CHALMERS

Residential biomass combustion

– emissions of organic compounds to air from wood pellets and other new alternatives

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Göteborg, Sweden, 2006

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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ISBN 91-7291-728-8
Doktorsavhandlingar vid Chalmers Tekniska Högskola, Ny serie nr 2410
ISSN 0346-718X

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Front cover: Five sequential stages of incomplete combustion of softwood pellets; initial smouldering, early flaming, late flaming, after-flame smouldering and final glowing
Back cover: Sampling in the chimney pipe of a residential pellet burner

Printed by Chalmers Reproservice
Göteborg, Sweden 2006

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ABSTRACT

It is important to increase the use of biofuels for residential heating in order to decrease the use of fossil fuels and their impact on global warming. The smoke from the combustion of biomass contains a large number of compounds, which to varying degrees can affect the environment and human health. In this study, specific organic compounds were therefore analysed in the smoke from the selected fuels and combustion appliances using various gas chromatographic and mass spectrometric techniques.

Softwood pellets are increasingly common as a residential fuel in Sweden and annually almost 500 000 tonnes are used. Measurements showed that the emissions from different stages of incomplete laboratory burning of softwood pellets differ greatly in amount and composition. Initial smouldering and flaming burning emitted methoxyphenols with an antioxidant effect in high concentrations, whereas glowing burning emitted the carcinogenic benzene and polycyclic aromatic hydrocarbons in low concentrations.

With the increasing demand for wood pellets, alternative fuels, such as oats, wheat straw and peat, are of great interest. Results from incomplete combustion of these fuels on a laboratory scale indicate that they give rise to relatively low emissions of organic compounds, almost as low as those from softwood pellets. High concentrations of furan-related compounds and anhydrosugar were emitted during the initial smouldering of oats, while high concentrations of methoxyphenols were emitted from wheat straw and peat/wood pellets.

The emissions from the combustion of softwood pellets in residential appliances were generally low and wood pellets are environmentally well suited to replace traditional firewood and oil boilers. The combustion of softwood pellets in two stoves and one boiler gave rise to emissions of methoxyphenols together with aromatic hydrocarbons. The combustion in pellet burners was more complete and emitted benzene and other aromatic hydrocarbons in low concentrations. The large variations observed in emissions from different residential pellet burning appliances make it important to choose the best available appliance and to install and maintain it correctly.

The studied ecolabelled wood boiler showed high combustion efficiency. The emissions of compounds hazardous to health and the environment were low and the boiler is therefore recommended as an environmentally sound option for residential firewood combustion.

Keywords: Burning, smoke, firewood, oats, wheat straw, peat, stove, boiler, ecolabel, benzene, methoxyphenol, hydrocarbon

Biobränsleeldning i villa

– emissioner av organiska ämnen till luft från träpellets och andra nya alternativ

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SAMMANFATTNING

För att kunna minska användningen av fossila bränslen och deras bidrag till växthuseffekten är det viktigt att öka andelen biobränslen för villauppvärmning. Rök från förbränning av biomassa innehåller ett mycket stort antal ämnen som kan påverka miljön och hälsan. I denna studie analyserades därför specifika organiska ämnen i rök från olika bränslen och förbränningsutrustningar med hjälp av gaskromatografi och masspektrometri.

Villauppvärmning med träpellets ökar i Sverige och uppgår nu till nästan 500 000 ton årligen. Mätningar visade att emissionerna från olika stadier av ofullständig förbränning av träpellets i laboratorieskala varierade mycket. Under antändnings- och flameldningsstadierna emitterades höga koncentrationer av metoxifenoler med antioxidanteffekt. Låga koncentrationer av cancerogena ämnen som bensen och polycykliska aromatiska kolväten bildades under glödeldningsstadiet.

Med en stigande efterfrågan på träpellets ökar nu intresset för alternativa bränslen, såsom havre, vetehalm och torv. Ofullständig förbränning av dessa bränslen i laboratorieskala ger upphov till relativt låga emissioner av organiska ämnen, nästan lika låga som från träpellets. Höga koncentrationer av furanrelaterade ämnen och anhydrosocker erhölls under antändningsstadiet för havre och höga koncentrationer av metoxifenoler under antändningsstadiet för vetehalm och torv/träpellets.

