

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Insulation materials in district heating pipes

Environmental and thermal performance of
polyethylene terephthalate and polyurethane foam

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CHALMERS UNIVERSITY OF TECHNOLOGY
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Insulation materials in district heating pipes : Environmental and thermal performance
of polyethylene terephthalate and polyurethane foam
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Cover: Close-up of PET foam

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ABSTRACT

District heating can contribute to increased energy efficiency in society. The environmental impact can be reduced by minimising the heat losses in the district heating pipes during distribution of the heat to the customers. Today, the most commonly used type of district heating pipe has a steel or copper media pipe, surrounded by polyurethane (PUR) foam insulation and a protective outer casing of polyethylene. The heat losses increase over time due to diffusion of blowing agents out of and air into the insulating foam. In this thesis, the long-term environmental and thermal performance of different insulating materials was studied. The diffusion mechanisms of cyclopentane, a commonly used blowing agent in PUR foam, were compared to those of a new gas, 1,1,1,3,3-pentafluorobutane (HFC-365mfc). The performance of polyethylene terephthalate (PET) foam as a possible replacement alternative to PUR foam was also investigated. The environmental impact from global warming, acidification and resource depletion was studied for the first three phases (pipe production, network construction and network use) of the life-cycle of different pipe alternatives by means of life-cycle assessment (LCA). The LCA-study of PET foam insulated pipes is theoretical, since only foam boards can be produced today.

The diffusion characteristics of HFC-365mfc in PUR foam were found to be similar to those of cyclopentane. District heating pipes insulated with HFC-365mfc blown PUR foam may have less environmental impacts due to heat losses than cyclopentane blown foam, but the high global warming potential of HFC-365mfc render its use questionable. If it is assumed that the entire HFC-365mfc content in the PUR foam were to be released to the atmosphere, the use of this gas for pipe insulation can not be justified as an option to cyclopentane blown foam.

The determined effective diffusion and solubility coefficients of blowing agents and air are lower in PET foam than in PUR foam. The environmental performance of pipes insulated with high-density carbon dioxide blown PET foam ($157 \text{ kg} \cdot \text{m}^3$) is similar to pipes insulated with carbon dioxide blown PUR foam ($86 \text{ kg} \cdot \text{m}^3$). If PET foam of lower density could be produced, it would be a potential competitor to pipes insulated with cyclopentane blown PUR foam. A future trend towards increased recycling of PET can be expected in Europe, possibly as a result of increased PET consumption and current regulations. Recycled PET has also the advantage of a lower price than virgin PET and PUR.

Keywords: District heating pipe, insulation, polyurethane foam, polyethylene terephthalate foam, mass transport, thermal performance, cyclopentane, 1,1,1,3,3-pentafluorobutane, HFC-365mfc

LIST OF PUBLICATIONS

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

- I Diffusion of cyclopentane in polyurethane foam at different temperatures and implications for district heating pipes**
Maria E. Olsson, Ulf Jarfelt, Morgan Fröling, Sara Mangs and Olle Ramnäs
Journal of Cellular plastics, 38 (2002) 177-188

- II Transport of 1,1,1,3,3-pentafluorobutane (HFC-365mfc) in rigid polyurethane foam and polyethylene**
Sara Mangs, Morgan Fröling, Olle Ramnäs and Ulf Jarfelt
Cellular Polymers, 21 (2002) 155-164

- III PET (polyethylene terephthalate) foam as insulation material for district heating pipes**
Sara Mangs, Olle Ramnäs and Ulf Jarfelt
Proceedings of The 9th International Symposium on District Heating and Cooling, Espoo Finland, August 30-31, 2004

- IV Mass transport of cell gases in carbon dioxide blown PET (polyethylene terephthalate) foam insulation**
Sara Mangs, Olle Ramnäs and Ulf Jarfelt
Cellular Polymers, 24 (2005) 115-126

- V Environmental comparison of DH pipes - PET and PUR foam insulated district heating pipes**
Sara Mangs, Camilla Persson, Morgan Fröling, Olle Ramnäs and Ulf Jarfelt
Euroheat and Power, 3 (2006)26-31



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1 INTRODUCTION

1.1 Goal and scope

The aim of this thesis is to investigate the long-term thermal and environmental performance of district heating pipes insulated with foam made of polyethylene terephthalate (PET) and polyurethane (PUR). Two main comparisons have been considered:

- cyclopentane and 1,1,1,3,3-pentafluorobutane (HFC-365mfc) as blowing agents in PUR foam
- PET and PUR foam insulation

The insulating capacity of district heating pipes deteriorates over time due to the mass transport of insulating gas out of and air into the foam insulation. The main part of the work was focused on determining the thermal aging characteristics of the foams. During the use of district heating pipes, emissions from the heat produced to compensate for the heat losses gives rise to environmental impacts. From an environmental perspective, the entire life-cycle of the pipes: pipe production, network construction, network use and post-use handling (figure 1.1) is of importance, although the use phase produces the greatest environmental impacts [Fröling 2002a, Fröling 2004a, Fröling 2004b, Persson 2005c] and **V**.

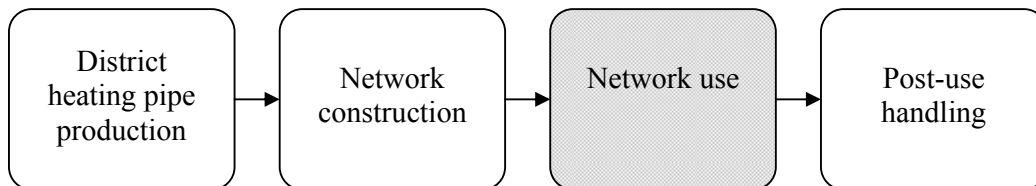


Figure 1.1 *The life-cycle of a district heating pipe. The shaded box indicates the main focus of this doctoral thesis.*

In paper **I**, the diffusion characteristics of cell gases in cyclopentane blown PUR foam and in the high density polyethylene (HDPE) casing surrounding the foam in district heating pipes are determined. This is a type of pipe commonly used today. In paper **II**, the mass transport properties of a new blowing agent, HFC-365mfc, is studied. The

aging characteristics of PET foam, a possible future alternative to PUR foam, were analysed in papers **III** and **IV**. Finally in paper **V**, the environmental impacts of district heating pipes insulated with PET and PUR foam are compared by life cycle assessment (LCA) methodology, in which all stages of the lifetime of a district heating pipe are considered, with the exception of waste management.

1.2 Outline of the thesis

Chapter 2 provides background information about district heating. The foam (rigid PUR and PET foam) and casing materials (LDPE and HDPE) used in or considered for district heating pipes, are described in chapter 3. Some general characteristics of the various blowing agents used in foam production are also described in chapter 3. Chapter 4 covers the research results and theories concerning heat transfer mechanisms and mass transport of cell gases in insulating foams and casing materials in district heating pipes. In chapter 5, the environmental impacts of insulating materials and blowing agent in the foam are discussed from a life cycle perspective.

1.3 The research group

This work was performed within the framework of a cross-disciplinary research project between the divisions of Chemical Environmental Science and Building Technology at Chalmers University of Technology and the Swedish National Testing and Research Institute, and was financially supported by the Swedish District Heating Association and the Swedish Energy Agency. The research collaboration started in 1990 with studies on CFC-free polyurethane insulated district heating pipes and continued with studies on long-term thermal performance and life-cycle assessment in addition to mechanical investigations of district heating pipes. Today, the focus is on the development of new types of pipe constructions and materials.

2 DISTRICT HEATING

2.1 A 19th century technology with potential for the future

District heating is used to heat buildings in areas with high population density and a cold climate. Water, or steam in a few older systems, is heated in large centralized plants and transported through a pipe network which is buried in the ground (figure 2.1). In the buildings connected to the district heating network, the heat is in general transferred to the internal space heating system and to the tap water system by means of heat exchangers. The cooled water is then transported back to the heat production plant. In a modern system, with water as the energy carrier, the hot water temperature is about 80-100 °C and the return flow of water about 40 °C.

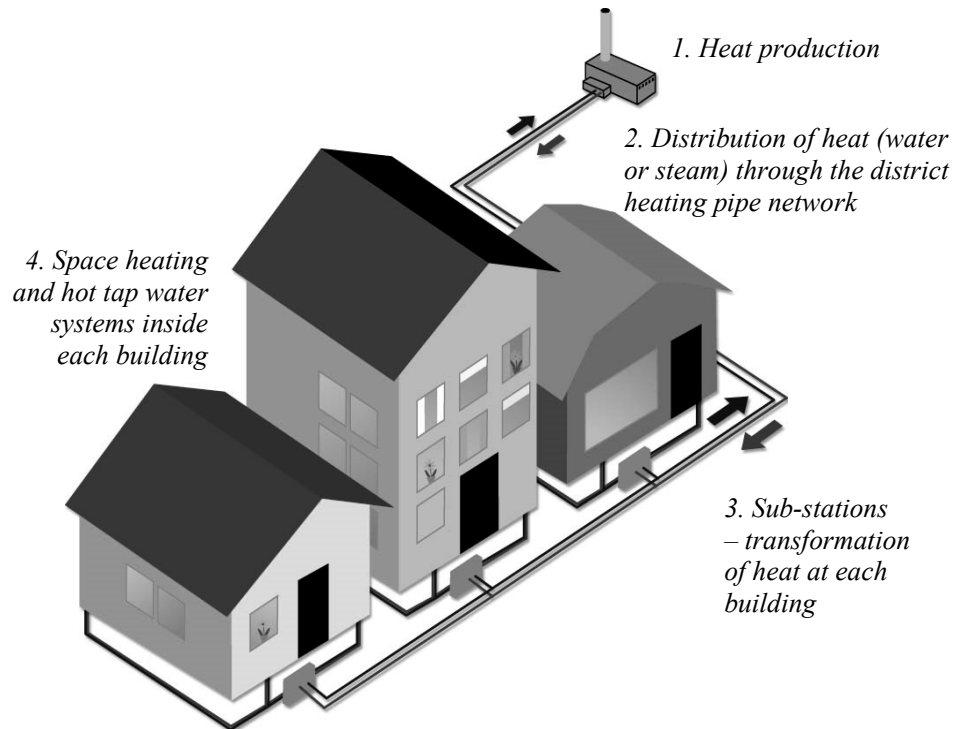


Figure 2.1 The district heating system. The picture is taken from the homepage of the Swedish District Heating Association [Swe DH 2005a].

The technology was first development in the United States in the 1870's and then spread to Europe where several large systems were built during the first half of the 20th century [Werner 1989]. Today, district heating supplies about 100 million people in Europe. The amount of district heat delivered is increasing in many countries [Euroheat & Power 2003]. District heating is most widespread in Scandinavia, Russia, Central and Eastern Europe. In Central and Eastern Europe the market share is about 40 % while Western Europe has about 10 %. In Sweden, district heating is delivered to almost half of all buildings [Swe DH 2005a]. In 2003, the delivered heat was 47.7 TWh and forecasts indicate that it will increase by a further 10 TWh by 2010, both due to the planned enlargement of existing systems and the introduction of new systems.

Despite the fact that the idea of district heating is more than a century old, it is open to new innovations and technology. The distribution system has been developed over the years. Very old systems used steel pipes within concrete or asbestos boxes insulated with, for example mineral wool or cellular concrete foam [Fredriksen 1993]. Some forty years ago pre-fabricated pipes were introduced. Today they are the most commonly used pipes in newly constructed district heating networks. The inner pipe is normally made of steel or copper and surrounded by PUR foam insulation and an outer HDPE casing (figure 2.2). When the pipe is buried under ground, the casing protects the foam against both water and mechanical pressure. The rigid PUR foam insulation consists of closed cells initially containing an insulating gas and a small amount of air. Today, the most commonly used blowing agents in PUR foam used in district heating pipes are cyclopentane and carbon dioxide. Chlorofluorocarbons (CFCs) were used until their ozone depletion effect was discovered and international action was taken to restrict them. Sometimes a foil is placed between the outer casing and the PUR foam in order to decrease the diffusion of cell gases and slow down the effect of aging on the insulation capacity.

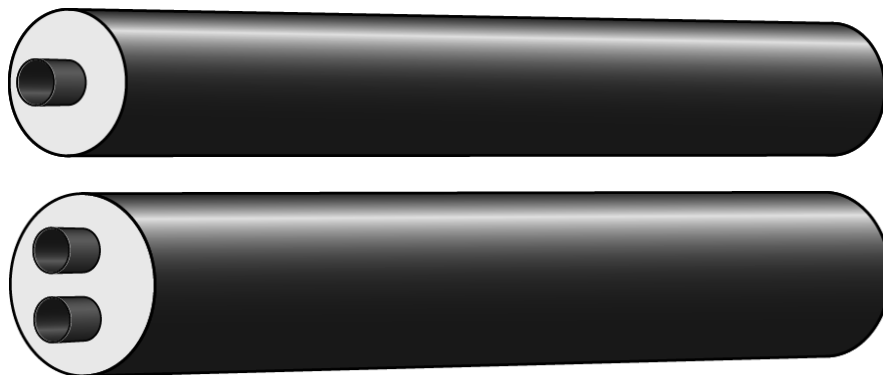


Figure 2.2 The district heating “single pipe” (top picture) and “twin pipe” (bottom picture). These commonly used pipes have steel or copper media pipes surrounded by polyurethane foam insulation and a high density polyethylene casing.

In some district heating networks, two or more media pipes are placed within the same casing pipe (figure 2.2). In this “twin pipe” system, one media pipe is used for transporting hot water from the heat production facility to the consumer, while the other is used for the return flow of water. The so-called “flexible” district heating pipes of quite small dimensions are used in the proximity of buildings. These can be bent to some extent due to the fact that semi-flexible PUR foam and low density polyethylene (LDPE) is used in the pipes.

Various pipe dimensions are used in different parts of the network. The outer diameter of the pipes varies from less than 100 mm to almost 1000 mm. Large pipes are used as main pipes close to the heat production plants where large heat flows are distributed, while smaller pipes are installed in the vicinity of the end users.

2.2 District heating and sustainable development

In the last decades it has become very evident that human activities have an extremely harmful impact on eco-systems, both locally and globally. Since the “World Commission on Environment and Development” (often called “the Brundtland commission”) in the 1980s first defined sustainable development as “...the development that meets the needs of the present without compromising the ability of future generations to meet their own needs”, several international initiatives have been taken to solve some of our most serious global environmental problems [WCED 1987]. One of them is the Kyoto Protocol to the United Nations Framework Convention on Climate Change [UNFCCC 2005], in which many of the world’s nations agreed to reduce their emissions of greenhouse gases due to their effects on the global climate. District heating has great potential to keep pace with the changes in a society moving towards a higher degree of ecological sustainability. A variety of fuels and heat sources with low net emissions of carbon dioxide can be utilised, e.g. wood waste, natural geothermal heat sources and refuse incineration plants. Making use of surplus heat from industry and incorporating combined heat and power (CHP) technology can also contribute to increased energy efficiency in society. In a CHP plant, the heat from combustion of a fuel is used to produce electricity and the remaining heat employed in for example district heating systems. In a report published by the International Energy Agency, it is argued that the high energy efficiency achieved by CHP in combination with district heating systems can be of significant value in the short term as a means of fulfilling the Kyoto agreement in Europe [Werner 2002].

Western European district heating systems are mainly powered by fossil fuels: 34 % coal, 31 % natural gas and 6 % oil [Euroheat & Power 2003]. Only 11 % of the heat generated comes from renewable resources and 10 % from waste heat. The remaining 8 % is unspecified. The use of different types of heat sources and fuels varies a great deal between different countries (figure 2.3). In Sweden, the proportion of low carbon dioxide emitting fuels and technologies (solid biofuels, biogas, refuse incineration, waste heat, heat pumps and CHP) increased from 60 % in 1997 to 74 % in 2003

[Euroheat & Power 2003, Swe DH 2005b]. The reported energy efficiency of the district heating system was 88 % in 2003 [Swe DH 2005b]. Losses occur in the heat production and during distribution due to pump energy and heat losses in the pipes' insulation [Fredriksen 1993].

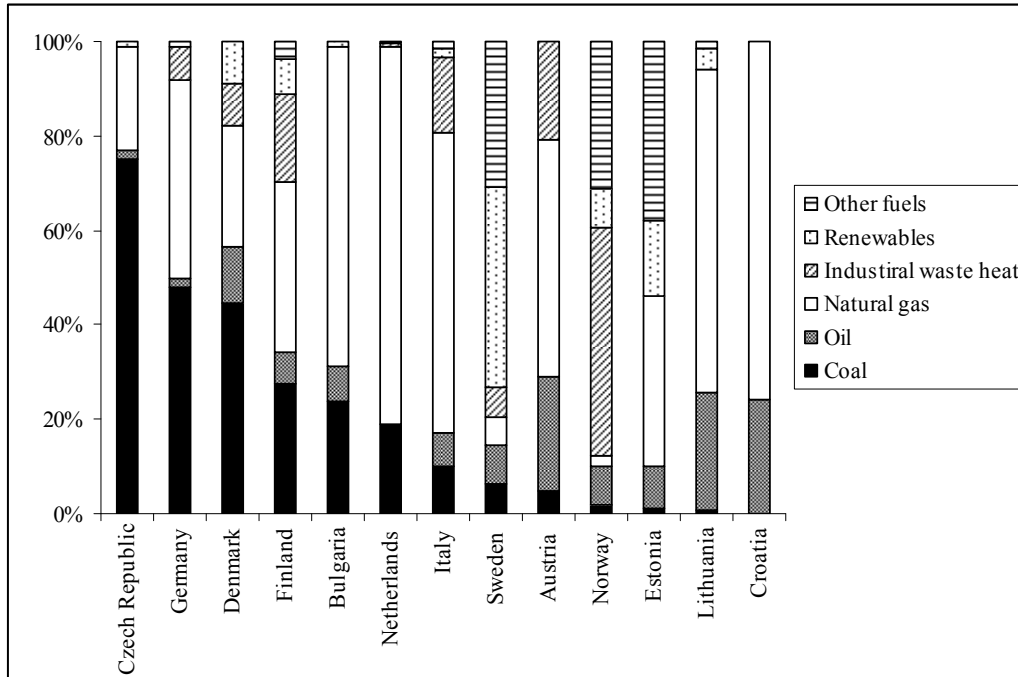


Figure 2.3 Fuels used in district heating in Europe in 2001 [Euroheat & Power 2003].

3 INSULATION AND CASING MATERIALS IN DISTRICT HEATING PIPES

3.1 District heating pipe production

A common production technique for PUR foam insulated district heating pipes is a production line, where each pipe is manufactured individually. The pipes are produced to in lengths of 6 to 16 m and the thickness of the PUR foam for each dimension can be varied according to the intended application [Schlenter 1996]. The HDPE casing is first produced in a continuous process where HDPE granules are melted and extruded into a cylindrical shape and then cut to the desired length. The media pipe is centred in the casing, after which the PUR foam formulation is injected through a hole in the casing in the middle of the pipe or from one of the ends. The foam is created as a result of chemical reactions of the components in the formulation. When the PUR foam expands, it adheres to the surface of the steel pipe and the HDPE casing. There are two types of continuous production techniques. In the “spray process”, layers of PUR foam formulation are sprayed onto the steel pipe and the HDPE casing is either extruded or wound around the insulation. In the continuous moulding process, the foam formulation is laid on a PE sheet with the steel pipe centred above it. The sheet is pulled into a pipe-shaped mould as the PUR foam expands. The HDPE casing is then extruded onto the pipe. Finally the pipes are cut to the desired lengths.

Production of PET foam insulated district heating pipes is still being developed. So far, only boards of a thickness up to about 5 cm can be produced in an extrusion process developed by the Italian company BC Foam. It is possible that the extrusion process may be developed for the purpose of producing district heating pipes.

3.2 Polyurethane foam

Polyurethane is a widely used material. In Western Europe in 2003, PUR constituted about 5 % or 2.7 million tonnes of the total annual consumption of plastics (figure 3.1) [APME 2004]. There has been a steady increase since 1995, when consumption was 1.8 million tonnes [APME 1997, 2000, 2001, 2002, 2003, 2004]. The great

possibilities of adjusting the material properties, e.g. density, flexibility and stiffness, opens up for a variety of different applications, such as coatings in the appliance industry, soles for shoes, glue, mattresses, vehicle seats and insulation. In many countries rigid PUR foam is commonly used as insulation material in the construction industry due to its low thermal conductivity compared to other materials and the fact that it can be foamed on site.

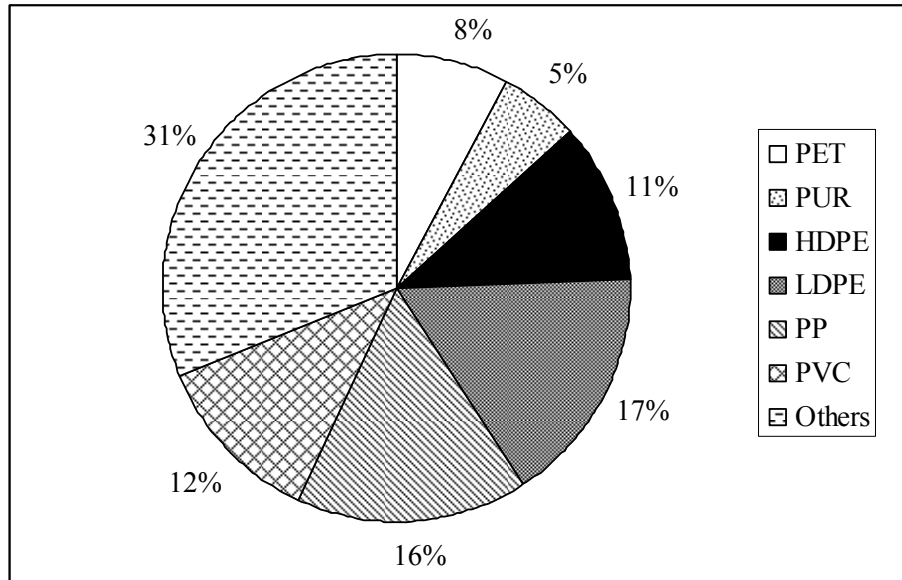


Figure 3.1 Distribution of consumption of different plastics in Western Europe in 2003 [APME 2004]. “LDPE” = low density polyethylene, “PP” = polypropene, “PVC” = polyvinyl chloride, “Others” includes for example polystyrene, polyamides and amino polyesters.

PUR foam is formed by simultaneous polymerisation and expansion in a formulation containing an isocyanate, a polyol and a blowing agent with a low boiling point (figure 3.2). The polyol contains two or more hydroxyl groups.

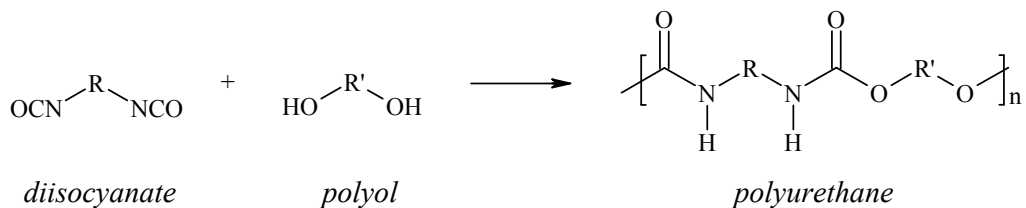


Figure 3.2 Polymerisation reaction of polyurethane.

The heat from the exothermic reaction vaporizes the blowing agent, thus creating the PUR foam cell structure. Due to the fact that small amounts of water are always present and/or added, gaseous carbon dioxide is formed in a reaction with the isocyanate, which contributes to the formation of the cells. It is important that there is a balance between the foam expansion and the polymerisation. A polymerisation that is too slow can result in foam collapse. In order to control this process a catalyst affecting the polymerisation reaction is often used.

Because of their high reactivity and favourable price, MDI (diphenylmethane diisocyanate, figure 3.3) and pMDI (polymeric by-products of MDI) are the main isocyanates used for rigid foam production today [Grünbauer 2004]. Isocyanates are highly toxic and can cause allergic reactions in humans [Bakke 2001]. Therefore, handling of isocyanates is problematic in the working environment. Isocyanate molecules can also be released if the chemical links are broken due to heating of PUR foam, e. g. when district heating pipes are welded together during the construction of the district heating network [Bergström 2002].

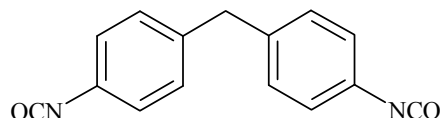


Figure 3.3 MDI, diphenylmethane 4,4'-diisocyanate.

The density of the foam is determined by the hydroxyl functionality of the polyol [Glicksman 1989]. Short chain polyols with high functionality produce a PUR foam with more cross-links and thus a more rigid and high density product. Soft, elastomeric foam with an open cell structure and low density is formed by using polyols with longer chains and lower functionality. Water is also involved in reactions that create a harder, but more fragile foam structure. For thermal insulation applications, the heat conduction in the solid polymer must be minimized, thus the density should be kept as low as possible without jeopardising the strength of the foam. Normally, the density of the PUR foam in district heating pipes is about $60\text{-}70\text{ kg}\cdot\text{m}^{-3}$.

The constituents used for rigid PUR foam production are normally derived from fossil, non renewable resources. It is, however, possible to produce polyols from renewable resources. Baser et al. showed that closed cell rigid PUR foam for insulation purposes can be produced by using castor oil as the polyol [Baser 1993]. Dahlke et al. also suggest sunflower and rapeseed oil produced by the German company HOBUM Oleochemicals, as a base for polyols [Dahlke 1998]. Palm oil and soybean oil, produce thermally stable foams with good mechanical properties [Chian 1998, Guo 1999, Javni 2000]. In order to function as a polyols, palm oil and soybean oil has to undergo chemical processes. The hydroxyl functionality of the soybean polyol is rather low and would consequently produce a semi-rigid foam. Guo et al. therefore suggest the addition of hydroxyl containing crosslinkers and/or water in order to obtain a rigid foam structure.

The price of palm oil and soybean oil, 470 and 620 US dollars per tonnes in 2004 respectively [The Hindu 2005], is lower than that of castor oil, which was 800 US dollars per tonne in 2004 [The World Bank Group 2005]. In order to be a sustainable polyol option, the oils must be produced in an environmentally sustainable way. Soybean oil is the world's most popular vegetable oil and is mainly produced in the US (38%) and Brazil (26%) [Rainforestweb 2005, World Rainforest Movement

2005]. The second most popular vegetable oil is palm oil with 85 % of the total world production in Malaysia and Indonesia. The total agricultural area for these oils increased significantly between 1990 and 2002, 26% for soybean oil and 43 % for palm oil. In South East Asia and Brazil, agricultural land for the production of soy beans and oil palms has been made available by cutting down large areas of rainforests. Besides the loss of biodiversity, a high level of pesticides and herbicides is often used in these large monocultures.

The increased global use of PUR also results in higher amounts of waste, for which there are several recycling methods. Flexible foams can, for example, be ground into a powder and blended into the foam formulation for the production of new PUR products, or granulated and joined together by means of a binder and used, for example, as carpet underlay, athletic mats and interior vehicle parts [API 2005, Quinlan 1994]. Polyols can be extracted from PUR foam by means of chemical processes: glycolysis, aminolysis and hydrolysis. In glycolysis, low molecular recycled polyols are created by dissolving PUR scrap and sometimes a catalyst in glycol (e.g. ethylene glycol, 1,2-propylene glycol, triethylene glycol) in a reactor at about 170-220 °C [Borda 2000, Murai 2003]. The glycolysis reaction is believed to occur in accordance with the reaction illustrated in figure 3.4 below (in this case with ethylene glycol).



Figure 3.4 Glycolysis reaction of polyurethane.

Aminolysis (figure 3.5), which is performed in a similar manner to glycolysis is assumed to follow the exchange reaction below [Kanaya 1994].

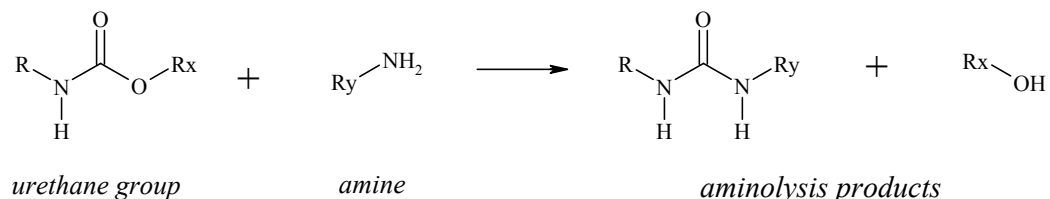


Figure 3.5 Aminolysis reaction of polyurethane.

Shin et al. introduced recycled polyols from glycolysis, 10-30 % by weight of the total polyol content, in PUR foam formulation with cyclopentane and water as blowing agents [Shin 1998]. The foams had as good or even better dimensional stability and up to 9 % lower thermal conductivities than those prepared from virgin materials. The low foam thermal conductivity was probably due to the small cell sizes which reduces the contribution of radiation within the cell voids.

3.3 High density polyethylene

The total amount of polyethylene used in Europe (both high and low density polyethylene) amounted to about 28 % of the total plastic consumption in 2003 (figure 3.1) [APME 2004]. Low density polyethylene, LDPE (17 %), is used for films, bags, toys, coatings, containers and pipes, while HDPE (11 %) is used for pipes, containers, toys, household goods, industrial wrappings and films.

The basic structure of polyethylene is the ethylene unit ($-\text{CH}_2\text{CH}_2-$). The less branched the chain backbone, the harder the material and the higher the density. By definition HDPE has a density of $940 \text{ kg}\cdot\text{m}^{-3}$ or more. According to the European standard, HDPE casings of rigid PUR foam insulated district heating pipes should have a density of at least $944 \text{ kg}\cdot\text{m}^{-3}$ [EN253:2003]. The branching and molecular weight are the main factors that influence the physical and mechanical properties. Polyethylene is partially crystalline, and the rate of flexibility of the material decreases in line with increasing crystallinity. In common with most plastics, PE is derived from crude oil.

3.4 Polyethylene terephthalate

There has been a worldwide increase in the consumption of PET during the last decade [APME 2004, 2005]. Between 1995 and 2001 the total consumption of PET in the world increased from about 3 million to almost 8 million tonnes. Today, the use of PET exceeds that of PUR in Western Europe (figure 3.1). PET used for bottles and film in Europe has increased almost threefold since 1995, while the use of the material for textile fibres has remained more or less static (figure 3.6) [APME 1997, 2000, 2002, 2004]. PET recycling is also expected to increase due to the European Commission's Packaging and Packaging Waste Directive, which includes higher targets for mechanical recycling of plastic packages all over Europe [European Council 1994, 2005]. PET is a thermoplastic and can thus be remelted into new products. Since production of food packages from recycled material is restricted for hygienic reasons, new fields of application for recycled PET such as foam production, can be developed.

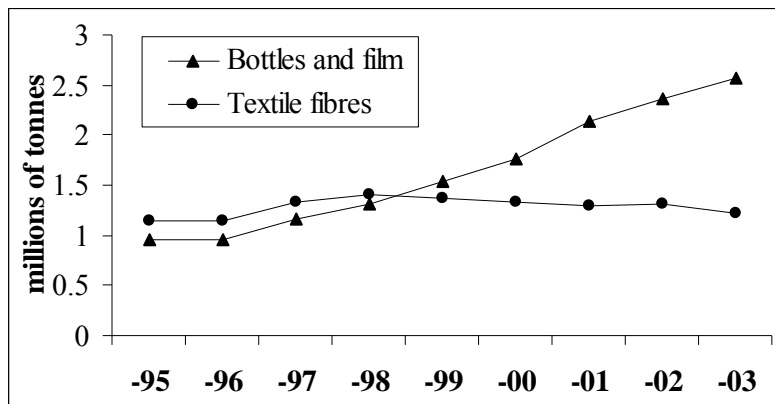


Figure 3.6 Consumption of PET in Western Europe [APME 1997, 2000, 2002, 2004].

PET (figure 3.7) was developed by the British Calico Printers company 1941 and was originally used for synthetic fibers [Bousted 2002]. Films have been produced since the mid-1960s and the PET bottle blowing technique was introduced in the 1970s.

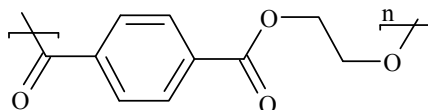


Figure 3.7 Polyethylene terephthalate

Polyesters are obtained by a reaction between acid and alcohol (figure 3.8). Terephthalic acid or di-methyl terephthalate and ethylene glycol are used in the production of PET and the reaction takes place in the presence of a catalyst. *P*-xylene derived from catalytic reforming of naphta is used to produce terephthalic acid and di-methyl terephthalate and ethylene made from cracked natural gas or the naphta fraction from crude oil is used to produce ethylene glycol, and. [Bousted 2002]. For both reaction routes a polycondensation reaction follows. A short liquid state polycondensation creates an amorphous material suitable for fibres and film. Semi-crystalline material for bottles and PET foam is achieved by longer period of polycondensation [Xanthos 2000].

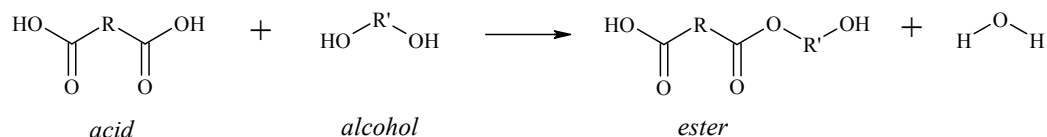


Figure 3.8 Principal polymerisation reaction of polyethylene terephthalate.

The production of PET foam boards is shown in figure 3.9. The polymer granules are dried and mixed with a nucleating agent (talcum 0.5 % by mass) before entering the extruder. The blowing agent (approx. 1 % by mass) is mixed under high pressure (70-80 bar) into the polymer melt in the extruder and kept under pressure until the melt exits through the die where the extrusion pressure is about 45-50 bar. In the atmospheric pressure following the die lips, the blowing agent is transformed from the liquid to the gaseous phase, creating the foam cells.

The price of virgin materials follows the fluctuations in the cost of raw oil. In 2004 the prices of PET and PUR were about the same, at around 1.8 EUR/kg [III]. The price for recycled PET was significantly lower, around 0.5 EUR/kg. Recycled PET has, however, been shown to be unsuitable for foam production, due to contamination of other plastics and degradation of the material during the recycling process [Japan 2000, Xanthos 2000]. The problem is that the viscosity of recycled PET is too low and the melt strength inferior compared to virgin material. Foams of a very high

quality have been achieved in experiments where recycled PET was chemically modified by means of multifunctional branching agents (e.g. tetraglycidyl diamino diphenyl methane or pentaerythritol) [Japon 2000, Smith 1990, Xanthos 2000].

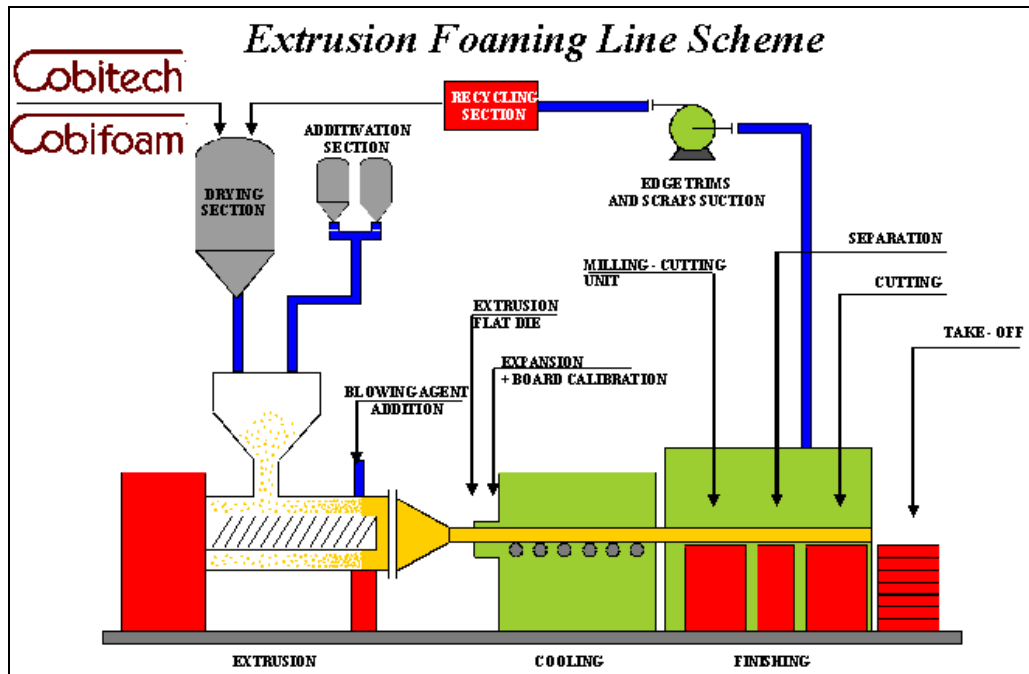


Figure 3.9 Schematic illustration of a process plant used to produce PET foam sheets [M&G Polymers 2004].

Studies show that PET undergo chemical degradation by hydrolysis if exposed to humidity or water at high temperatures (85 and 120 °C), which results in increased embrittlement [Foulc 2005, Oreski 2005]. In district heating pipes, this could become a problem for the PET foam close to the media pipe where the temperature is elevated.

The lowest density of PET foam achieved today is about 90 kg·m⁻³ (average value of a 3 cm thick board) [III]. The compressive strength of this foam was determined to 580 kPa, which is considerably higher than the required value for PUR foam in district heating pipes, namely 300 kPa [EN253:2003]. One function of the HDPE casing in district heating pipes is to protect the PUR foam insulation from external mechanical pressure. Due to the high compressive strength of PET foam it may be possible to use PET foam insulated pipes without casing or with a casing of PET. Production techniques have not yet been developed, but the casing could, for example, be produced by melting the outer layer of the insulation. Fewer materials in a product makes the waste treatment of pipes taken out of use considerably easier.

3.5 Blowing agents – physical and environmental properties

Table 3.1 presents some technical and environmental features of previously and currently used blowing agents in PUR and PET foam insulations. It is desirable that a blowing agent has a fairly high vapour pressure, thus making it possible to introduce more gas in the foam. A higher gas content leads to a slower deterioration of the insulation capacity over time. The thermal conductivity of the blowing agent has a major impact on the foam thermal conductivity and should be as low as possible to ensure foam with good insulating capacity. The atmospheric lifetime is an important environmental factor, since substances with a long life can potentially cause more environmental damage such as ozone depletion and global warming. The ozone depletion potential (ODP) for the blowing agents with CFC-11 as a reference substance and the global warming potential (GWP) with carbon dioxide as reference substance are presented in table 3.1.

The chlorofluorocarbons (CFCs) were used in the first types of PUR foam insulated district heating pipes. Their effect on the ozone layer led to a shift towards hydrochlorofluorocarbons (HCFCs) and carbon dioxide. Today, cyclopentane, often in combination with carbon dioxide, is the main blowing agent in European PUR foam insulated district heating pipes. In the United States pentafluoropropane (HFC-245fa) is used as replacement for HCFCs. Pentafluorobutane (HFC-365mfc) is a gas that has been considered for Swedish district heating pipes and was therefore investigated in this research project. In the development of PET foam, tests with different blowing agents have been performed in pilot plants. The gases used have been carbon dioxide, difluoroethane (HFC-152a), (chlorodifluoroethane) HCFC-142b and chlorodifluoromethane (HCFC-22).