Emissionerna från förbränning av träpellets i villautrustningar var generellt låga och pelletspannor, brännare och kaminer är därför miljömässigt väl lämpade att ersätta oljepannor och traditionella vedpannor. Förbränning av träpellets i två kaminer och en panna gav upphov till utsläpp av metoxifenoler tillsammans med aromatiska kolväten. Förbränningen i pelletsbrännare var mer fullständig och gav låga emissioner av bensen och andra aromatiska kolväten. Den stora skillnad som observerats mellan emissioner från olika villautrustningar för pellets gör det viktigt att välja bästa möjliga utrustning och att installera och underhålla den väl.

Den studerade miljömärkta vedpannan var kopplad till en ackumulatortank och hade hög förbränningseffektivitet. Emissionerna av miljö- och hälsofarliga ämnen var låga och pannan rekommenderas därför som ett miljövänligt alternativ för villauppvärmning.

List of publications

This thesis is based on the following publications, appended in the thesis and referred to in the text by their Roman numerals:

I **Oxidative pyrolysis of integral softwood pellets**
Maria Olsson, Jennica Kjällstrand and Göran Petersson
Journal of Analytical and Applied Pyrolysis 2003, 67, 135-141

II **Specific volatile hydrocarbons in smoke from oxidative pyrolysis of softwood pellets**
Maria Olsson, Olle Ramnäs and Göran Petersson
Journal of Analytical and Applied Pyrolysis, 2004, 71, 847-854

III **Benzene emitted from glowing charcoal**
Maria Olsson and Göran Petersson
The Science of the Total Environment, 2003, 303, 215-220

IV **Specific chimney emissions and biofuel characteristics of softwood pellets for residential heating in Sweden**
Maria Olsson, Jennica Kjällstrand and Göran Petersson
Biomass and Bioenergy 2003, 24, 51-57

V **Chimney emissions from small-scale burning of pellets and fuelwood - examples referring to different combustion appliances**
Jennica Kjällstrand and Maria Olsson
Biomass and Bioenergy 2004, 27, 557-561

VI **Low emissions from wood burning in an ecolabelled residential boiler**
Maria Olsson and Jennica Kjällstrand
Atmospheric Environment 2005, *in press*

VII **Emissions of organic compounds from the combustion of oats – a comparison with softwood pellets**
Maria Olsson
Manuscript submitted to Bioresource Technology 2005

VIII **Wheat straw and peat for fuel pellets – organic compounds from combustion**
Maria Olsson
Biomass and Bioenergy 2005, *in press*

Results related to this thesis are also presented in:

Emissions from burning of softwood pellets
Maria Olsson and Jennica Kjällstrand
Biomass and Bioenergy 2004, 27, 607-611

Wood pellets as residential biofuel (In Swedish: Träpellets som småskaligt biobränsle)
Maria Olsson
Report for the Swedish Energy Agency. Chemical Environmental Science, Chalmers University of Technology, Göteborg, Sweden, 2001

Wood pellets - sustainable heating for residences
Maria Olsson
In proceedings of the Annual Meeting of the World Student Council for Sustainable Development, Chalmers, Göteborg, Sweden, March 2004. Also published in Vision, 2(1), 2004, available at www.wscsd.org/ejournal

Emissions from five sequential combustion stages of softwood pellets
Maria Olsson
Proceedings of World Bioenergy 2004, Jönköping, Sweden, June 2004

Combustion of oats for heating (In Swedish: Eldning av havre för uppvärmning)
Maria Olsson, Olof Arkelöv and Kent-Olof Söderqvist
Report for the Federation of Swedish Farmers, LRF Skaraborg, Box 114, SE-532 22 Skara, Sweden, 2004, available at www.lrf.se

New raw materials for pellets - organic compounds from combustion
Maria Olsson
Proceedings of 14th European Biomass Conference and Exhibition, Paris, France, October 2005

Pellets R&D in Europe – an overview
Maria Olsson and Johan Vinterbäck
Report for the projects Pellets for Europe and EnergyCentre.Info/Pellets, 2005, available at www.PelletCentre.Info

Table of contents

1 Introduction

In this thesis, measurements of the emissions of organic compounds from the combustion of wood pellets are presented, together with results from other new residential biomass alternatives. The impact of these emissions on health and the environment are also discussed. The main focus is on the combustion of softwood pellets, both on a laboratory scale and in residential appliances. Further, alternative raw materials for pellet production as well as the burning of firewood in an ecolabelled wood boiler were studied.