3.5.1 The phase-out of chlorofluorocarbons

The 1950s marked the start of the use of CFCs in different technical applications, such as refrigerators, air conditioners, aerosol containers, packaging materials, cleaning solvents and insulation materials. For insulation purposes, this type of gases had some very good technical qualities such as low thermal conductivity ($7.4\text{-}8.2 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at $25 \text{ }^\circ\text{C}$ for CFC-11), relatively high vapour pressure and are not inflammable [Brodth 1995, Chemnetbase 2005, Heinemann 2000, Shankland 1990a].

In the late 1970s, it was found that the CFCs and the HCFCs, had the very undesirable effect of depleting the ozone layer in the stratosphere [The Montreal Protocol 2005]. The ozone layer is 10-50 km above the Earth's surface and protects the Earth from the dangerous short wave UVB radiation by absorbing the energy. The effects of higher radiation are, for example, increased rates of skin cancer, damage to the immune system of both humans and animals, decreased marine algae production and diminished crop growth.

The first international agreement setting out a legal framework restricting the use of ozone depleting substances in industrialised countries was the “Montreal Protocol on Substances that Deplete the Ozone Layer” in 1987 [The Montreal Protocol 2005]. Since then, further amendments have been adopted in London (1990), Copenhagen (1992), Montreal (1997) and Beijing (1990). By September 2002, 183 countries had ratified the Protocol. Production and use of CFCs have been phased out in industrialised countries, while developing countries are following phase-out programs, culminating in a complete ban by 2010. In the case of HCFCs which have an ozone depletion potential of about 1-11 % of that of CFC-11 [World Meteorological Org 2002], the phase-out will be completed by 2030 in industrialised countries and by 2040 in developing countries, although some countries have voluntarily agreed on tighter phase-out schedules. Even though CFCs have been phased out in Sweden, district heating pipes containing these gases are still in use. The total amount of CFC-11, the most potent ozone depleting substance, is estimated to 2000 tonnes in Sweden and about 8100 tonnes in all the Nordic countries [Svanström 1996]. The gases are released to the atmosphere as they diffuse out of the foam, which however, is a very slow process.

3.5.2 Blowing agents in PUR foam

Carbon dioxide is often used in combination with cyclopentane in PUR foam. An advantage of carbon dioxide is that it is created during foaming by adding a small amount of water to the PUR foam formulation. The main disadvantages of carbon dioxide is its high thermal conductivity ($16.3\text{-}16.6\text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at $25\text{ }^{\circ}\text{C}$) compared to other blowing agents (table 3.1) [Albouy 1998, Brodt 1995, L'air liquide 1976, Shankland 1990a] and its fast diffusion out of the foam leading to a rapid decrease in insulation capacity [I]. Solely carbon dioxide blown PUR foam is normally only used for pipes of large dimensions. Cyclopentane has lower thermal conductivity than carbon dioxide ($11.3\text{-}13.8\text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at $25\text{ }^{\circ}\text{C}$) [Brodt 1995, Volkert 1995] as well as a much slower rate of diffusion [I]. The vapour pressure of cyclopentane is though below 1 bar at room temperature (0.42 bar at $25\text{ }^{\circ}\text{C}$) [Chemnetbase 2005]. In addition to cyclopentane, iso-pentane with a vapour pressure of 0.917 bar at $25\text{ }^{\circ}\text{C}$ and a thermal conductivity of $14.8\text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at $25\text{ }^{\circ}\text{C}$ [Chemnetbase 2005, Volkert 1995] is sometimes added into the foam formulation in order to increase the total amount of hydrocarbons in the foam cells. Another gas sometimes used in PUR foam is n-pentane, which has a higher vapour pressure (0.68 bar at $25\text{ }^{\circ}\text{C}$) than cyclopentane, but somewhat higher thermal conductivity ($14.8\text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at $25\text{ }^{\circ}\text{C}$) [Chemnetbase 2005, Volkert 1995]. From a technical point of view, a disadvantage of hydrocarbons is their flammability, and thus extra precautions must be taken during handling and processing operations. Although produced from fossil resources, hydrocarbons have no ozone depletion effect and very low global warming effect. A report by Galvin et al. summarizes the results of toxicological studies carried out on rats, mice and rabbits since the 1940s [Galvin 1999]. From these studies it was concluded that cyclopentane is practically non-toxic and has no significant mutagen effects.


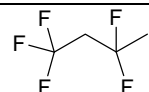
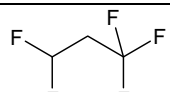
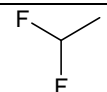
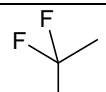
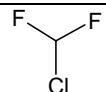
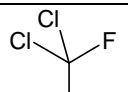
Hydrofluorocarbons (HFCs) have been used as replacement options in several technical applications including PUR foam insulation. The gases in this group are non-ozone depleting but have rather high global warming potentials, up to 10,000 times higher than carbon dioxide [IPCC 2001a, Naik 2000]. In order to restrict the use of HFCs, taxates have been introduced in Denmark, Norway and Austria. In Denmark the goal is to phase out HFCs by 2006, and other European countries are expected to follow [Danish EPA 2002]. Taxes or regulations on the use of HFCs have not yet been introduced in Sweden [Swedish EPA 2005].

In the USA, HCFCs used for production of new insulation foams were phased out in 2003, and HFC-245fa (EnovateTM3000) is produced and marketed as a replacement option by the American company Honeywell. As it is a non-flammable gas, it is possible to use the same equipment as for the production of PUR foam blown with dichlorofluoroethane (HCFC-141b) [Bogdan 2001]. The German company Bayer AG has patents in Europe, the USA and Canada for methods to produce PUR foam with HFCs as blowing agent [Bayer AG Leverkusen 1990, 1996]. Honeywell has acquired a world wide licence from Bayer AG with exclusive rights for USA and Canada, while Solvay has acquired a world licence excluding the USA and Canada. Solvay produces a range of HFCs marketed under the name Solkane®, of which HFC-365mfc is one of their main products intended for PUR foam insulation [Solvay Fluor 2005]. Due to the flammability of HFC-365mfc, the Solvay company has developed non flammable mixtures with 7 % and 13 % heptafluoropropane (HFC-227ea). At Solvay's French production plant in Tavaux, all hydroflouroalkanes are manufactured by means of hydrofluorination of a chlorinated precursor [Zipfel 1999]. At the end of 2002, a plant with an annual HFC-365mfc production capacity of 15,000 tons commenced operation in Tavaux in France. The price of HFC-365mfc and HFC-245fa is higher than that of cyclopentane. Since the chemicals used for the PUR formulation differ due to the blowing agent used, the total cost must be considered.

The vapour pressure of HFC-365mfc and HFC-245ea is higher than that of cyclopentane, which may result in a higher concentration of these gases in the foam. The thermal conductivity of HFC-365mfc ($10.6 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at $25 \text{ }^\circ\text{C}$) is of about the same as that of cyclopentane and lower than that of HFC-245fa ($12.2\text{-}13.5 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at $25 \text{ }^\circ\text{C}$) (table 3.1). When HFC-365mfc is mixed with HFC-227ea, the thermal conductivity of the gas mixture increases to $10.7\text{-}10.9 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at $25 \text{ }^\circ\text{C}$ [Zipfel 2002].

A toxicological study of HFC-365mfc shows low toxicity and no significant mutagenicity [Zipfel 1999]. Studies on HFC-245ea show that the substance is of low toxicity, non-mutagenic and not a teratogen [Honeywell 2005].

Table 3.1 Physical and environmental properties of different insulating gases used as blowing agents in PET and PUR insulation foam.

	Carbon dioxide	Cyclopentane	HFC-365mfc	HFC-245fa	HFC-152a	HCFC-142b	HCFC-22	CFC-11
								
	CO ₂	C ₅ H ₁₀	CF ₃ CH ₂ CF ₂ CH ₃	CHF ₂ CH ₂ CF ₃	CHF ₂ CH ₃	CClF ₂ CH ₃	CHClF ₂	CCl ₃ F
CAS registry no	124-38-9	287-92-3	406-58-6	460-73-1	75-37-6	75-68-3	75-45-6	75-69-4
Molecular weight, g·mole⁻¹	44.0	70.1	148.1	134.0	66.1	100.5	86.5	137.4
Boiling point (°C)	-78.5 ^a	49.3 ^a	40.2 ^b	15.3 ^r	-25 to -24.1 ^{a,c,d,e,l}	-10 to -9.2 ^{a,c,d,f}	-40.8 ^{a,c,d}	23.7 ^a
Vapour pressure at 25 °C (bar)	64.3 ^c	0.42 ^c	0.47 (20°C) ^b	1.23 (20°C) ^r	6.0-6.1 ^{c,d,e}	3.4-3.5 ^{c,e}	10.4 ^{c,e}	1.1 ^c
Thermal conductivity of gas phase at 25 °C (mW·m⁻¹·K⁻¹)	16.3-16.6 ^{c,f,g,h}	11.3-13.8 ^{i,h,v}	10.6-11.6 ^{b,v}	12.2-14.8 ^{b,j}	13.4-14.7 ^{c,d}	9.4-12.1 ^{c,f,j}	10.6-11.7 ^{c,f,h,j}	7.4-8.2 ^{f,h,j}
Flammability limits in air (vol%)	None	1.5 – 8.7 ^k	3.5-13.3 ^{l,t}	None ^b	3.7-20.2 ^{c,m,n}	9.0-14.8 ^{c,m,n}	None ^c	None ^f
Atmospheric lifetime (years)		<0.01 ^{u,s}	8.6-10.7 ^{o,p,q}	7.2-8.4 ^{o,p,q,s}	1.4-1.8 ^{n,o,p,q}	17.9-22.4 ^{n,o,p,q}	11.9-15.8 ^{n,o,p,q}	45-50 ^{o,p,q}
Ozone Depletion Potential, 100 years	0	0	0	0	0	0.014-0.07 ^q	0.034-0.055 ^q	1
Global Warming Potential, 100 years	1	<10 ^u	782-953 ^{o,p,q}	950-1020 ^{o,p,q}	120-149 ^{o,p,q}	1957-2400 ^{o,p,q}	1700-1780 ^{o,p,q}	4600-4749 ^{o,p,q}

a) [Knovel Corp 2005]

b) [Zipfel 2002]

c) [Albouy 1998]

d) [Creazzo 1995]

e) [Chemnetbase 2005]

f) [Shankland 1990a]

g) [L'air liquide 1976]

h) [Brodt 1995]

i) [Volkert 1995]

j) [Heinemann 2000]

k) [Galvin 1999]

l) [Solvay Fluor 2005]

m) [Decaire 1994]

n) [Barthélemy 1993]

o) [Naik 2000]

p) [IPCC 2001b]

q) [World Meteorological Org 2002]

r) [Honeywell 2005]

s) [Seifert 2003]

t) [Zipfel 1999]

u) [Heilig 1994]

v) [Merten 1997]

3.5.3 Blowing agents in PET foam

The production of PET foam is still on a pilot scale. HCFC-142b, HCFC-22, HFC-152a, carbon dioxide and nitrogen have been used as blowing agents due to their satisfactory performance in the production process. Other gases may be considered in the future as the production process develops. Table 3.2 summarizes the foam densities achieved when using the various gases. The lowest density of foam board produced to date, about $90 \text{ kg}\cdot\text{m}^{-3}$, was achieved with a mixture of HCFC-142b and HCFC-22 [III], which cannot be considered as a solution for the future due to the ozone depletion potential of these gases. HFC-152a, which produces a foam with a density of $120 \text{ kg}\cdot\text{m}^{-3}$, has a thermal conductivity in the same range as HFC-245fa and cyclopentane as well as a somewhat lower global warming potential than HFCs (table 3.2). Inhalation experiments on rats indicate that HFC-152a has very low acute toxicity [Keller 1996]. Carbon dioxide blown foam has been produced with densities down to about $140 \text{ kg}\cdot\text{m}^{-3}$. Nitrogen as blowing agent produces PET foam up to densities of $400 \text{ kg}\cdot\text{m}^{-3}$ and is not intended to be used for insulation purposes, but as construction material.

Table 3.2 The lowest densities of the studied PET foams blown with different gases [II, III].

PET foam blown with:	Foam density $\text{kg}\cdot\text{m}^{-3}$
HCFC-142b/HCFC-22 *	91
HFC-152a	120
Carbon dioxide	144
Nitrogen	330

* Volume ratio HCFC-142b/HCFC-22: 60/40

4 INSULATION PERFORMANCE OF DISTRICT HEATING PIPES

4.1 Introduction

This chapter deals with the main factors affecting the long-term thermal performance of district heating pipes. Chapter 4.2 contains a review of the scientific literature on the heat transfer mechanisms in polymeric foams. The main research results on the thermal characteristics of PET and PUR foams presented in papers **I**, **II**, **III** and **IV** based on established theories on heat and mass transport in polymeric materials are summarised in chapter 4.3.

4.2 Heat transfer mechanisms in district heating pipes

The temperature difference between the inside of the media pipe (T_2) and the surrounding ground (T_1) is the driving force behind the heat flow through a district heating pipe (figure 4.1). If the materials are assumed to be homogeneous and isotropic, Fourier's law of heat conduction describes the heat flux q ($\text{W}\cdot\text{m}^{-2}$), through the pipe (distance r , m), with the thermal conductivity λ ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) as the proportional coefficient:

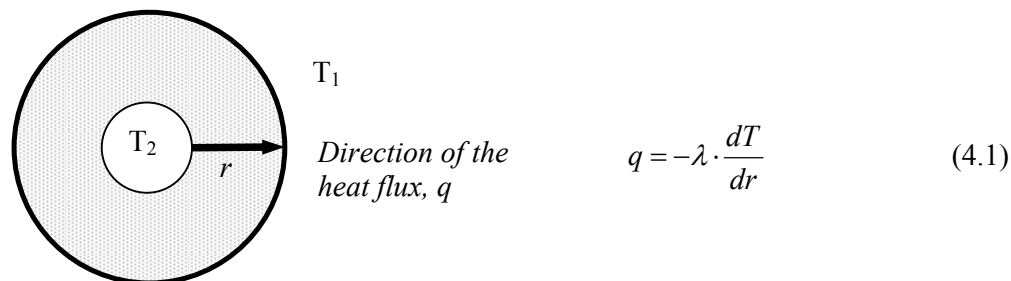


Figure 4.1 Heat flux, q ($\text{W}\cdot\text{m}^{-2}$), through a district heating pipe, $T_2 > T_1$.

Different district heating network constructions are used, such as the three examples shown in figure 4.2. Heat losses in a district heating network can be calculated by using finite elements or finite differences [Jonson 2001, Persson 2005a]. Simplified formulas for the steady-state heat flow from twin and single pipe systems has been developed [Wallentén 1999]. Persson and Claesson have derived a similar multipole model that can be applied to all kinds of single pipe constructions [Persson 2005b]. The low thermal conductivity of the insulating foam (20-40 mW·m⁻¹·K⁻¹ at 20 °C) [II, III, IV] compared to the surrounding ground (about 1500 mW·m⁻¹·K⁻¹ at 20 °C) reduces the heat losses from the the hot water inside of the district heating pipe.

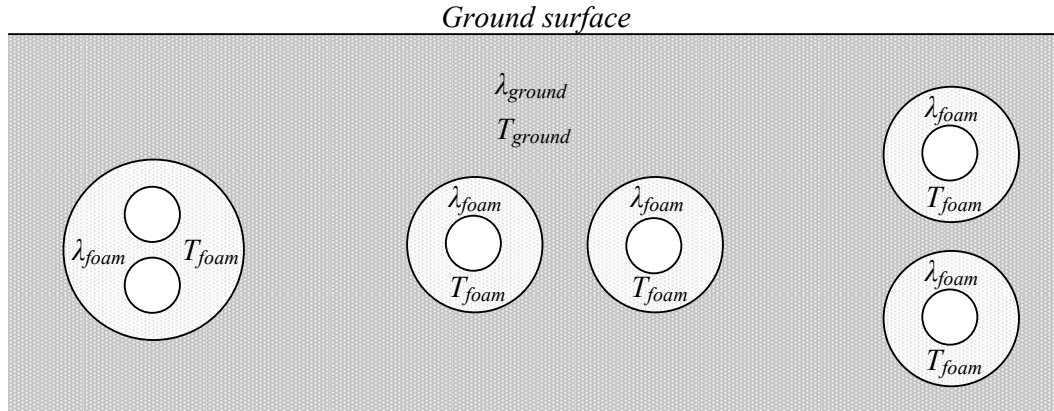


Figure 4.2 Examples of district heating pipe constructions. Twin pipe construction (left) and two types of single pipe constructions (middle and right).

The foam thermal conductivity of the foam can be described as the sum of the three main mechanisms (equation 4.2). The cell gas conduction is time dependent due to the change of cell gas composition as a result of diffusion. All mechanisms are temperature dependent, but this dependency is more pronounced for cell gas conduction and radiation.

$$\lambda_{foam}(t) = \lambda_{gas}(t) + \lambda_{pol} + \lambda_{rad} \quad (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}) \quad (4.2)$$

- where
- λ_{foam} total thermal conductivity of the foam
 - λ_{gas} thermal conductivity due to gas conduction
 - λ_{pol} thermal conductivity due to conduction in the polymer matrix
 - λ_{rad} thermal conductivity due to radiation

Convection only occurs if the temperature is low, the temperature gradient very high and the cell size exceeds 5 mm [Isberg 1988]. Convection is normally negligible in the PUR foam used in district heating pipes and in the studied PET foam qualities, due to their small cell sizes [Isberg 1988] and [IV]. If the cell gas pressure is high, the blowing agent may partially be present as a condensed liquid in the foam cells. The total volume of this liquid is very small and conduction in the liquid can thus be disregarded.

4.2.1 Radiation and conduction in the polymer matrix

Radiation

The thermal conductivity due to radiation, λ_{rad} , in a polymeric foam takes place in all directions from the surface of the cells, with the net energy transfer from the hot to the cold side. The process involves several mechanisms (scattering, reflection, emission and absorption) [Glicksman 1987, Glicksman 1997, Placido 2005]. The radiative heat flow is strongly dependent on the temperature. Other factors that influence λ_{rad} are the radiative properties of the cell walls and the cellular structure, such as cell shape, void fraction, surface area to volume ratio of the cells, distribution of the cell sizes around the mean value, fraction of the polymer material in walls between two cells and fraction of polymer material in struts (the region of thicker walls between three cells) [Glicksman 1997]. Generally λ_{rad} decreases with smaller cell size [Glicksman 1997, Wu 1999b]. In a one-dimensional case, the Rosseland equation can describe the radiative heat transfer (equation 4.3) [Siegel 2001]. The extinction coefficient, K , describes the overall absorption ability of the material.

$$\lambda_{rad} = \frac{16}{3K} \cdot \sigma \cdot T^3 \quad (4.3)$$

where	K	extinction coefficient	(m^{-1})
	σ	Stefan Boltzman's constant	($5.7 \cdot 10^{-8} W \cdot m^{-2} \cdot K^{-4}$)
	T	mean foam temperature	(K)

Several models have been developed to calculate the extinction coefficient. The fact that the cell walls in polymeric foams are transparent to infrared radiation, while the thicker polymeric material of the struts functions as a barrier to the radiation is taken into account in an advanced model of the extinction coefficient for cellular foams [Glicksman 1991a, Glicksman 1997]. Experimental measurements of low density PUR foams (about $30-50 kg \cdot m^{-3}$), where the cell size parameters were determined by scanning electron microscopy (SEM), show very good agreement with the model [Eeckhaut 1996]. The coefficients describing the cell morphology and the absorption ability of the solid polymer included in the model may differ between PET and PUR foam.

Based on Glicksman's theory and experimental measurements, Nielsen developed a simplified model for the extinction coefficient of rigid PUR foams qualities used in district heating pipes (equation 4.4) [Nielsen 1998].

$$K = \rho_{foam} \cdot \left(0.0878 \cdot \frac{1}{d \sqrt{\rho_{foam}}} + 3.76 \right) \quad (4.4)$$

where	ρ_{foam}	foam density	($kg \cdot m^{-3}$)
	d	cell diameter	(m)

Olsson suggested a relationship between the extinction coefficient and foam density, based on literature data for PUR foam of densities between 20 kg·m⁻³ and 60 kg·m⁻³, (equation 4.5) [Olsson 1998].

$$K = 1700 + 70 \cdot (\rho_{foam} - 30) \quad (4.5)$$

Conduction in the polymer matrix

The contribution to the heat flow due to conduction in the foam matrix, λ_{pol} , depends both on the thermal conductivity of the solid polymer material and the amount and distribution of the material, such as the fraction of solid in the struts and the distribution of cell sizes of the foam [Glicksman 1997]. Glicksman proposes a model for closed cell foams based on the assumption of cubic cells (equations 4.6-4.8) [Glicksman 1989].

$$\lambda_{pol} = \left(\frac{2}{3} - \frac{f_s}{3} \right) \cdot (1 - f_g) \cdot \lambda_{pol}^{solid} \quad (4.6)$$

$$f_s = \left(\frac{\rho_{pol}^{solid}}{\rho_{foam}} \right) \cdot \left(\frac{8.62}{d^2} \right) \cdot A_{strut} \quad (4.7)$$

$$f_g = \frac{\rho_{pol}^{solid} - \rho_{foam}}{\rho_{pol}^{solid} - \rho_{gas}} \approx 1 - \frac{\rho_{foam}}{\rho_{pol}^{solid}} \quad (4.8)$$

where f_s	fraction of solid material in the struts	(-)
f_g	void/gas fraction of the foam	(-)
λ_{pol}^{solid}	thermal conductivity of the solid polymer	(W·m ⁻¹ ·K ⁻¹)
ρ_{pol}^{solid}	density of the solid polymer	(kg·m ⁻³)
	($\rho_{PET} = 1380 \text{ kg·m}^{-3}$, $\rho_{PUR} = 1200 \text{ kg·m}^{-3}$)	
ρ_{foam}	density of the foam	(kg·m ⁻³)
ρ_{gas}	density of the cell gas	(kg·m ⁻³)
A_{strut}	mean cross-sectional area of a strut	(m ²)
d	mean foam cell diameter	(m)

Nielsen derived a model for heat conduction in PUR foam that assumes a different distribution of heat conduction in the cell walls and struts compared to Glicksman (equation 4.9) [Nielsen 1998]. Comparison with experimental values showed that the model is suitable for foams with a void fraction of over 0.9 which represents PUR foam densities below 120 kg·m⁻³.

$$\lambda_{pol} = (0.48 \cdot f_s + 0.66 \cdot (1 - f_s)) \cdot (1 - f_g) \cdot \lambda_{polymer}^{solid} \quad (4.9)$$

The mean foam cell diameter and the area of the struts can be determined by SEM of a two-dimensional cross-section of the foam. The characteristics of the foam are often calculated by modelling the cells as pentagonal dodecahedrons [Glicksman 1997, Placido 2005]. A majority of the solid polymer in PUR foam is in the struts, but the amount varies with foam density and the blowing agent used. In studies by

Biedermann et al., the strut fraction of closed cell PUR foams from district heating pipes with densities close to $60 \text{ kg}\cdot\text{m}^{-3}$ was 92-95 % [Biedermann 2001a, Biedermann 2001b].

Comparison of PET and PUR foam

The thermal conductivity of solid PUR polymer (λ_{PUR}) from district heating pipes was determined by Nielsen et al. to $0.21 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at $23 \text{ }^\circ\text{C}$, with a linear increase with increased temperature of $0.2 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}\cdot\text{C}^\circ$ between $0 \text{ }^\circ\text{C}$ and $150 \text{ }^\circ\text{C}$ [Nielsen 2000]. Literature values of the thermal conductivity of solid PET polymer (λ_{PET}) are similar to λ_{PUR} . The type of PET (molecular weight and structure) and the degree of crystallinity have been shown to affect λ_{PET} . Depending on the molecular properties, Valcárcel et al. showed that λ_{PET} can either decrease or increase with increased degree of crystallinity [Valcárcel 1999]. Choy et al. determined λ_{PET} for a crystallinity of 40 % to about $0.22 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at room temperature. The carbon dioxide blown PET foams studied in **IV** had a similar degree of crystallinity (35-37 %). Other reported values of λ_{PET} at $20 \text{ }^\circ\text{C}$ are $0.19 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for both amorphous and post consumer material [Chen 1977, Lopez 2004]. A linear relation fitted to the values reported for the post consumer PET between $20 \text{ }^\circ\text{C}$ and $100 \text{ }^\circ\text{C}$, shows a decrease with increased temperature of $0.5 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}\cdot\text{C}^\circ$ [Lopez 2004]. According to equations 4.6-4.8 and given assuming that λ_{PET} and λ_{PUR} and the cell characteristics are approximately the same, λ_{pol} for PET and PUR foam are similar.

Typically, the contribution to the thermal conductivity in PUR foam from λ_{rad} is about four times higher than from λ_{pol} for densities normally used in district heating pipes (about $70 \text{ kg}\cdot\text{m}^{-3}$) [Smits 1991]. For PUR foam qualities used in district heating pipes, smaller cells generally decrease λ_{rad} , while higher foam density provides a greater contribution to λ_{pol} [Glicksman 1991a, Glicksman 1991b, Olsson 1998]. Figure 4.3 shows a tendency towards increasing values with increasing density for the PET foam qualities studied in **III** and **IV** (cell size: 0.4-0.5 mm, densities 91-157 $\text{kg}\cdot\text{m}^{-3}$).

Assuming a typical PUR foam used in district heating pipes¹, equations 4.3, 4.4 and 4.9 give a contribution to $\lambda_{pol} + \lambda_{rad}$ of $9.8 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at room temperature. Based on previous measurements of foam thermal conductivities for PUR foam insulated district heating pipes, the contribution is approximated to about $10\text{-}12 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. The lowest value of $\lambda_{pol} + \lambda_{rad}$ in PET foam at room temperature was $14.4 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for a foam with the density of 120 kg (blown with HFC-152a) [**III**, **IV**].

The average cell diameter of the studied PET foams was determined to 0.4 - 0.5 mm and no dependency on density was observed. The cells in the foam with the lowest density ($91 \text{ kg}\cdot\text{m}^{-3}$) were, however, elongated in some regions. Biedermann et al. reported cell sizes of 0.13-0.43 mm for closed cell PUR foam (densities 57-63 $\text{kg}\cdot\text{m}^{-3}$) from district heating pipes [Biedermann 2001a]. If PET foam with lower density and smaller cells can be developed, it would be possible to achieve $\lambda_{rad} + \lambda_{pol}$ in the same range as for PUR foam in the district heating pipes produced today.

¹ Foam density: $70 \text{ kg}\cdot\text{m}^{-3}$, strut fraction: 92 %, cell diameter: 0.4 mm, λ_{pol} : $0.21 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at $23 \text{ }^\circ\text{C}$

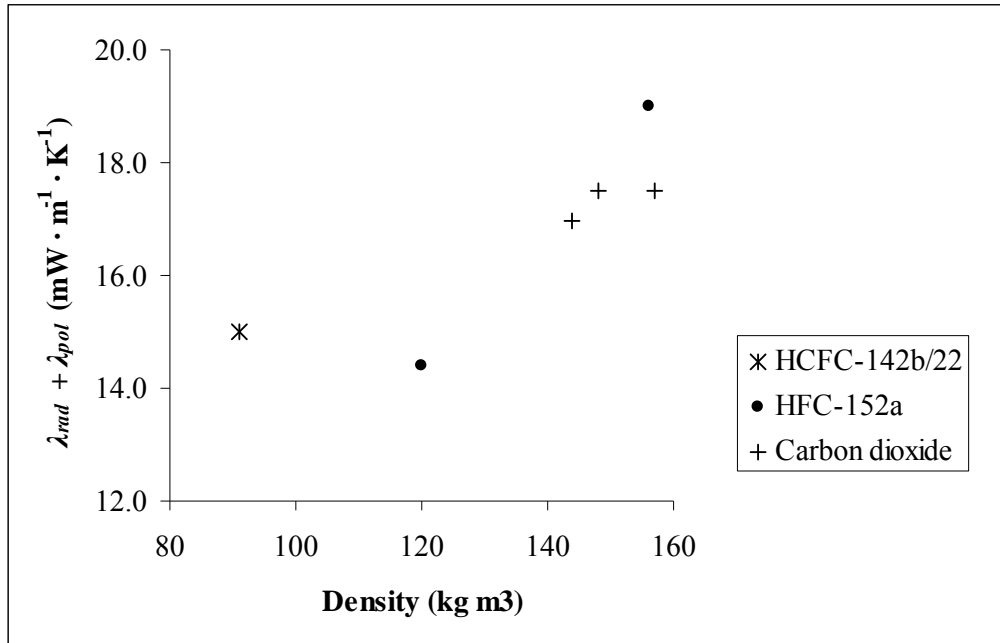


Figure 4.3 Approximate contributions to the foam thermal conductivity due to radiation and conduction in the solid polymer ($\lambda_{rad} + \lambda_{pol}$) at 25 °C in PET foam blown with HCFC-142b/22, HFC-152a and carbon dioxide (cell size 0.4-0.5 mm) [III,IV]. The values presented in III were recalculated using the Brokaw equation and gas thermal conductivities from [Albouy 1998] and [L'air liquide 1976].

4.2.2 Conduction in the cell gas

The foam thermal conductivity is strongly affected by the cell gas conductivity, λ_{gas} . In the studied PET foams (densities 91-157 kg·m⁻³), λ_{gas} contributed 45-60 % to the foam thermal conductivity [III, IV]. In PUR foam (densities 35-80 kg·m⁻³) it can account for up to 65-80% of the foam thermal conductivity [Olsson 1998]. In new foam, the cells mainly contain blowing agent.

Temperature dependency

The thermal conductivity of the gases increases with increasing temperature, which is illustrated for oxygen, nitrogen, carbon dioxide, HFC-245fa, HFC-365mfc and cyclopentane in figure 4.4. The thermal conductivities of cyclopentane presented in the literature show great variation. Values of between 11.3 and 13.8 m·W·m⁻¹·K⁻¹ have been reported at room temperature [Brodt 1995, Merten 1997]. In figure 4.4, cyclopentane data from four different references are shown: 10 °C from [Fleurent 1995], 25 °C from [Volkert 1995], 50 °C from [Takada 1999] and 62-145 °C from [Heinemann 2000], with a suggested polynomial formula fitted to the values.

The thermal conductivity of a gaseous compound at a certain temperature can be calculated according to several advanced models [Laesecke 1992, Marrucho 2003, Poling 2000]. In Reid et al. a simple model for calculating the thermal conductivity at a certain temperature, is presented (equation 4.10) [Reid 1977]. The accuracy between this model and literature values is higher for low temperature differences.

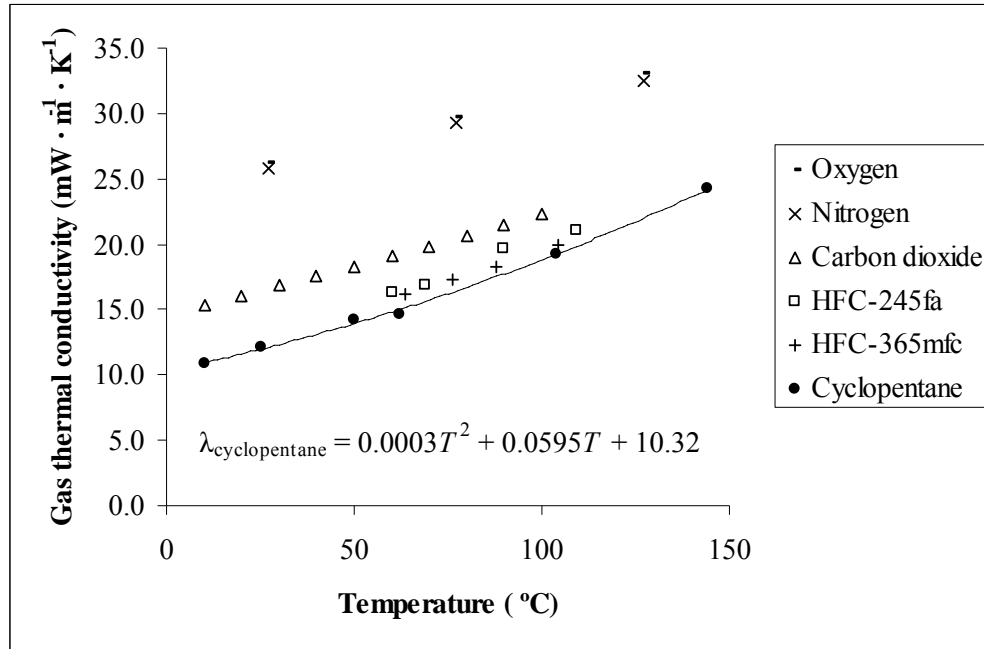


Figure 4.4 Temperature dependency of the gas thermal conductivity of nitrogen, oxygen, carbon dioxide [L'air liquide 1976], HFC-245fa [Dohrn 1999], HFC-365mfc [Marrucho 2002] and cyclopentane [Fleurent 1995, Heinemann 2000, Takada 1999, Volkert 1995].

$$\frac{\lambda_{T_1}}{\lambda_{T_2}} = \left(\frac{T_1}{T_2} \right)^{1.786} \quad (4.10)$$

where λ_{T_i} gas thermal conductivities at T_i ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)
 T_i temperatures (K)

Thermal conductivity of cell gas mixtures

Several models have been developed in order to calculate the thermal conductivity of cell gas mixtures at low pressures [Mason 1958, 1959, Merten 1997, Nielsen 1998, Poling 2000, Reid 1977]. Both the thermal conductivity of each gas component in the mixture and the interactions between the molecules must be taken into account. Difficulty in describing the thermal conductivity of the mixture occurs when one or more of the gases involved are polar. The Wassiljewa equation from 1904 is commonly used to calculate λ_{gas} (equation 4.11) [Reid 1977]. Equation 4.12 was derived by Wassiljewa for binary gas mixtures [Merten 1997].

$$\lambda_{gas} = \frac{\sum_{i=1}^m y_i \lambda_i}{\sum_{j=1}^m B_{ij} y_j} \quad (4.11)$$

$$B_{ij} = \frac{1}{\sqrt{2}} \left(\frac{s_i + s_j}{2s_i} \right)^2 \sqrt{\frac{M_i + M_j}{M_j}} \quad (\text{valid for binary gas mixtures}) \quad (4.12)$$

where	λ_{gas}	thermal conductivity of the gas mixture	$(W \cdot m^{-1} \cdot K^{-1})$
	λ_i	thermal conductivity of component i	$(W \cdot m^{-1} \cdot K^{-1})$
	y_i	molar fractions of component i	(-)
	B_{ij}	Wassiljewa function	(-)
	s_i	molecule diametre	(m)
	M_i	molecular mass of component i	$(g \cdot mol^{-1})$

Mason and Saxena proposed a modified equation where the gas viscosities also are taken into account (equation 4.13) [Reid 1977]. Sometimes an equation for B_{ij} based on critical temperatures and pressures are used [Poling 2000].

$$B_{ij} = \frac{\left[1 + \left(\frac{\eta_i}{\eta_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2}{\left[8 \cdot \left(1 + M_i / M_j \right) \right]^{1/2}} \quad (4.13)$$

where η_i gas viscosity of component i (Pa·s)

Lindsay and Bromley's equation also includes the boiling temperature of the components [Reid 1977]. Brokaw suggested an empirical model (equation 4.14) [Reid 1977]. As an approximation of the cell gas mixtures in PUR insulating foams, Isberg proposed a simplification of the Brokaw equation, where the Brokaw coefficient is set to 0.5. This model is very accurate for mixtures of air and CFC-11 (equation 4.15) [Isberg 1988].

$$\lambda_m = q \cdot (y_1 \cdot \lambda_1 + y_2 \cdot \lambda_2) + (1-q) \cdot (y_1 / \lambda_1 + y_2 / \lambda_2)^{-1} \quad (4.14)$$

where q the Brokaw coefficient

$$\lambda_{gas} = 0.5 \cdot \left(\sum_{i=1}^n y_i \lambda_i + \frac{1}{\sum_{i=1}^n \frac{y_i}{\lambda_i}} \right) \quad (4.15)$$

In the extended corresponding states theory (ECST), the thermal conductivity is expressed as the sum of energy transfer due to translation effects and internal degrees of freedom [Marrucho 2005].

Thermal conductivity properties of cyclopentane and HFC-365mfc

Merten and Rotermund compared thermal conductivities of mixtures various blowing agents and carbon dioxide or air measured at 40 °C with values calculated by models from the literature (Wassiljewa, Mason and Saxena, Lindsay and Bromley and Brokaw) [Merten 1997]. It was concluded that the models can deviate considerably from measurements. The mean deviations from the measured values of mixtures of cyclopentane and carbon dioxide were 0.14 to 0.50 $mW \cdot m^{-1} \cdot K^{-1}$. The Brokaw

equation gave the highest deviation. In mixtures with air the deviation was 0.73 to 0.75 $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Marrucho et al. also found deviations between measured thermal conductivities of mixtures of cyclopentane and nitrogen and calculated values based on ECST [Marrucho 2005]. It is obvious that the thermal conductivities of some gas mixtures are difficult to predict with existing models. When accurate values are required, measured values should be used.

The measured gas thermal conductivities of HFC-365mfc and cyclopentane at 40 °C in mixtures with carbon dioxide and air are shown in figure 4.5 [Merten 1997]. The higher vapour pressure of HFC-365mfc compared to cyclopentane makes it possible to obtain a higher fraction for HFC-365mfc (up to 63 % at 25 °C) than for cyclopentane (up to 42 % at 25 °C) [Chemnetbase 2005, Marrucho 2002]. Consequently, it is possible to achieve a lower gas thermal conductivity for the mixture of air with HFC-365mfc than with cyclopentane (upper lines in figure 4.5). The gas thermal conductivity of the carbon dioxide and HFC-365mfc mixture will, however, always be approximately the same or higher than that of cyclopentane (lower lines in figure 4.5). The concentration of carbon dioxide is high in new PUR foam, but its rate of diffusion out of the foam is more rapid than the inward diffusion of air and the outward diffusion of blowing agent. According to Merten and Rotermund's measurements new foams blown with carbon dioxide and a high amount of HFC-365mfc could thus have the same or higher cell gas thermal conductivity as a cyclopentane blown foam. When the carbon dioxide has left the foam, the cell gas thermal conductivity of the HFC-365mfc blown foam could become lower than that of the cyclopentane blown foam.