1.1 Background

The residential use of wood and other biomass fuels has a long history. Today, increased use of such fuels is encouraged in view of global warming and the predicted future shortage of fossil fuels. Most wood boilers presently used for residential heating in Sweden are old and often emit large quantities of organic compounds.

New residential biomass combustion alternatives, such as wood pellets and highly efficient wood boilers, have entered the market over the last ten years. The emissions from such new alternatives can be significantly lower than those from traditional alternatives.

In view of the increasing demand for wood pellets, alternative fuels are of great interest. Some of them, such as oats, can be directly combusted in adapted pellet burning appliances, whereas others, such as wheat straw and peat, are suitable for pellet production.

Despite the fact that biofuels are considered environmentally friendly and the total emissions to air from modern residential combustion appliances can be very low, it is important to study the emissions of individual compounds. Smoke from the combustion of biofuels is a complex mixture of organic compounds with varying environmental and health effects. It is essential to determine the individual hazardous compounds in the smoke and to understand how to minimise the emissions of them. Although it is desirable to increase the use of biofuels both for environmental and economic reasons, it is also important to protect the local environment from hazardous emissions.

Knowledge about the smoke constituents is also necessary when setting regulations and developing better biomass combustion technologies. The organic content of the smoke from the combustion of the selected fuels was therefore analysed both on a laboratory scale and in residential appliances.

1.2 Outline

This thesis is based on eight articles (**I-VIII**). Their relation to each other is illustrated in Figure 1. All articles focus on the emissions of organic compounds from modern residential biomass burning and their effects on health and the environment.

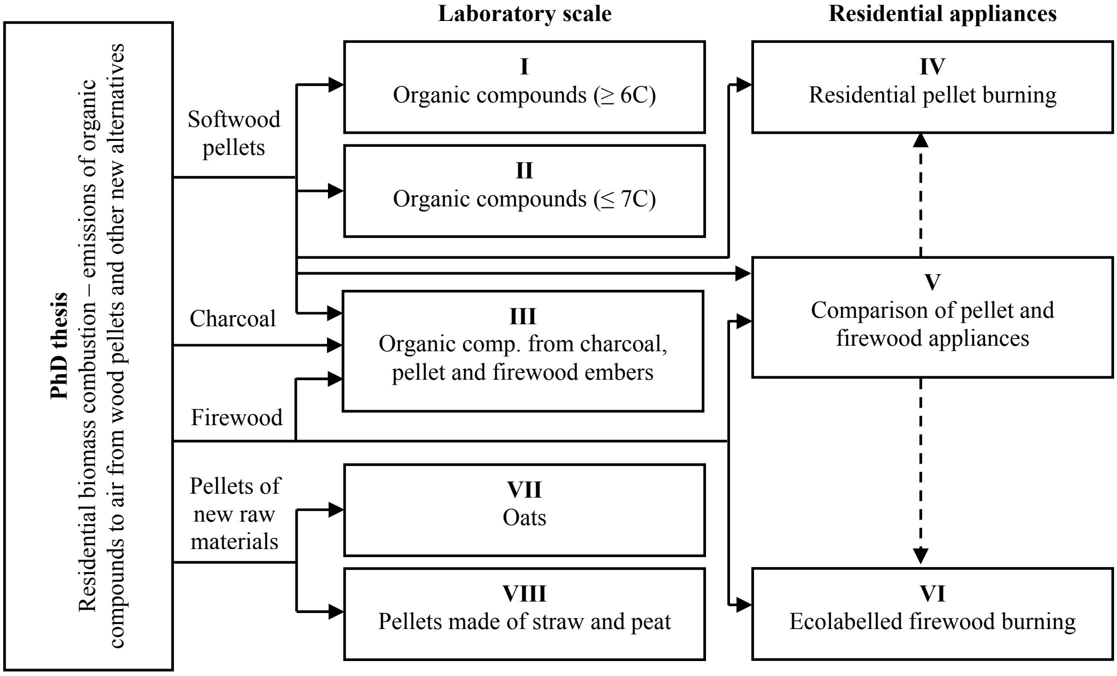

Figure 1: Overview of articles.