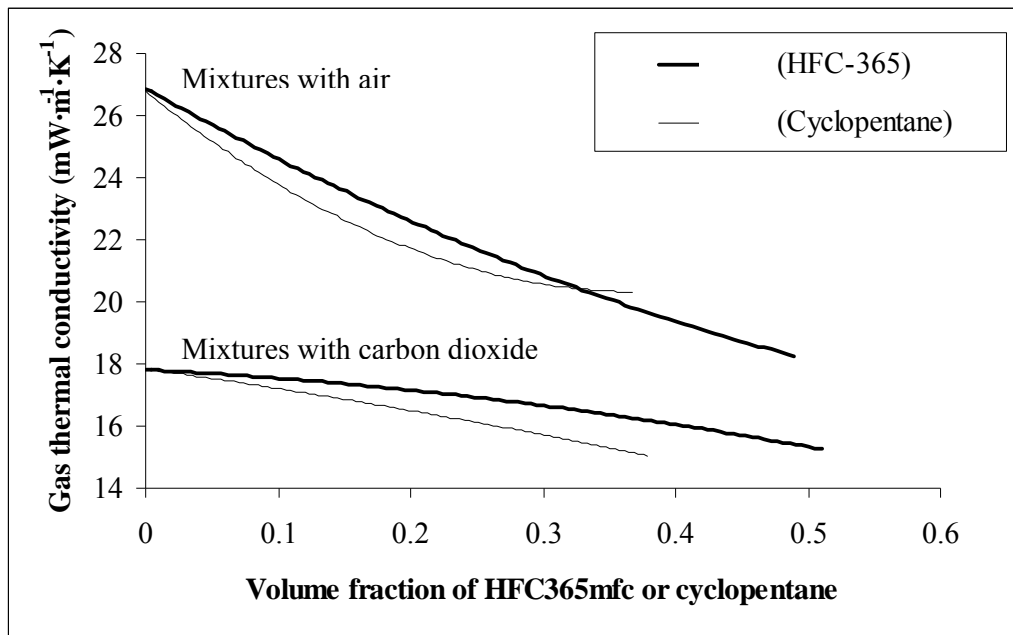


Figure 4.5 Thermal gas conductivity for HFC-365mfc and cyclopentane in mixtures with air and carbon dioxide at 40 °C (mixtures prepared at 25 °C) The figure is based on tables 2, 6 and 7 and figures 5, 12 and 14 in [Merten 1997].

4.3 Long-term thermal performance of district heating pipes

4.3.1 Changes in thermal conductivity over time

The increase in λ_{foam} over time in a closed cell polymer foam is caused by the change in the cell gas mixture due to diffusion, which is exemplified for PUR foam in figure 4.6 [I-IV]. In both PET and PUR foam, carbon dioxide leaves the foam faster than air (oxygen and nitrogen) enters it [I,III,IV]. The diffusion of physical blowing agents (e.g. cyclopentane or HFCs) out of the foam is comparatively slow [I-III]. The thermal conductivity of air at 25 °C is about $26 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is considerably higher than that of the blowing agents (carbon dioxide: 16.4, cyclopentane: 12.1-13.8, HFC-365mfc: $10.6 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). The diffusion process thus lead to an increase in λ_{foam} until the whole foam is completely filled with air and devoid of blowing agent. The time required to complete the process depends on the initial cell gas composition as well as on the characteristics of the foam, e.g. density and degree of crystallinity [I-IV]. The HDPE casing of PUR foam insulated district heating pipes has been found to affect the diffusion rate of some gases, by acting as a barrier [I,II]. Thus, in order to determine the thermal aging of a district heating pipe, the transport of cell gases both in the insulating foam and the casing material must be taken into account.

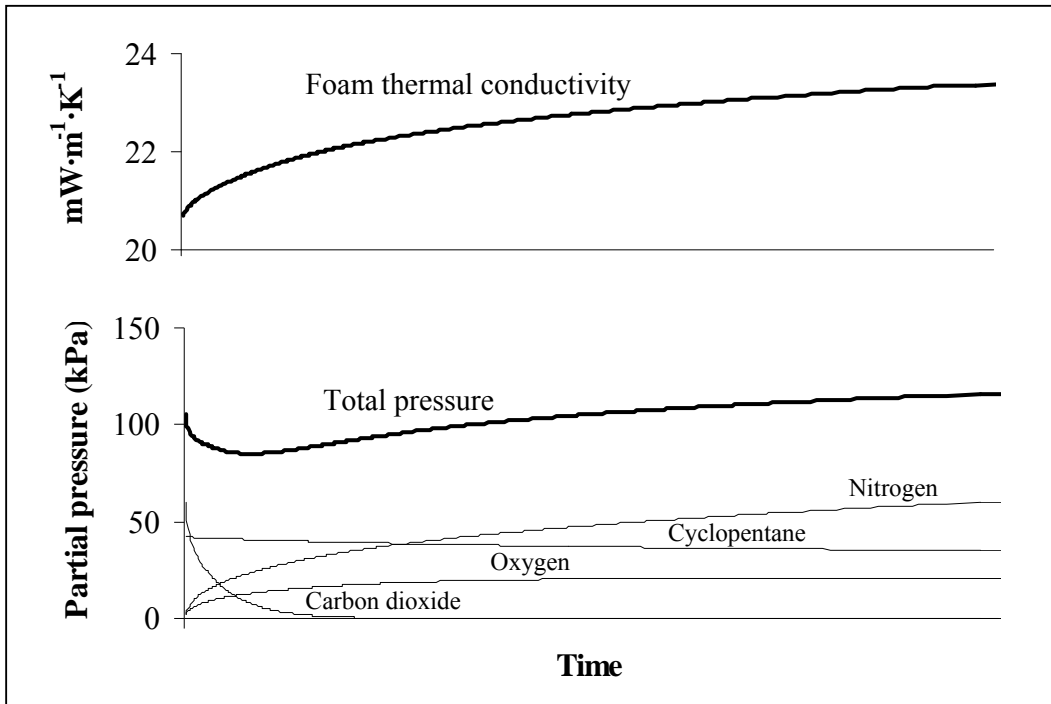


Figure 4.6 The partial pressure changes of cell gases in a PUR foam slab due to diffusion (lower graph) and its effect on λ_{foam} (upper graph) at room temperature.

A fraction of the cell gases are present dissolved in the polymer matrix and as liquid in the cells if the vapour pressure of the gas is exceeded. The fraction of blowing agent starts to decrease after excess liquid has evaporated and diffused out of the foam. Liquid blowing agent can act as a buffer, slowing down the process of deterioration of the insulating capacity of the foam. The cell gas content in newly produced PUR foam insulated district heating pipes from various producers was analysed in a study initiated by the Swedish district heating association. Up to 45 % by weight of the cyclopentane content in the foam cells was present as liquid in the foam cells.

4.3.2 Mass transport in polymeric membranes

Mass transport in polymeric materials is a complex process, where the materials and/or the penetrating molecules can interact in different ways, causing disturbances that complicates a description of the process by means of theoretical models [Rogers 1986]. Experimentally determined parameters describing diffusion of a gas are only valid for a specific polymer with its unique molecular characteristics (degree of crystallinity, polymer chain length and branching etc.) and the amount of additives that may be present. The situation becomes even more complicated when the polymer has a closed cell structure, but several models have been developed to experimentally determine and theoretically describe such cases [Brodt 1995, du Cauzé de Nazelle 1995].

At a microscopic level, the diffusion process in insulating foam takes place from cell to cell through the thin membrane surrounding each cell. The casing material surrounding district heating pipes can also be considered as a membrane. The driving force behind the mass transport of a gas through a membrane is the partial pressure gradient of the gas over the membrane, with net mass transfer in the direction from the side with the highest partial pressure to the side with the lowest (figure 4.7). The total mass flow at a certain time of gas component i through an isotropic membrane, can be described by Fick's first law of diffusion (equation 4.16).

$$J_i = -P_{pol,i} \cdot \frac{\partial p_i}{\partial x} \quad (4.16)$$

1)	where J_i	mass flow	(mole·m ⁻² ·s ⁻¹)
	$P_{pol,i}$	polymer permeability coefficient	(mole·m ⁻¹ ·s ⁻¹ ·Pa ⁻¹)
	p_i	partial pressure	(Pa)
	x	distance in the direction of the diffusion	(m)

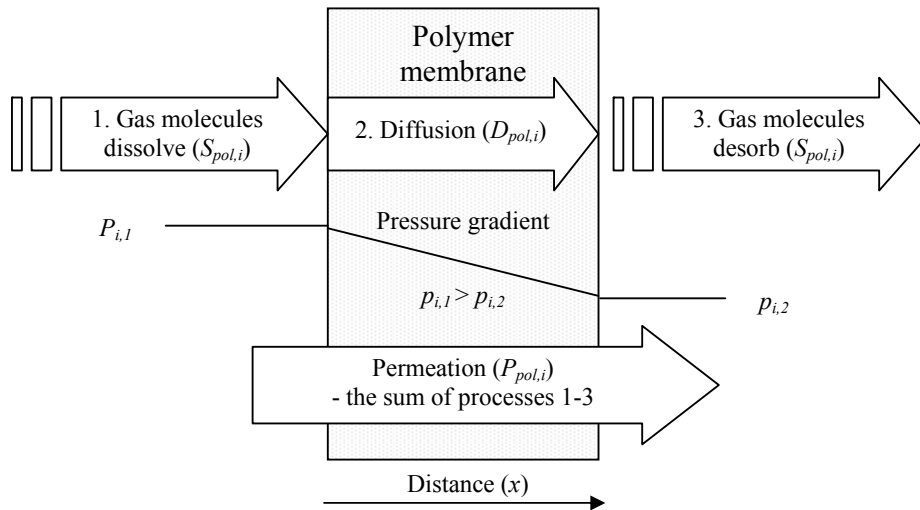


Figure 4.7 Permeation of gas component i through a polymer membrane.

Permeation can be divided into a three-stage process [Rogers 1986]. At first the gas is dissolved at the surface of the membrane, a process that is characterized by the polymer solubility coefficient ($S_{pol,i}$). The dissolved gas diffuses through the membrane, described by the polymer diffusion coefficient ($D_{pol,i}$). The diffusion step can be considered as a sequence of small jumps, each involving a potential barrier. The surrounding polymer chain segments are rearranged in each step, which involves a number of van der Waal interactions. Finally, the gas molecules desorb from the other side of the membrane surface. Under ideal conditions, the dissolved gas at the boundary of the membrane is in equilibrium with the gas outside the membrane, as described by Henry's law (equation 4.17). The permeability coefficient is the product of the solubility and the diffusion coefficients (equation 4.18). Fick's first law of diffusion can thus be rearranged into equation 4.19. All coefficients are specific for every penetrant in a given polymer.

$$c_{pol,i} = S_{pol,i} \cdot p_i \quad (4.17)$$

$$P_{pol,i} = S_{pol,i} \cdot D_{pol,i} \quad (4.18)$$

$$J_i = -D_{pol,i} \cdot \frac{\partial c_{pol,i}}{\partial x} \quad (4.19)$$

where

$c_{pol,i}$ concentration of gas in the polymer (at the membrane surface) ($\text{mole} \cdot \text{m}^{-3}$)

p_i partial pressure (outside the membrane surface) (Pa)

$S_{pol,i}$ polymer solubility coefficient ($\text{mole} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$)

$D_{pol,i}$ polymer diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$)

The change in the concentration of a penetrant at any point within the membrane is given by Fick's second law of diffusion (equation 4.20). In this differential equation the diffusion coefficient is a constant and thus independent of time, distance and concentration of the sorbed penetrant.

$$\frac{\partial p_i}{\partial t} = -D_{pol,i} \cdot \frac{\partial^2 p_i}{\partial x^2} \quad (4.20)$$

These mathematical descriptions of the diffusion process assume homogeneous materials and do not take into account the normal variations in the structures of a polymeric material. Often the diffusion coefficient is not constant. A common case is that $D_{pol,i}$ is dependent on the concentration of the sorbed penetrant in the polymer, (equation 4.21) [Rogers 1986].

$$\frac{\partial p_i}{\partial t} = \frac{\partial}{\partial x} \left(-D_{pol,i}(c_{pol,i}) \cdot \frac{\partial p_i}{\partial x} \right) \quad (4.21)$$

The equation can be rewritten as equation 4.22. By performing experiments within small intervals of $c_{pol,i}$, the second term in the equation can be omitted [Rogers 1986]. The concentration dependency can then be obtained from several mean diffusion coefficients determined over each interval.

$$\frac{\partial p_i}{\partial t} = -D_{pol,i}(c_{pol,i}) \frac{\partial^2 p_i}{\partial x^2} - \left(\frac{\partial D_{pol,i}(c_{pol,i})}{\partial x} \cdot \frac{\partial p_i}{\partial x} \right) \quad (4.22)$$

Another approach often used to describe diffusion in polymers is the free-volume theory, originally presented by Cohen and Turnbull in 1959 and developed by several researchers since then [Duda 1996]. In these models, the polymer volume can be divided into an occupied and a free part that is created by thermal fluctuations, through which molecules can penetrate. Generally, an increase in temperature provides energy for enhanced movement of the polymer segments, which can also be described as an enlargement of the total free-volume [Rogers 1986].

If the diffusion is assumed to follow Fick's and Henry's laws, the temperature dependency of $P_{pol,i}$, $S_{pol,i}$ and $D_{pol,i}$ can be described by Arrhenius types of relationships (equations 4.23-4.25), where E_P , E_S and E_D are the activation energies [Rogers 1986].

$$P_{pol,i} = P_0 \cdot \exp\left[\frac{-E_P}{R \cdot T}\right] \quad (4.23)$$

$$S_{pol,i} = S_0 \cdot \exp\left[\frac{-E_S}{R \cdot T}\right] \quad (4.24)$$

$$D_{pol,i} = D_0 \cdot \exp\left[\frac{-E_D}{R \cdot T}\right] \quad (4.25)$$

where P_0, S_0, D_0 , pre-exponential factors
 E_P, E_S, E_D activation energy for each process (J·mole⁻¹)
 R the gas constant (J·K⁻¹·mole⁻¹)
 T temperature (K)

Deviations occur when other factors affect the mobility of the polymer chains, such as interactions between the penetrant and the polymer or between penetrants, increased mobility at the glass transition or melting temperature and defective structures such as voids and microcracks [Lewis 2003, Rogers 1986].

4.3.3 Mass transport in closed cell polymeric foams

Mass transport in a closed cell foam involves permeation through the cell walls as well as transport within the cell voids and is dependent both on the properties of the gas and on the structural characteristics of the foam e.g. foam density, cell size distribution, cell elongation, cell orientation and the thickness of the cell walls [Brodth 1995, du Cauzé de Nazelle 1995]. The overall mass transfer of gas component i in the foam can be characterized by the effective diffusion coefficient ($D_{eff,i}$) and the effective permeability coefficient ($P_{eff,i}$) are used if the foam is assumed to be a homogeneous material. Models of diffusion in closed cell foams can be divided into two categories: continuous and discrete [Alsoy 1999]. The models presented below are one dimensional, but can easily be extended to more dimensions. The temperature dependency of $P_{eff,i}$ and $D_{eff,i}$ can be assumed to follow the Arrhenius relationships in the same way as $P_{pol,i}$ and $D_{pol,i}$ (equations 4.23 and 4.25).

In the continuum approach, which was first developed by Francis J. Norton in 1967, the foam is considered as a homogeneous, continuous medium [du Cauzé de Nazelle 1995, Fröling 2002a, Norton 1967, Olsson 2001a]. The model is based on the following assumptions:

1. The effective diffusion coefficient of each gas in the polymer ($D_{pol,i}$) is independent of its respective concentrations in the polymer. Thus a linear concentration gradient across the cell walls is assumed and both Fick's law and Henry's are valid.
2. The diffusion processes of the different gases are independent of each other.
3. No pores exist in the cell walls
4. The mass storage capacity of the gas in the foam is represented exclusively by the storage capacity of the cell voids, i.e. no gas is considered to be dissolved in the polymer.

Fick's first and second laws with the effective diffusion and permeability coefficients (equations 4.26 and 4.27) can then describe the mass transport of a gas in the foam, analogous with the theory for mass transport through a membrane described in chapter 4.4.1. The relationship between the coefficients is described by equation 4.28.

$$J_i = -D_{eff,i} \cdot \frac{\partial c_i}{\partial x} = -P_{eff,i} \frac{\partial p_i}{\partial x} \quad (4.26)$$

$$\frac{\partial p_i}{\partial t} = -D_{eff,i} \cdot \frac{\partial^2 p_i}{\partial x^2} \quad (4.27)$$

$$P_{eff,i} = S_{void,i} \cdot D_{eff,i} \quad (4.28)$$

where	$D_{eff,i}$	effective diffusion coefficient	$(m^2 \cdot s^{-1})$
	$P_{eff,i}$	effective permeability coefficient	$(mole \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1})$
1)	c_i	cell gas concentration of component i	$(mole \cdot m^{-3})$
	p_i	cell gas pressure of component i	(Pa)
	$S_{void,i}$	“solubility” in the cell voids, $=1/(R \cdot T)$	$(mole \cdot m^{-3} \cdot Pa^{-1})$

The membrane permeation model describes the diffusion as a cell to cell process that follows Fick's law [Brodt 1995, du Cauzé de Nazelle 1995, Norton 1982]. Different models of the foam structure can be used, from simple cubic cell structures to modelled networks of polyhedrons with imperfections [du Cauzé de Nazelle 1995].

Equation 4.29, which is derived from the mass balance of one cell, may be used to calculate D_{eff} , where a geometrical factor F_{geo} , summarizes the structural properties of the foam [Bart 1993, Brodt 1995]. A minimum of F_{geo} is obtained by assuming that the polymer material is distributed as plane sheets, which gives equation 4.30 [Brodt 1995]. More advanced F_{geo} can be calculated by modelling the cells as spheres, cubes or truncated octahedrons [Brodt 1995, du Cauzé de Nazelle 1995]. Equation 4.31 displaces the case of truncated octahedrons [Brodt 1995].

$$D_{eff,i} = \frac{D_{pol,i} \cdot S_{pol,i} \cdot F_{geo}}{f_g / (RT) + (1 - f_g) \cdot S_{pol,i}} \quad (4.29)$$

$$F_{geo,min} = \frac{1}{1 - f_g} = \frac{d}{m} \quad (4.30)$$

$$F_{geo} = \frac{3.69}{1 - f_w f_g} \quad (4.31)$$

where	$D_{eff,i}$	effective diffusion coefficient in the foam	($m^2 \cdot s^{-1}$)
	$D_{pol,i}$	diffusion coefficient in the polymer	($m^2 \cdot s^{-1}$)
	$S_{pol,i}$	solubility coefficient in the polymer	($mole \cdot m^{-3} \cdot Pa^{-1}$)
	F_{geo}	geometrical factor	(-)
	R	gas constant = 8.314	($Pa \cdot m^3 \cdot mole^{-1} \cdot K^{-1}$)
	T	temperature	(K)
	f_g	void/gas fraction of the foam	(-)
	f_w	fraction of polymer in the struts	(-)
	d	cell diameter	(m)
	m	membrane thickness	(m)

The membrane permeation model and the continuum model can be combined. If the cell gases are considered ideal, the relationship between the effective diffusion coefficient and the effective permeability coefficient can be written according to equation 4.32. In the case of insulating foams, the void fraction is often close to 1, since the volume of the polymer is very small. Equation 4.29 can then be reduced to equation 4.33. Combining equations 4.32 and 4.33 yields an approximate expression for calculating P_{eff} from the polymer diffusion and solubility coefficients as well as the geometrical coefficient (equation 4.34).

$$D_{eff,i} = P_{eff,i} \cdot R \cdot T \quad (4.32)$$

$$D_{eff,i} = D_{pol,i} \cdot S_{pol,i} \cdot F_{geo} \cdot R \cdot T \quad (4.33)$$

$$P_{eff} = D_{pol} \cdot S_{pol,i} \cdot F_{geo} \quad (4.34)$$

Applying equation 4.34 to equation 4.29 eliminates F_{geo} . Rearrangement of the equation produces an equation for P_{eff} , where the first product originates from the gas in the voids and the second from the gas dissolved in the polymer matrix (equation 4.37).

$$P_{eff,i} = D_{eff,i} \left[\frac{f_g}{R \cdot T} + S_{pol,i}(1 - f_g) \right] \quad (4.35)$$

There are controversies about the type of models that should be used to determine effective diffusion coefficients in closed cell polymer foams. Attempts have been made to compare the discrete models with experimental data from the literature, in order to determine their validity [Alsoy 1999, Pilon 2000]. Discrepancies have been revealed, but it should be borne in mind that the diffusion coefficients are very much dependent on the characteristics of the polymer [Pilon 2000]. In the case of PUR foam, many different polyols and isocyanates can be used, but the types of precursors used are rarely specified in the literature. It is argued that the discrete models fail to correctly describe the diffusion process for the heavier blowing agents due to their deviations from Henry's law. Therefore a discrete unsteady-state model taking the concentration dependency into account was suggested by [Alsoy 1999].

4.3.4 Study of mass transport in PET and PUR foam

The effective diffusion coefficients of the cell gases in insulating foams can be determined by measuring the change in partial pressures over time and applying the commonly used diffusion theories [Svanström 1997b]. This method (described below) was used in **I-IV** to determine D_{eff} for air and blowing agents in PET and PUR foams. Other methods for the determination of D_{eff} are measurements of the changes in foam thermal conductivity [Booth 1996]; indirect sorption experiments where the pressure change in the atmosphere surrounding a sample is recorded [Brodt 1995, Brodt 1993, Mitalis 1991, Page 1992]; determination of the gas flow in a foam sample due to an imposed pressure gradient [Shankland 1990b]; and gravimetric studies [Booth 1996, Booth 1993, Cuddihy 1967]. The time needed to determine the diffusion process can be speeded up by reducing the size of the foam samples or increasing the temperature [Isberg 1988, Svanström 1997b].

Experimental procedures

The effective diffusion coefficients of the cell gases (carbon dioxide, oxygen, nitrogen and physical blowing agents) in PET and PUR foam were determined by means of aging experiments on foam cylinders (diameter 20.8 mm, length 40-65 mm), taken from foam slabs or district heating pipes [I-IV]. The cylinder ends were sealed by gluing aluminium plates with epoxy or by applying a mixture of beeswax and paraffin in order to prevent longitudinal diffusion. The cylinders were stored at different temperatures (23 °C, 40 °C, 60 °C and 90 °C) and the cell gas content was determined after different lengths of time using the experimental set up illustrated in figure 4.8 [Svanström 1997b].

Dinitrogen oxide was flushed through the system in order to remove all oxygen after which nitrogen and then the foam cylinders were ground and the released cell gases collected in a glass syringe. The composition of the gas was analysed by gas chromatography. Since the volume of the foam cylinder and the volume of the released cell gases at ambient pressure are determined, it is possible to calculate the partial pressure of all the cell gases in the foam. The experimental procedure on the PUR foam samples took place at the same temperature as that at which the sample was stored, so that the equilibrium between the gas dissolved in the polymer matrix and the gas in the cells would not be changed. Friction during grinding caused the PET foam samples to melt if the temperature during grinding was too high. All PET foam samples were therefore analysed at room temperature. This is not expected to have a significant influence on the results, since the solubility of cell gases in PET is low (table 4.2) [III].

The solution of Fick's second law for a foam cylinder (equation 4.27 for cylindrical coordinates) was used to calculate the change in mean partial pressure of the cell gases in a PUR cylinder (equation 4.36) [Svanström 1997b]. The effective diffusion coefficient for each gas and sample was determined by fitting a calculated curve to the experimentally determined partial pressure change.

$$\bar{p}_i = p_{0i} \sum_{j=1}^{\infty} \frac{4 \cdot \exp(-\beta_{0j}^2 \cdot D_{eff,i} \cdot t)}{(\beta_{0j} \cdot a)^2} \quad (4.36)$$

where	\bar{p}_i	mean partial pressure of component i	(Pa)
	p_{0i}	initial partial pressure of component i	(Pa)
	a	cylinder radius	(m)
	$\beta_{0j} \cdot a$	roots of the zero order Bessel function	(-)
	t	time	(s)

The concentration of blowing agent in the polymer was determined by placing a quantity of PUR and of PET foam powder from a previous cell gas analysis into steel containers and expose them to a high temperature (280 °C) [Holmgren 2004]. After cooling, the gas mixture in the container was analysed by gas chromatography. $S_{pol,i}$ was calculated according to Henry's law (equation 4.17) using the calculated concentration of the cell gas in the polymer and the partial pressure determined from the previous cell gas analysis. The solubility coefficient of cyclopentane in PET, which is not used as a blowing agent in PET foam today, was determined by exposing ground PET foam to a known partial pressure of cyclopentane in a vessel until equilibrium was reached. Thereafter the procedure described above was applied in order to determine the concentration of the cell gas in the polymer [III].

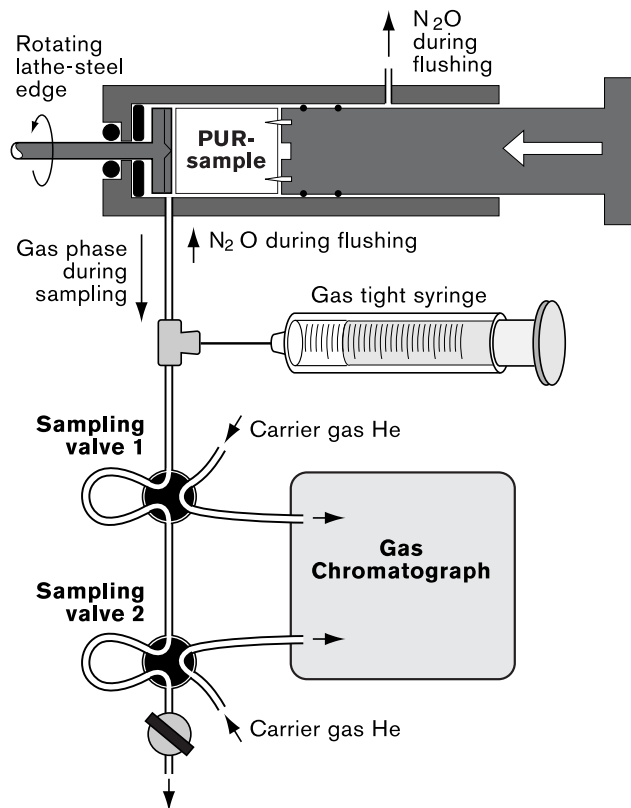


Figure 4.8 Experimental set up to determine the partial pressure of cell gases in PET and PUR foam.

Summary of results

The experimentally determined effective diffusion coefficients and activation energies based on the Arrhenius relationship in PUR and PET foams of different densities are shown in table 4.1 [I-IV]. Polymer solubility coefficients from experiments and the literature are presented in table 4.2. A review of literature values of effective diffusion coefficients in PUR foam for some blowing agents is presented in table 4.3.

All diffusion coefficients were determined for the first 100-3500 hours, depending on the diffusion rate. The shorter times were used for fast diffusing gases at high temperatures. Diffusion of oxygen, nitrogen and carbon dioxide in both PUR and PET foam and HCFCs in PET foam closely followed the theoretical diffusion model. Initially, a more rapid rate of diffusion than predicted by the theoretical model was obtained for cyclopentane and HFC-365mfc in PUR foam, possibly due to the interference of mechanisms other than diffusion. One explanation is the effects of the surface damage caused when the cylinders are taken from the foam slabs or district heating pipes.

Table 4.1 Experimentally determined effective diffusion coefficients (D_{eff}) and activation energies (E_D) for different cell gases in PUR and PET foam.

		Foam density $\text{kg}\cdot\text{m}^{-3}$		D_{eff} $\cdot 10^{-13} \text{ m}^2\cdot\text{s}^{-1}$				$E_{D_{eff}}$ $\cdot 10^3 \text{ J}\cdot\text{mole}^{-1}$
				23°C	40°C	60°C	90 °C	
PUR foam	Carbon dioxide	58-71	[I]	500		1300	14000 ^{a)}	40 ^{b)}
	Oxygen	58-71	[I]	150		650	4500 ^{a)}	40 ^{b)}
	Nitrogen	58-71	[I]	25		220	2000 ^{a)}	55 ^{b)}
	Cyclopentane	58-71	[I]	0.6	4	7	10 ^{a)}	35 ^{b)}
	HFC-365mfc	34-52	[III]	1.0				
PET foam	Carbon dioxide	157	[IV]	45	85	150	1000	25 ^{d)}
	Oxygen	157	[IV]	15	20	40	290	25 ^{d)}
	Nitrogen	157	[IV]	1.5	3.5	7.0	70	35 ^{d)}
	HCFC-22	91	[III]	1.7 ^{c)}				
	HCFC-142b	91	[III]	0.5 ^{c)}				

^{a)} New measurements from foam taken from a district heating pipe (foam density $58 \text{ kg}\cdot\text{m}^{-3}$).

^{b)} Calculated between 23 °C and 90 °C.

^{c)} Recalculated from [III], by taking a damaged outer layer of 0.4 mm into account.

^{d)} Calculated between 23 °C and 60 °C.

Long-term measurements of the partial pressure change of cyclopentane and HFC-365mfc in PUR foam cylinders (up to 16000 hours) showed deviations from the ideal diffusion model. Over time the diffusion seems to become increasingly slower. Lower diffusion coefficients would thus be obtained for a curve fitted to the values determined after long time compared to those presented in table 4.1. This may be caused by concentration or time dependency. Generally, the concentration dependency of diffusion coefficients in polymers increases with the size of the diffusing molecule [Duda 1996]. According to measurements by Hong et al., there are indications of lower diffusion and permeability coefficients in solid polyurethane with

decreasing concentration of blowing agent [Hong 2001]. In a study by Holmgren no relationship between the solubility coefficients of cyclopentane and the partial pressures of the gas in PUR foam cells was found [Holmgren 2004]. This was also the case in a small-scale study of HFC-365mfc in PUR foam [Mangs 2002].

Table 4.2 Solubility coefficients (10^{-3} mole·m⁻³·Pa⁻¹) at 23-25 °C in PUR and PET polymers.

	PUR	PET
Carbon dioxide	0.82-0.90 ^{a)}	1.33 ^{g)}
Oxygen	0.062 ^{a)}	0.058 ^{g)} ; 0.041 ^{h)}
Nitrogen	0.041 ^{a)}	0.076 ^{g)}
Cyclopentane	8.8 ^{b)} ; 11.4 ^{a)} ; 12.3 ^{c)} ; 18.5 ^{d)} ; 23.6 ^{d)}	2.4 ^[III]
HFC-365mfc	6.0 ^[III] ; 9.3 ^{e)} ; 9.7 ^{e)}	-
HCFC-22	1.8 ^{f)} ; 4.2 ^{e)}	0.4 ^[III]
HCFC-142b	4.0 ^{e)} ; 5.4 ^{e)}	0.5 ^[III]
HCFC-152a	3.8 ^{d)} ; 4.0 ^{d)}	0.3 ^[III]

a) [du Cauzé de Nazelle 1995]

b) [Holmgren 2004]

c) [Mangs 2002]

d) [Hong 2001]

e) [Hong 1998]

f) [du Cauzé de Nazelle 1995]

g) [Lewis 2003] Amorphous PET

h) [Liu 2004a] Amorphous PET

A literature review reveals great variations in the effective diffusion coefficients of carbon dioxide ($70-420 \cdot 10^{-13}$ m²·s⁻¹), oxygen ($40-700 \cdot 10^{-13}$ m²·s⁻¹) and nitrogen ($5.5-30 \cdot 10^{-13}$ m²·s⁻¹) in different types of PUR foams at 20-25 °C [Svanström 1997a]. The results of the present study are thus within this range (see table 4.1). The variations in the literature data may be due to the experimental method used as well as to the foam formulation and morphologies of each of the studied foams. The type of polyol in the PUR formulation has been shown to have a significant effect on both the diffusion and the solubility coefficient [Kaplan 1994].

Table 4.3 Effective diffusion coefficients of blowing agents at 20-25 °C in PUR foam published in the literature.

	Foam density kg·m ⁻³	D_{eff} ·10 ⁻¹³ m ² ·s ⁻¹	Reference
Cyclopentane	n.g.	0.5	[Thijs 1994]
	43-49	1-5	[Svanström 1997b]
	30.5	6.2	[Capella 1996]
	n.g.	8.3	[Bazzo 1994]
HFC-365mfc	n.g.	0.5	[Zipfel 1998]
	32-36	0.52	[Modesti 2005]
	n.g.	3.1	[Wu 1999a]
HFC-245fa	n.g.	0.39	[Wu 1999a]
	33-36	0.69-0.91	[Modesti 2005, Modesti 2004]
HCFC-22	n.g.	12	[Bazzo 1994]
	35	18	[du Cauzé de Nazelle 1995]
	n.g.	6.6-45	[Bhattacharjee 1995]
	n.g.	60	[Bart 1993]
HCFC-142b	n.g.	2.2	[Bazzo 1994]

n.g. = not given

Comparison of cyclopentane and HFC-365mfc in PUR foam

At room temperature, the determined effective diffusion coefficient of HFC-365mfc ($1.0 \text{ m}\cdot\text{s}^{-1}$) is about twice as high as that of cyclopentane ($0.6 \text{ m}\cdot\text{s}^{-1}$). It should be borne in mind that D_{eff} increases with decreasing foam density, since less material gives lower resistance to gas transport [Brodt 1995], and that the density of the studied HFC-365mfc blown foams ($34\text{-}52 \text{ kg}\cdot\text{m}^{-3}$) is lower than that of the cyclopentane blown foams ($58\text{-}71 \text{ kg}\cdot\text{m}^{-3}$).

Effective diffusion coefficients for cyclopentane in PUR foam found in the literature vary between 0.5 and $8.3\cdot 10^{-13} \text{ m}^2\cdot\text{s}^{-1}$ (table 4.3). The densities were though not given for all foams. The value of HFC-365mfc is similar to those reported by Zipfel et al. and Modesti et al., ($0.5\text{-}0.52 \text{ m}\cdot\text{s}^{-1}$) while the value given by Wu et al. is slightly higher ($3.1 \text{ m}\cdot\text{s}^{-1}$) [Modesti 2005, Wu 1999a, Zipfel 1998]. The diffusion coefficients of HFC-245fa presented in table 4.3 are similar to the HFC-365mfc values. Studies of the long-term thermal performance of HFC-245fa blown PUR foam report a slower or similar aging performance compared to that of cyclopentane blown PUR foam [Doerge 2001, Seifert 2003].

Despite the fact there are large discrepancies in the literature between the solubility coefficients for cyclopentane in PUR, these coefficients are all higher than those determined for HFC-365mfc (table 4.2). The value reported by Holmgren, which was achieved using the same procedure as for HFC-365mfc, is however similar. In one study, D_{pol} of HFC-365mfc in PUR polymer at $24 \text{ }^\circ\text{C}$ were determined to 3.2 and $4.4\cdot 10^{-16} \text{ m}^2\cdot\text{s}^{-1}$ [Hong 2001]. In the same study, the cyclopentane values were: 4.6 and $5.1\cdot 10^{-16} \text{ m}^2\cdot\text{s}^{-1}$. Two gases with similar S_{pol} , and D_{pol} , such as HFC-365mfc and cyclopentane will have about the same value of D_{eff} in foams with the same cellular structure (equation 4.29 and 4.33).

Comparison of PET and PUR foam

The determined effective diffusion coefficients of carbon dioxide, oxygen and nitrogen are about 10-30 times lower in PET foam than in PUR foam for all temperatures studied (table 4.1). The largest difference between the foams is obtained for nitrogen. In **IV** the changes in gas thermal conductivity over time for 35 mm thick carbon dioxide blown PET and PUR foam boards at different temperatures were calculated according to the determined diffusion coefficients. The calculated aging of the PET foam board was approximately 10 times slower than that of the PUR foam board. The density of the carbon dioxide blown PET foam for which D_{eff} were determined was high ($157 \text{ kg}\cdot\text{m}^{-3}$), which gives slower diffusion of gases and an unfavourably high contribution to λ_{foam} from conduction in the polymer matrix.

In order to predict the performance of carbon dioxide blown PET foam of lower density, a new study of the density dependency of the effective diffusion coefficients of carbon dioxide at 60°C was performed. Foam cylinders with a density of $123\text{kg}\cdot\text{m}^{-3}$ (HFC-152a blown) and $95\text{kg}\cdot\text{m}^{-3}$ (HCFC-142b/22 blown) were placed in a steel vessel with a constant slow flow of carbon dioxide. The cell gas composition of the

cylinders was determined after different lengths of time with the method described above, and a curve for the inward diffusion was fitted to the values. In figure 4.9 the determined effective diffusion coefficients for carbon dioxide are shown together with those determined for foam with a density of $157 \text{ kg}\cdot\text{m}^{-3}$ in **IV**. The oxygen and nitrogen values for foam densities of 120 and $157 \text{ kg}\cdot\text{m}^{-3}$ are from **III** and **IV**. The equations in the figure are approximations of the density dependency of the effective diffusion coefficients. Calculating an approximate value of D_{eff} for carbon dioxide in PET foam of a density of $60 \text{ kg}\cdot\text{m}^{-3}$ result in $1000\cdot 10^{-13} \text{ m}^2\cdot\text{s}^{-1}$, which is very similar to the experimentally determined value ($1300\cdot 10^{-13} \text{ m}^2\cdot\text{s}^{-1}$) of PUR foam with a density of $58\text{-}71 \text{ kg}\cdot\text{m}^{-3}$ [**I**]. The calculated values for oxygen and nitrogen in PET foam (240 and $30\cdot 10^{-13} \text{ m}^2\cdot\text{s}^{-1}$) are lower than those in PUR foam (650 and $220\cdot 10^{-13} \text{ m}^2\cdot\text{s}^{-1}$), although the former figures are more uncertain.

The effective diffusion coefficients of HCFC-22 ($1.7\cdot 10^{-13} \text{ m}^2\cdot\text{s}^{-1}$) and HCFC-142b ($0.5\cdot 10^{-13} \text{ m}^2\cdot\text{s}^{-1}$) were also determined for PET foam with a density of $91 \text{ kg}\cdot\text{m}^{-3}$. The literature values for these gases in PUR foam are 12 to $60\cdot 10^{-13} \text{ m}^2\cdot\text{s}^{-1}$ for HCFC-22 and $2.2\cdot 10^{-13} \text{ m}^2\cdot\text{s}^{-1}$ for HCFC-142b (table 4.3).

The solubility coefficients in table 4.2, which is a summary of both experimental studies and literature values, show a tendency towards lower values for the heavier blowing agents in PET compared to PUR, contributing to lowering the permeability of PET foam in accordance with diffusion theories (equations 4.33 and 4.34). The values of carbon dioxide and air are similar in PET and PUR. Dissolved blowing agent may act as a buffer, thus maintaining the concentration of blowing agent in the foam cells. However, high amounts of blowing agents in PUR foam lead to decreased compression strength of the foam according to [Singh 1998].

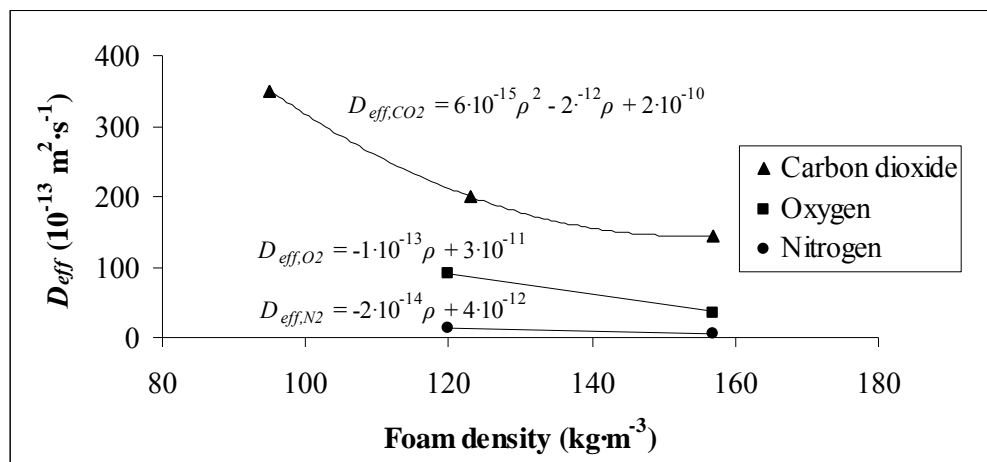


Figure 4.9 The effective diffusion coefficients of carbon dioxide, oxygen and nitrogen in PET foams of different densities (ρ) at $60 \text{ }^\circ\text{C}$. The values of carbon dioxide at $95 \text{ kg}\cdot\text{m}^{-3}$ and $123 \text{ kg}\cdot\text{m}^{-3}$ are from a new study while the other values are from **III** and **IV**.