In **I**, organic compounds (≥ 6C) were studied in smoke from laboratory scale experiments on flaming and burning softwood pellets from three different manufacturers. The emissions of organic compounds (≤ 7C) from five sequential combustion stages of softwood pellets are presented in **II**. In **III**, the emissions of organic compounds from glowing charcoal, pellet embers and firewood embers were studied.

Measurements of the emissions of organic compounds (≥ 6C) from residential pellet combustion appliances are presented in **IV**. In **V**, the emissions from different wood pellets and firewood combustion appliances are compared. The results of an assessment of the emissions of organic compounds from an ecolabelled residential wood boiler are presented in **VI**.

In **VII**, the emissions of organic compounds from five sequential combustion stages of oats and softwood pellets are compared. A similar comparison of the emissions of straw pellets, peat/wood pellets and softwood pellets is presented in **VIII**.

2 Residential biomass combustion

Approximately 14 % of the world's energy use is derived from biomass and in developing countries the corresponding figure is 35 % (Demirbas 2004). Due to global warming and the predicted future shortage of fossil fuels, society is attempting to achieve a sustainable energy supply by increasing the use of alternative fuels.

In accordance with the Kyoto Protocol, the industrialised nations have agreed to decrease their emissions of greenhouse gases by 5 % by 2008-2012, based on the 1990 emission levels (UNFCCC 1997). The corresponding figure for the European Union member states is 8 %. In order to achieve this, it will be necessary to increase the efficiency of energy use and to replace fossil fuels with biomass and other renewable energy sources. The European Commission's white paper for a community strategy and action plan sets a strategy to double the share of renewable energy in the gross domestic energy consumption in the European Union by 2010, from the present 6 % to 12 % (European Commission 1997). The change from fossil fuels to biofuels is an effective way of decreasing the Swedish carbon dioxide emissions (Bohlin *et al.* 1998).

Sweden is one of the leading biofuel users in the European Union (Ericsson and Nilsson 2004), and in 2003 its total energy consumption was 400 TWh, of which 15 % was derived from biofuels (Swedish Energy Agency 2004). In Sweden, as in many other countries, numerous homes are heated by means of small-scale wood burning. At present, biomass combustion accounts for more than 10 TWh of the 65 TWh used for heating purposes in one, two or multi dwelling buildings (SCB Statistics Sweden 2004). Biomass heating is now a more common residential heating option than light fuel oil (SCB Statistics Sweden 2004). At present, about 300 000 biofuel boilers and 350 000 stoves or open fireplaces are used for the heating of Swedish residences (SBBA 2005).

Today, most wood boilers used for residential heating in Sweden are old and the emissions can be high (Hansson 2003). Over the last ten years new alternatives for residential biomass combustion, such as wood pellets and highly efficient wood boilers, have entered the market. The exposure to air pollutants is decreased when exchanging old wood boilers for pellet appliances (Boman *et al.* 2003b). Wood pellets are a biofuel that is much in demand for residential heating and hot water production and this fuel is used in more than 80 000 Swedish homes (SBBA 2005). Alternative fuels are of great interest in view of the increasing demand for wood pellets. Some of them can be directly combusted in adapted pellet burning appliances, whereas others are suitable for pellet production.

Preparing food over glowing charcoal may be the most common use of biofuels for many people, in Sweden and other countries, exposing mainly the cook to high emissions of organic compounds. The annual Swedish use of charcoal for this purpose has been estimated to 10 000-15 000 tonnes (Wijkmark 2003).

2.1 Firewood

Until just under a hundred years ago, wood burning was the predominant residential heating option in Sweden (**V**, **VI**). In the 1950s, oil burning became very popular and to a great extent replaced wood burning. Due to the oil crises in the 1970's, oil burning became less popular. Since then, oil burning has decreased in popularity with increasing oil prices and environmental awareness, and once again biofuels are in demand.

Most wood boilers used for residential heating in Sweden are old and often emit large quantities of organic compounds. Today, all new wood boilers installed in urban areas of Sweden must comply with the emission limits set by the authorities. More than 90 % of all boilers sold today are environmentally approved for use in urban areas (SBBA 2005).

The development of highly efficient wood boilers has increased over the past few years (Strehler 2000). A high temperature and sufficient air supply, mixing and residence time in the combustion area is required for complete combustion of organic compounds. Highly efficient residential boilers have ceramic combustion chambers and are constructed for reversed combustion.