The carbon dioxide blown PET foam of a density of $157 \text{ kg}\cdot\text{m}^{-3}$ had a degree of crystallinity of 35 % [II]. Studies on mass transport of oxygen in PET show that the diffusion, permeability and to some extent solubility coefficients decrease with increasing crystallinity [Hedenqvist 1996, Lin 2002, Liu 2004b, Natu 2005, Qureshi 2000, Sekelik 1999]. Including copolymers in PET can also reduce the gas transport in the polymer [Hibbs 2004, Polyakova 2001a, Polyakova 2001b, Sekelik 1999]. About 0.5 % talcum by mass is added to the foam formulation during PET foam production. Sekelik et al. has showed that P_{pol} , D_{pol} and S_{pol} of oxygen in PET with isophthalate copolymer is reduced when the amount of talcum in the polymer is increased [Sekelik 1999]. The mass transport properties of carbon dioxide and oxygen in PET are impaired if the polymer is oriented, as for example is the case in drawn or blown PET bottles [Lewis 2003, Liu 2004a, Liu 2004b, McGonigle 2001, Qureshi 2000].

Activation energies in PET and PUR foam

The activation energies of the diffusion coefficients of carbon dioxide, oxygen and nitrogen in PUR foam calculated in accordance with the Arrhenius relationship are higher in PUR than in PET foam (table 4.1). The diffusion coefficients at different temperatures and the curves calculated in accordance with the Arrhenius relationship are also shown in figure 4.10. The diffusion coefficients above the polymer glass transition temperatures (T_g), determined to $78 \text{ }^\circ\text{C}$ in the PET foam [I], were excluded from the calculations, since the apparent activation energy normally increases above T_g [Duda 1996]. In one study of the diffusion of carbon dioxide, oxygen and nitrogen in PET (35-46 % crystallinity), higher activation energies were obtained above than below T_g [Michaels 1963], similar to the PET foam presented in figure 4.10. Other studies of diffusion characteristics of carbon dioxide and air in PET and other polymers show similar results [Koros 1978, Yasuda 1977]. McBride et al. have studied the diffusion of carbon dioxide, oxygen and nitrogen in polyurethane block polymers and found discontinuities from the Arrhenius relationship around T_g [McBride 1979]. The glass transition temperature in PUR foam used for district heating pipes is probably above the studied interval [Bergström 1996].

4.3.5 Study of mass transport in HDPE casing materials

The diffusion coefficient of HFC-365mfc in HDPE was determined by storing a sample of HDPE casing in an atmosphere saturated with HFC-365mfc at 23°C and atmospheric pressure [II]. A calculated curve obtained by solving Fick's second law for an infinite slab was fitted to the measured weight increase, which gives a polymer diffusion coefficient of $0.23\cdot 10^{-13} \text{ m}^2\cdot\text{s}^{-1}$. The calculated curve asymptotically approaches a value of approximately 0.7 % by weight, and the solubility coefficient of HFC-365mfc in HDPE was calculated to $0.81\cdot 10^{-3} \text{ mole}\cdot\text{m}^{-3}\cdot\text{Pa}^{-1}$ based on this value.

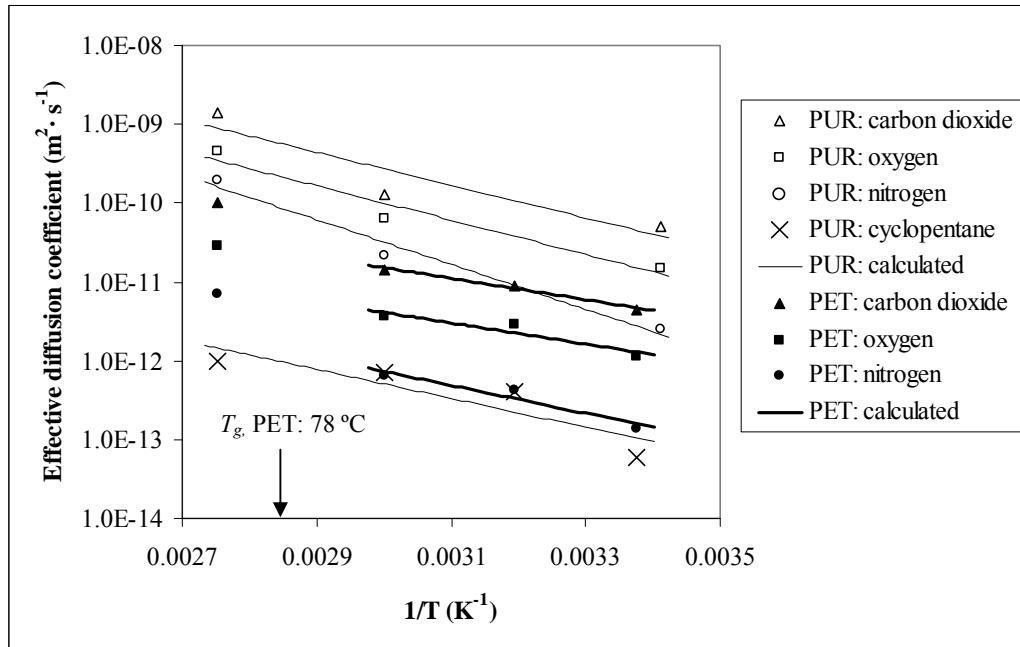


Figure 4.10 Effective diffusion coefficients of cell gases in PUR foam (density 58-71 kg·m⁻³) and PET foam (density 157 kg·m⁻³) at different temperatures. The lines were calculated assuming an Arrhenius relationship between 23 °C and 60 °C [I,III,IV]. The glass transition temperature (T_g) for the PET foam (78 °C) is indicated.

The procedure for determination of the diffusion and solubility coefficients of cyclopentane in HDPE was analogous with that of HFC-365mfc, although in this case the sample was removed from the saturated atmosphere, and the weight decrease due to desorption was measured [I]. The diffusion coefficient of cyclopentane in HDPE was also shown to increase with increasing cyclopentane content in the polymer. Therefore D_{eff} was determined for different contents of cyclopentane. For a cyclopentane content representative of a district heating pipe at 23 °C, D_{eff} was determined to $1 \cdot 10^{-13}$ m²·s⁻¹. The solubility coefficient was determined to $2.3 \cdot 10^{-3}$ mole·m⁻³·Pa⁻¹ by measuring the weight increase of HDPE samples stored for about one month in autoclaves containing a certain amount of cyclopentane.

A steady-state transmission method described in [Olsson 2001b], was used to determine the permeabilities of oxygen, nitrogen and carbon dioxide in HDPE at different temperatures (5-40 °C) [I].

4.3.6 Mass transport in district heating pipes

In order to evaluate the diffusion characteristics of different gases in district heating pipes insulated with PUR or PET foam, the influence of both the foam and the casing must be considered. The mass transfer resistance is a combination of the permeability coefficient of the gas component i in each material and the thickness of the material. The Biot number can be used to determine in which of the materials the dominating mass transfer resistance occurs, for a homogeneous foam slab and a polymer membrane [Brodt 1995]. If the Biot number for a gas component (equation 4.37), is equal to 1, it means that the resistance of that gas is the same in both materials. $Bi_i < 1$ means that the dominant resistance is found in the casing material, and $Bi_i > 1$ that the dominant resistance is in the polymer foam.

$$Bi_i = \frac{P_{pol,i}^{case} \cdot L_{foam}}{L_{case} \cdot P_{eff,i}^{foam}} \quad (4.37)$$

where	Bi_i	the Biot number for gas component i	(-)
	$P_{pol,i}^{case}$	permeability coefficient in casing material	(mole·m ⁻¹ ·s ⁻¹ ·Pa ⁻¹)
1)			
	$P_{eff,i}^{foam}$	permeability coefficient in the foam	(mole·m ⁻¹ ·s ⁻¹ ·Pa ⁻¹)
1)			
	L_{case}	casing thickness	(m)
	L_{foam}	foam thickness	(m)

Table 4.4 shows the permeability coefficients used to calculate the Biot numbers for different material combinations. The permeability coefficients in the table refer to a temperature of 20-25 °C. The temperature at the surface of a district heating pipe will be lower (about 15 °C) and there will be a temperature gradient across the foam (about 40-100 °C at the media pipe). For a district heating pipe in use, the P_{pol} values are thus lower and P_{eff} values higher than those in table 4.4. Higher P_{eff} value reduces the Biot number. A casing thickness of 3 mm and a foam thickness of 40 mm were assumed. The main barrier to mass transport of carbon dioxide, oxygen and possibly nitrogen in a district heating pipe insulated with PUR foam is in the HDPE casing material, while the foam has the highest resistance to cyclopentane and HFC-365mfc. In another study by Olsson et al., the determined permeabilities of gases in HDPE and PUR foam from district heating pipes show that the main resistance to carbon dioxide is in the casing, while for oxygen and nitrogen it is in the foam [Olsson 1999]. For PET foam insulated pipes with PET casing, the main resistance to all gases is in the foam. The values of the low density PET foam are, however uncertain. The results are dependent on the pipe dimension. If the thickness of the insulations was doubled for all combinations of materials, the main resistance to all gases would be in the foam for both PET and PUR foam insulation.

Today it is common to put a diffusion barrier between the PUR foam insulation and the LDPE casing in flexible pipes. In these pipes, fast axial transport of cell gases out

of the foam has been observed, which may be caused by poor fastening between the material layers [Reidhav 2005].

The purpose of the casing material is to protect the PUR foam from water uptake and mechanical pressure. In **III**, the compressive strength of PET foams of different densities was determined. A foam with a density of $84 \text{ kg}\cdot\text{m}^{-3}$ had a compressive strength of 580 kPa. The required value for PUR foam in district heating pipes is 300 kPa [EN253:2003]. PET foam insulated district heating pipes may not require casing for mechanical reasons. A casing could, however retard the long-term aging of the insulation properties. Studies show that surface modifications of PET can reduce the permeation of gases. Plasma-ion implementation of PET films significantly reduced the permeabilities of carbon dioxide and oxygen compared to untreated polymer [Sakudo 2005]. By applying a silica-like layer, a low permeability of oxygen was achieved [Zhu 2005].

Table 4.4 Permeabilities ($10^{-16} \text{ mole}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$) and calculated Biot numbers at 20-25 °C for a foam thickness of 40 mm and a casing material thickness of 3 mm.

Pipe material	Cell gas	P_{pol} casing	P_{eff} foam	Biot number
PUR foam ($\rho_{foam} = 58\text{-}71 \text{ kg}\cdot\text{m}^{-3}$) HDPE casing	Carbon dioxide	8.6 ^{a)}	290 ^{c)}	0.4
	Oxygen	1.9 ^{a)}	49 ^{c)}	0.5
	Nitrogen	0.65 ^{a)}	10 ^{c)}	0.9
	Cyclopentane	23 ^[I]	0.5 ^{d)}	600
	HFC-365mfc	0.19 ^[II]	0.6 ^[II]	4
PET foam ($\rho_{foam} = 157 \text{ kg}\cdot\text{m}^{-3}$) PET casing	Carbon dioxide	1.1 ^{b)}	7.2 ^{e)}	2
	Oxygen	0.28 ^{b)}	0.11 ^{e)}	30
	Nitrogen	0.052 ^{b)}	0.014 ^{e)}	50
PET foam ($\rho_{foam} = 60 \text{ kg}\cdot\text{m}^{-3}$) PET casing	Carbon dioxide	1.1 ^{b)}	8.6 ^{f)}	1.7
	Oxygen	0.28 ^{b)}	0.15 ^{f)}	25
	Nitrogen	0.052 ^{b)}	0.001 ^{f)}	69

^{a)} [Olsson 2001b] and **[I]**

^{b)} P_{pol} calculated from equation 4.18 with D_{pol} and S_{pol} from [Lewis 2003]

^{c)} [Olsson 1999]

^{d)} P_{eff} calculated from equation 4.35, D_{eff} from **[I]**, S_{pol} from [Holmgren 2004], $f_g = 0.95$

^{e)} P_{eff} calculated from equation 4.35, D_{eff} from **[IV]**, S_{pol} from [Lewis 2003], $f_g = 0.88$

^{f)} P_{eff} calculated from equation 4.35, D_{eff} calculated with equations in figure 4.9 and activation energies from **[IV]**, S_{pol} from [Lewis 2003], $f_g = 0.96$

5 LIFE CYCLE PERSPECTIVE ON DISTRICT HEAT DISTRIBUTION

5.1 District heat distribution from cradle to grave

The life cycle of a district heating distribution system from the extraction of raw materials from the nature (cradle) to the waste treatment at the end of the product lifecycle (grave) can be divided into four main phases (figure 1.1): production of district heating pipes, construction of district heating pipe network, distribution of heat, and waste management of pipes taken out of use (post-use handling). This division was used in V, where PET foam and PUR foam insulated pipes were compared by means of life cycle assessment (LCA) and in previous studies on district heat distribution [Fröling 2002a, Fröling 2004a, Fröling 2004b, Persson 2005c]. Waste management was not considered in any of these studies, since to date, pipes have not been taken out of use in a large scale.

The LCA methodology is outlined in the ISO 14040 international standard. The objective of LCA is to quantify the environmental impacts of emissions, resource use and waste from all processes and transports involved during the whole life cycle of a product or service on ecological systems and human health [Baumann 2004, Hauschild 1998, Nord 1995]. The identified emissions are classified and characterised into different impact categories such as global warming potential (GWP), photo oxidant creation potential (POCP), acidification potential (AP) and depletion of finite resources (RD) based on scientific criteria. Sometimes different weighting methods, e.g. EcoIndicator99 or Ecoscarcity, which summarises the different impacts into one figure, are used. This step is not always performed, as it is rather subjective.

LCA can be used to identify the processes, components and systems of a product or service that are the major contributors to environmental impacts or resource depletion. Different products/processes can be compared in order to choose the best alternative. LCA can provide guidance for long-term strategic planning and policy decisions both in the private and public sector. It should be noted that LCA only takes technical aspects into account and does not include studies on economic and social effects. An LCA study always involves simplifications and assumptions.

5.2 Comparison of insulation materials in district heating pipes

5.2.1 System description and inventory

An LCA of district heating pipes with different insulation and casing materials was performed [V]. The different types of pipes included in the study are shown in table 5.1. The objective was to investigate whether PET foam insulated district heating pipes have the potential to compete with traditional cyclopentane blown PUR foam insulated pipes from an environmental perspective. The study of PET foam insulated pipes is hypothetical, since it is not yet possible to produce these pipes. The high density carbon dioxide blown PET foam was considered due to the fact that its long-term thermal performance has been extensively investigated. Low density foam was included, since it is a possible development alternative. Foam made from recycled PET represents an interesting possibility for the future. A comparison was made with pipes insulated with carbon dioxide blown PUR foam, despite the fact that this is not commonly used today. The study is also included pipes insulated with HFC-365mfc blown PUR foam.

Table 5.1 Types of district heating pipes included in the LCA study.

Pipe alternative	Foam type	Foam density (kg·m ⁻³)	Blowing agent	Casing material
PUR (cp)	PUR	86	Cyclopentane/ carbon dioxide	HDPE
PUR (365)	PUR	86	HFC-365mfc/ carbon dioxide	HDPE
PUR (CO₂)	PUR	77	Carbon dioxide	HDPE
PET (HD, vir)	Virgin PET	157	Carbon dioxide	Virgin PET
PET (HD, rec)	Recycled PET	157	Carbon dioxide	Recycled PET
PET (LD, vir)	Virgin PET	86	Carbon dioxide	Virgin PET
PET (LD, rec)	Recycled PET	86	Carbon dioxide	Recycled PET

The functional unit was 1 meter of pipe construction, which includes 1 meter of flow pipe and 1 meter of return pipe over a period of 30 years. Pipes of the DN100/225 dimension were studied (steel tube outer diameter/thickness: 114/3.6 mm, casing pipe outer diameter/thickness: 225/3.4). Three impact categories were considered: GWP (kg CO₂-equivalents), AP (kg SO₂-equivalents) and RD (kg·year⁻¹). Pipe production, network construction and network use were included in the study.

Pipe production inventory data were taken from a previous study on PUR foam insulated district heating pipes [Fröling 2004a]. The production was assumed to be the same for pipes insulated with PET foam, with the exception of the PET foam production itself, which was approximated with foam board production [V]. Production of virgin PET granules for foam and casing pipe was taken from an APME report [Bousted 2002] while the PET recycling process was approximated with a study on polyethylene packages recycling in Sweden [Carlsson 2002]. Only the main materials (steel pipe, insulating foam, pipe casing and copper wire) and energy use were included in the study of the pipe production, since a previous study of PUR foam

insulated pipes shows that they contribute with 90 % or more to the environmental impacts. A study on PUR foam boards blown with HFC-365mfc showed that, during foam manufacture, the contribution of the blowing agent is higher in terms of GWP and similar in terms of AP when compared to n-pentane blown boards [Krähling 2000]. The GWP per mass of HFC-134a was about the same as cyclopentane in another LCA study [Katz 2003]. Due to lack of inventory data for production HFC-365mfc, these data were, however, assumed to be the same as those used in this study for cyclopentane. Network construction data for urban and green areas were taken from [Fröling 2004b] and assumed to be the same for all pipe alternatives.

Heat generated by the average Swedish district heat mix in the year 2000 and use of natural gas combustion (heat only boilers) were considered during the use phase. The Swedish district heat mix consists of 32 % renewable fuel, 29 % waste incineration, 15 % heat pumps, 6 % oil, 5 % peat, 5 % natural gas, 4 % coal and 4 % electricity [Swe DH 2005a]. Natural gas combustion was chosen because it was the major primary energy source for district heat in several European countries in 2001 [Euroheat & Power 2003]. The average thermal conductivities of the foams and the total heat losses from the DH networks over the 30 year period were calculated according to a method described in [Persson 2005a]. The following temperatures were used: 80 °C for the media flow pipe, 40 °C for the media return pipe and 15 °C in the soil surrounding the casing pipe (mean annual value). Explicit finite differences were used for the gas transport through the foam, and the casing was considered as surface resistance. A stationary temperature profile was used for each time step in which the diffusion was calculated, The initial partial pressures of the cell gases for each type of foam used in the pipes are presented in table 5.2.

Table 5.2. Initial partial pressures of cell gases at 20-25 °C of the studied foam types (cp = cyclopentane, 365 = HFC-365mfc).

Foam quality		Initial partial pressures (kPa)			
		cp or 365	Carbon dioxide	Oxygen	Nitrogen
PUR foam (25 °C) [Swe DH 2004]	cp/carbon dioxide blown	42*	67	0.4	0.7
PUR foam (25 °C) [Marrucho 2002, Swe DH 2004]	365/carbon dioxide blown	57*	52	0.4	0.7
PUR foam (20 °C) [Svanström 1999]	Carbon dioxide blown		122	0.2	0.7
PET foam (20 °C) [IV]	Carbon dioxide blown [#]		80	2.5	2.5

* 20 % by mass of the total cyclopentane or HFC-365mfc content (gas + liquid) in the cells as liquid.

[#] The same initial partial pressures are assumed for all PET foam types.

The transport coefficients used to calculate the change in the cell gas mixture over time in the foam cells are presented in table 5.3. For all foams, λ_{gas} was calculated using Wassiljeva's equation with modification by Mason and Saxena [Reid 1977]. For the PUR foams, and the low density PET foam, λ_{pol} was calculated by means of a matrix conduction model [Nielsen 1998] and λ_{rad} according to the Rosseland equation [Siegel 2001]. In the case of high density PET foam, an equation taken from [IV] was used.

Table 5.3. Coefficients used to calculate cell gas transport in the insulation and casing materials based on Arrhenius relationships. Two temperature intervals are given for PET because of the change in diffusion characteristics at or close to the glass transition temperature [IV]. (cp = cyclopentane)

	Temp. (°C)	cp	HFC- 365	Carbon dioxide	Oxyg.	Nitrog.
PUR foam¹						
D_0 ($10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$)	15-80	0.170	0.0444	480	341	10300
E_D ($10^3 \text{ J} \cdot \text{mole}^{-1}$)	15-80	35.3	32	39.9	41.7	54.3
PET foam²						
D_0						
HD foam ($10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$)	15-60			231	9.83	161
	60-80			0.140	0.103	0.881
LD foam ($10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$)	15-60			52.8	5.62	50.9
	60-80			0.324	0.558	2.83
E_D ($10^3 \text{ J} \cdot \text{mole}^{-1}$)	15-60			26.7	21.8	34.1
	60-80			63.6	66.4	77.1
PE³						
P_{pol} ($10^{-16} \text{ mole} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$)	23	23.0	0.19	8.60	1.90	0.650
E_P ($10^3 \text{ J} \cdot \text{mole}^{-1}$)	15-60	9.94	9.94	27.0	34.8	39.2
PET⁴						
P_{pol} ($10^{-16} \text{ mole} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$)	25			1.23	0.311	0.0579
E_P ($10^3 \text{ J} \cdot \text{mole}^{-1}$)	15-60			33.6	33.6	33.6

¹⁾ HFC-365mfc: D_{eff} at room temperature is from [II] E_D is calculated from [Zipfel 1998].

²⁾ LD foam: the density dependency of the diffusion coefficients was calculated according to the equations in figure 4.9. E_D was assumed to be the same as for HD foam.

³⁾ Calculated from I, II and [Brodt 1995]. E_P of HFC-365mfc was approximated.

⁴⁾ P_{pol} is based on diffusion and solubility coefficients from [Lewis 2003]. E_P of all gases were approximated based on a value for oxygen calculated from [Liu 2004a].

5.2.2 LCA results

The characterised environmental impacts for all the pipe systems are reported in table 5.4. The dominating environmental impact during the studied parts of the life cycle is caused by the heat losses for all studied impact categories. The average heat losses during 30 years of use are shown in figure 5.1. PET foam insulated pipes have the same environmental impact irrespective of whether virgin or recycled material is used. The performance of pipes insulated with high-density PET is about the same as those insulated with carbon dioxide blown PUR foam. If the foam density is lowered,

PET foam can compete with cyclopentane blown PUR foam. These results illustrate the fact that gases generally diffuse more slowly in PET foam compared to PUR foam [III, IV]. Carbon dioxide is the fastest diffusing of all the blowing agents used today in insulating foam [I-IV]. It is likely that other gases can be utilized in PET foam in the future, thus further reducing the heat losses of PET foam insulated pipes. Compared to cyclopentane blown foam pipe insulation, HFC-365mfc blown PUR foam may perform better, mainly due to the higher vapour pressure of HFC-365mfc which allows more gas in the foam cells.

Table 5.4. Characterised environmental impacts of a 1 m DN100/225 pipe network (1m flow pipe and 1 m return pipe) over 30 years with regard to global warming potential (GWP, kg CO₂-equivalents), acidification potential (AP, kg SO₂-equivalents) and resource depletion (RD, kg-year⁻¹).

Pipe alternative	Pipe production			Network construction* (green area/urban area)			Network use, 30 years (Swedish fuel mix/natural gas)		
	GWP	AP	RD	GWP	AP	RD	GWP	AP	RD
PUR (cp)	63	0.31	0.65	22/39	0.20/0.37	0.20/0.34	500/1500	2.7/1.1	1.7/8.4
PUR (365)	63	0.21	0.65	22/39	0.20/0.37	0.20/0.34	450/1400	2.4/1.0	1.6/7.7
PUR (CO ₂)	62	0.30	0.64	22/39	0.20/0.37	0.20/0.34	620/1900	3.3/1.3	2.2/10.6
PET (HD, vir)	81	0.52	0.69	22/39	0.20/0.37	0.20/0.34	650/2000	3.5/1.4	2.3/11.0
PET (HD, rec)	41	0.11	0.32	22/39	0.20/0.37	0.20/0.34	650/2000	3.5/1.4	2.3/11.0
PET (LD, vir)	67	0.38	0.56	22/39	0.20/0.37	0.20/0.34	500/1500	2.7/1.1	1.8/8.5
PET (LD, rec)	41	0.10	0.32	22/39	0.20/0.37	0.20/0.34	500/1500	2.7/1.1	1.8/8.5

* Values from [Fröling 2004b].

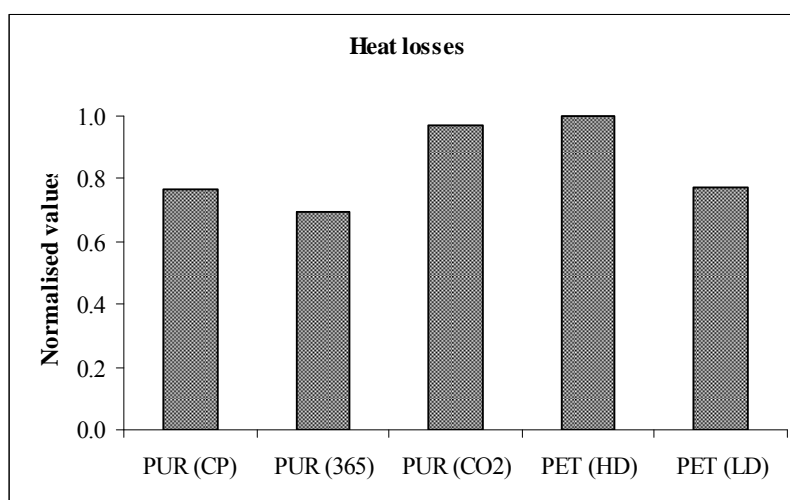


Figure 5.1. Heat losses of a 1 m DN100/225 pipe network (1m flow pipe and 1 m return pipe) over 30 years: Normalised values, PET(HD) = 1. The results are similar for both low and high-density PET foam, regardless of whether recycled material is used in the production.

Figure 5.2 a-c shows the environmental impacts characterised as GWP (a), AP (b) and RD (c) during the use phase for the Swedish heat mix and natural gas boilers as heat source. Due to the high amount of renewable fuels used for Swedish district heat production (32 %), the carbon dioxide emissions are about one third of those of the natural gas boiler system. The acidifying effect is, however higher in the Swedish case, since the heat mix contains small proportions of coal and peat (4 and 5 % respectively). A system based exclusively on fossil fuels result in a resource depletion that is almost five times higher than the Swedish heat mix.

The high global warming potential of HFC-365mfc makes its use questionable. If the total amount of HFC-365mfc (0.22 kg) in the PUR foam of the studied system (2 m DN100/225 pipes) were to be emitted to the atmosphere after 30 years, it would result in 220 kg CO₂-equivalents (GWP_{100years} = 1000) [IPCC 2001b, Naik 2000, World Meteorological Org 2002]. In the system heated with the Swedish fuel mix, foam blown with HFC-365mfc makes a 50 kg lower contribution to global warming in terms of CO₂-equivalents compared to cyclopentane blown foam. In the case of the system heated with the natural gas boiler, the emissions of CO₂-equivalents are 100 kg lower for the HFC-365mfc blown foam. With regard to the global warming and in comparison with cyclopentane blown PUR foam, this study cannot justify the use of HFC-365mfc in PUR foam insulated district heating pipes.

Pipe production and network construction constitute a small part of the environmental effects of the studied life cycle. Their relative contribution increases with higher proportions of renewable resources in the heat mix. Figure 5.3 shows the normalised values of the environmental impacts during production of the pipes studied. The difference between the pipes is mainly due to the type and amount of insulation material used, since the impact from the steel pipe, copper wire, casing material, blowing agent and energy used for pipe assembly are more or less identical. The high density PET foam results in the highest impacts, while low-density PET foam performs in a similar fashion to PUR foam. Utilisation of recycled PET has the potential to significantly reduce the impact compared to PUR foam.

Network construction is assumed to be similar for all pipe systems, although PET pipe installation techniques could differ. A large part of the environmental impacts are accounted for by the excavation work (up to 40 %) [Fröling 2004b]. In urban areas, deeper trenches and asphalt restoration are necessary, resulting in higher impacts compared to green areas. Research is performed in order to determine the minimum depth for pipe trenches without jeopardising the strength of roads and pipes [Nilsson 2005].

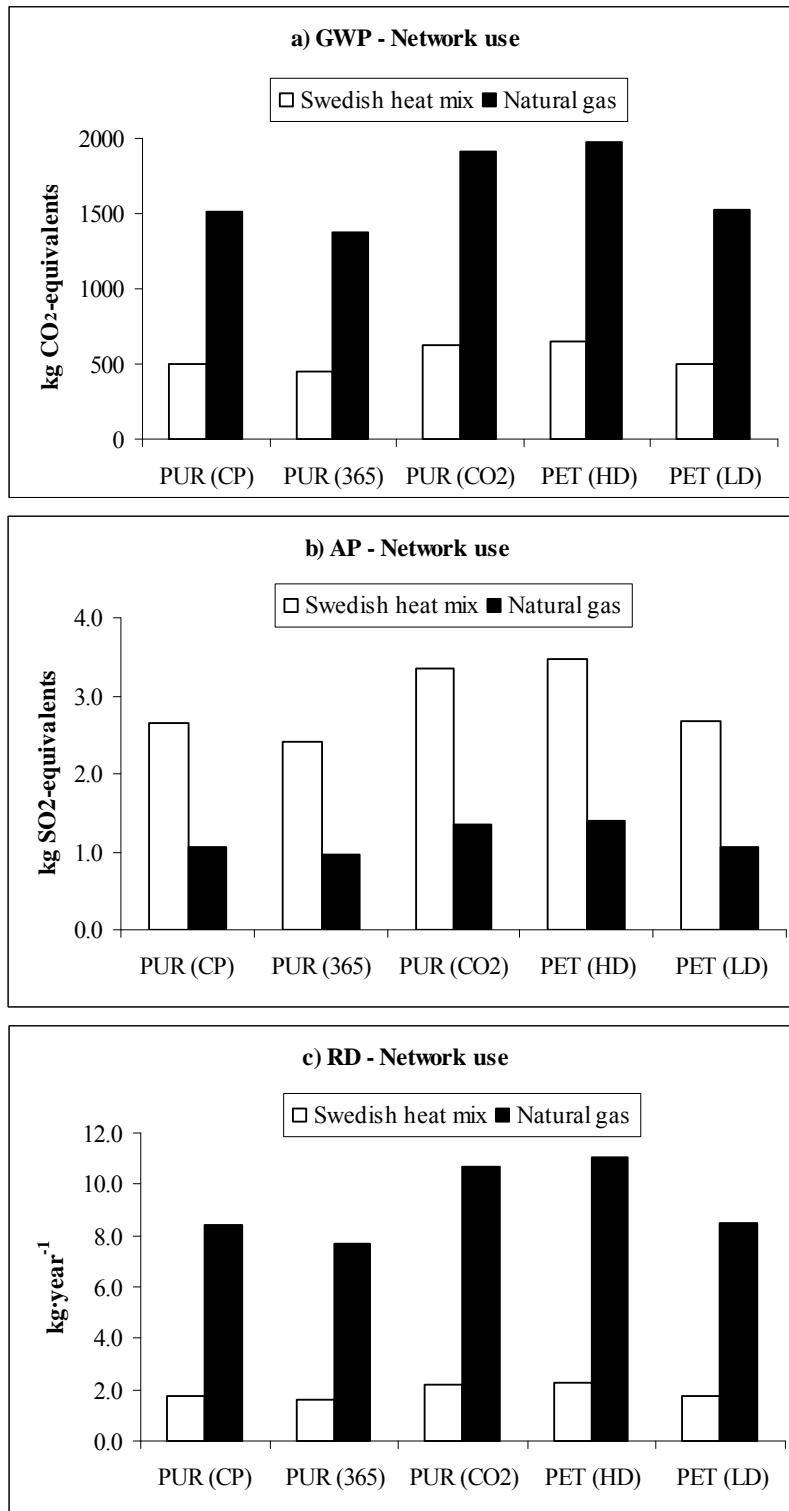


Figure 5.2. Characterised environmental impacts of a 1 m DN100/225 pipe network (1m flow pipe and 1 m return pipe) over a 30-year period with regard to **a)** global warming potential (GWP), **b)** acidification potential (AP) and **c)** resource depletion (RD).

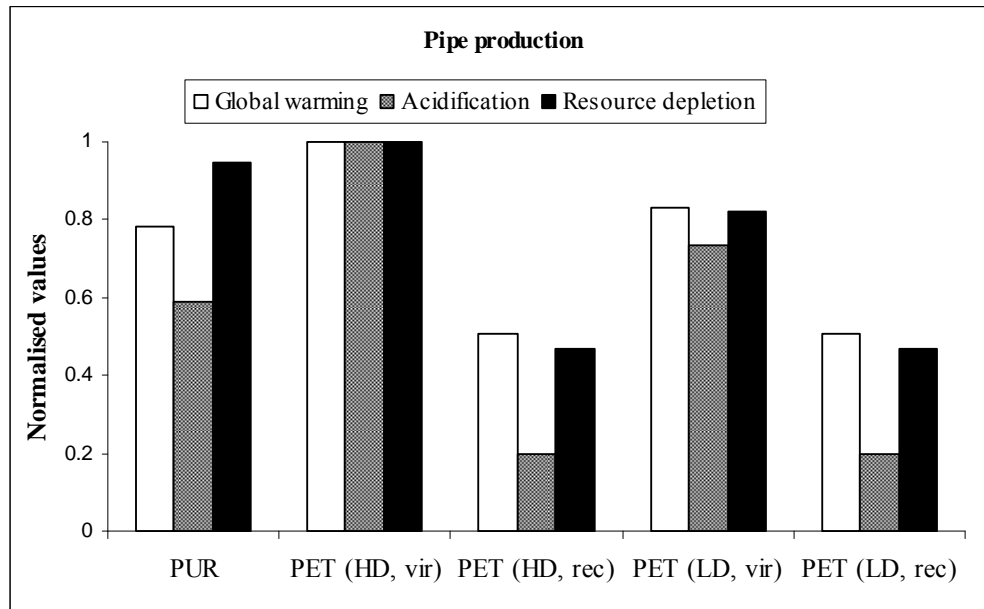


Figure 5.3. Characterised environmental impacts for pipe production: normalised values, $PET(HD) = 1$, for global warming potential, acidification potential, and resource depletion. The PUR foam insulated pipes gives a similar result for all studied blowing agents.

It has been shown that the total environmental impact from the first three phases of the life cycle of district heating pipes is very much dependent on how the heat is produced. In this thesis, pipes of the DN100/225 dimension were studied, and previous research shows similar results for other pipe dimensions [Fröling 2004a, Fröling 2002b, Fröling 2004b, Persson 2005c]. The relative contribution of each phase varies according to the dimension. Large pipes have a higher contribution related to the production while the use phase results in a lower one. Twin pipe systems generally gives rise to lower contributions related to pipe production (less material use), network construction (less excavation) and heat losses compared to single pipe systems. The results are, however dependent on the amount of insulation material used in the respective steel pipe dimension.

In one study different space heating alternatives (district heating, heat pump and pellet, oil and electricity furnaces) were compared [Bengtsson 2005]. The results were dependent on the heat mix in the district heating network and the delivered effect per metre of pipe, i.e. the population density of the residential area. Use of large amounts of bio-fuels makes district heating a good alternative in terms of GWP and RD, especially in densely populated areas. Only pellet furnaces and heat pumps (using the Swedish electricity mix) result in lower environmental impacts in these categories. Compared to electricity furnaces (Swedish electricity mix), district heating with natural gas boilers will result in lower impacts. In low density areas, oil furnaces may also perform better than district heating with natural gas boilers.

6 SUMMARY OF FINDINGS AND FUTURE RESEARCH

6.1 Comparison of cyclopentane and HFC-365mfc

Based on the experimentally determined coefficients and literature values it can be concluded that the diffusion characteristics of cyclopentane and HFC-365mfc in PUR foam are similar [I,II]. Additional studies of HFC-365mfc diffusion characteristics at high temperatures are recommended.

The LCA study reveals that, when the first three phases of the life cycle (pipe production, network construction and network use) are considered, pipe insulation consisting of HFC-365mfc blown PUR foam may reduce environmental impacts from global warming (GWP), acidification (AP) and depletion of resources (RD) compared to cyclopentane blown foam. This is mainly due to the higher vapor pressure of HFC-365mfc, which allows more insulating gas in the foam cells [Chemnetbase 2005, Zipfel 2002]. In comparison with cyclopentane, HFC-365mfc blown PUR foam as district heating pipe insulation only can not be justified, on account of the high contribution to global warming that would occur if all the HFC-365mfc in the pipes were to be released into the atmosphere.

6.2 Comparison of PET and PUR foam

The determined effective diffusion coefficients of carbon dioxide, oxygen and nitrogen are lower in PET foam than in PUR foam at 23-90 °C [IV]. According to the Arrhenius relationship, the activation energies of these gases are lower in PET foam compared to PUR foam [I, IV]. The determined solubility coefficients of blowing agents show a tendency towards lower values in PET than in PUR foam [I-III]. These experimental results gives that the decrease of insulating capacity of PET foam over time compared to PUR foam, due to the diffusion of cell gases, is slower.

The contribution to foam thermal conductivity due to radiation in the cells and conduction in the polymer matrix in the type of PET foam available today is higher than in the PUR foam used for district heating pipes [III, IV]. If PET foam with a

lower density and smaller cells could be developed, it might be possible to achieve the same values as those of for PUR foam.

The environmental performance (in terms of GWP, AP, RD) of pipes insulated with high-density PET foam is similar to pipes insulated with carbon dioxide blown PUR foam [V]. PET foam with a lower density has been shown to be a possible competitor to cyclopentane blown PUR foam for pipe insulation. Recycled PET has the potential to significantly reduce the impacts caused by pipe production compared to PUR foam. A future trend towards increased recycling of PET can be expected in Europe, possibly as a result of increased PET consumption and current regulations (the Packaging and Packaging waste directive). Recycled PET has also the advantage of a lower price than virgin PET and PUR. Problems due to degradation and contamination of other plastics can be solved by means of chemical modifications [Japon 2000, Smith 1990, Xanthos 2000].

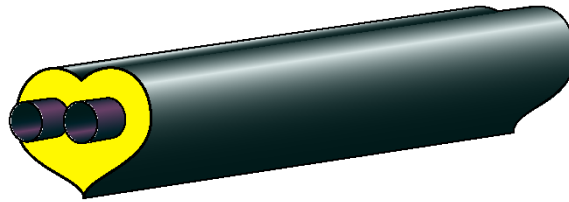
Due to its high compressive strength, pipes insulated PET may not require a casing [III]. Less different types of material would simplify the waste treatment of pipes taken out of use.

The literature reports that PET is subject to chemical degradation due to hydrolysis and becomes brittle when exposed to water at high temperatures [Foulc 2005, Oreski 2005]. The extent of these effects on foam used in district heating pipes and possible solutions to the problem should be investigated.

6.2 Other findings and comments

Differences between diffusion theories and the result of long-term experiments were noted in the case of HFC-365mfc. Such differences have been reported in the literature for heavy and slow diffusing blowing agents with relatively high polymer solubility coefficients [Duda 1996, Hong 2001]. Further studies of possible concentration dependencies are necessary in order to understand and simulate these mechanisms.

When calculating the long-term thermal performance of insulating foams, accurate cell gas thermal conductivity values are important. In the literature, gas thermal conductivity values for blowing agents are often inconsistent. The literature also makes it clear that the thermal conductivity of some gas mixtures is difficult to predict with existing models [Marrucho 2005, Merten 1997]. Further studies of the thermal conductivity of blowing agents and mixtures of gases would be a desirable contribution to this field.



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