Several countries have developed an environmental labelling system to help consumers choose environmentally friendly products. "The Swan" is the name of the Nordic ecolabel, which lays down the environmental criteria for wood boilers and stoves (Nordic Ecolabelling Board 2004a, 2004b). The criteria include; combustion efficiency, emissions to air, heating system design, material requirements, packaging, installation, operation instructions etc. The emission limits include organic gaseous carbon (OGC), carbon monoxide and particulate matter. Emission limits for wood boilers and stoves laid down by the Swan and the Swedish authorities are presented in Table 1.

Table 1: Present emission limits (mg m^{-3} dry gas) for wood boilers and stoves laid down by the Swedish authorities and the Swan (OGC = organic gaseous carbon, **VI**, Nordic Ecolabelling Board 2004a, 2004b, Swedish Board of Housing Building and Planning 2002).

	OGC	Carbon monoxide	Particles
Wood boilers (measured at 10 % O_2)			
- Swedish authorities (<50 kW)	150	-	-
- The Swan (<100 kW, major heat source)	70	2 000	70
Wood stoves (measured at 13 % O_2)			
- Swedish authorities	250	-	-
- The Swan (Heat accumulation)	180	2 500	3 [a]
- The Swan (No heat accumulation)	180	2 500	< 10 [a, b]

[a] (g kg^{-1} fuel),

[b] Average value, < 20 for each individual test

At present, two wood boilers and two wood stoves are ecolabelled (Figure 2). In 2001, the Baxi Solo Innova was the first wood boiler to be ecolabelled by the Swan and it was therefore a natural choice to use in a study of the emissions of organic compounds during combustion. The Baxi Solo Innova is designed for reversed combustion and is one of the most popular wood boilers in Sweden today, with almost 6 000 units installed (Baxi AB 2005).

Figure 2: The Nordic ecolabel the Swan together with an example of an ecolabelled wood boiler (middle, Baxi AB 2005) and a wood stove (right, Varde Ovne A/S 2005).

In a boiler with reversed combustion, the woodpile is burnt from below, and pieces of wood continuously drop down into the combustion chamber. This leads to uniform heat development throughout the burning cycle and has the advantage of longer burning intervals for one load of wood. The ceramic combustion chamber maintains a high combustion temperature during the whole burning cycle, resulting in decreased emissions during the flaming phase and increased energy yield during the glowing phase. Air intake in two steps guarantees a sufficient oxygen supply. Long gas-paths increase the residence time of the smoke gases, which is important for complete combustion of organic compounds and efficient heat transfer from the hot smoke gases. Heat storage in a large water tank makes it possible to run the boiler at a high effect without over-heating.

2.2 Wood pellets

Wood pellets offer many advantages and are therefore rapidly replacing light fuel oil and firewood for residential heating in Sweden. The properties of wood pellets differ a great deal from the properties of firewood. Wood pellets are a homogeneous fuel with low moisture content that allows even combustion with low emissions and high efficiency. Thanks to their low moisture content, the storage properties of wood pellets are good (Lehtikangas 2000). The transports of pellets are also cheaper and more convenient (Hillring and Vinterbäck 1998). The processing costs are partly offset by lower transport and storage costs due to the higher energy density (Wahlund *et al.* 2004). Another advantage of pellets compared to unprocessed biomass fuels is convenience for the customer. Pellets can be automatically fed into the burner, do not require splitting and form less ash.

Wood pellets also have several advantages compared to light fuel oil. They are a renewable fuel with no carbon dioxide emissions contributing to global warming. Furthermore, wood pellets are cheaper than oil and electricity and have a more stable price development. As pellets are a native fuel, they provide employment opportunities in Sweden. Some drawbacks compared to light fuel oil are the need for larger storage facilities, regular control and removal of ash.

2.2.1 Wood pellets in Sweden

As a background to this research project, the production and use of wood pellets was investigated in order to describe the Swedish pellet market (**IV**, Olsson 2001, 2004b).

Swedish wood pellets are produced from softwood sawdust and shavings. At present, there are more than 20 wood pellets production facilities in Sweden, with an annual total production of more than one million tonnes (PIR 2005). In Figure 3, major pellet producers are presented with their production during 2003 in thousands of tonnes (Olsson 2004b).

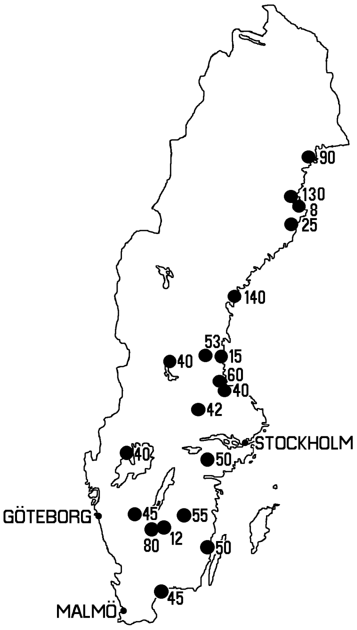

Figure 3: Production of wood pellets in Sweden in thousands of tonnes (Olsson 2004b).

Swedish wood pellet production started in the early 1980s with an annual production of 45 000 tonnes (Olsson 2002) and has increased dramatically ever since (Figure 4, total bars).

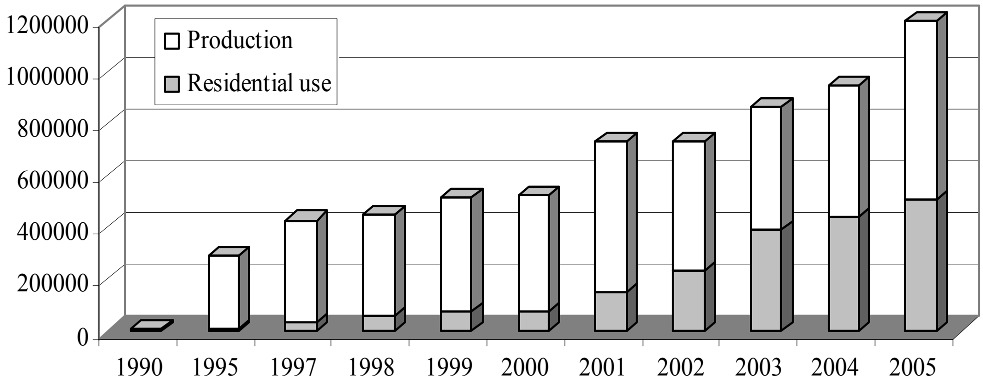

Figure 4: Swedish wood pellet production (total bars) and residential use (grey part of the bars) in tonnes (Olsson 2002, 2004b, PIR 2005).

The major proportion of the Swedish production of wood pellets is burnt in large-scale heating plants. However, according to the latest information from the pellet producers, approximately 500 000 tonnes are used for residential heating, which corresponds to 35 % of the total (Figure 4, grey part of the bar, PIR 2005). In 2004, around 57 000 residential pellet burners and boilers and about 10 000 pellet stoves were in use in Sweden (SBBA 2005). The prognosis for 2005 was an additional 15 000 burners and boilers, together with 2 000-3 000 new stoves (SBBA 2005). According to a previous study, there are great possibilities for a further increase in the shift to wood pellets (Carlson 2002).

Most of the residential pellet heating appliances have replaced firewood boilers. The reasons for the change from firewood to pellets are convenience, mainly due to the automatic fuel feed into the combustion appliance, and the fact that pellets are a cheap alternative. Today, the number of oil burners being replaced by pellet burners is increasing, due to pellets being an environmentally friendly alternative and cheaper than oil. The price of wood pellets for a small-scale customer in Sweden was approximately 50 € MWh^{-1} in 2005. The approximate cost of light fuel oil was above 100 € MWh^{-1} and electricity 110 € MWh^{-1}.

Sweden is not the only country where the production and use of wood pellets is significant. In Europe, Austria, Denmark, Finland, Estonia, Italy and Germany are also significant users and producers (Dahl *et al.* 2005).

Pellets have been used for residential heating for 20 years in the US and Canada, and there are over 60 producers. Today, more than 600 000 homes in the US and Canada use wood pellets for heat, mainly in stoves and fireplace inserts (PFI 2005). Unlike the Swedish market, the American market is dominated by the use of pellets in stoves as a secondary heat source (Vinterbäck 2000).

Of the pellets used in Sweden, 25 % are imported (PIR 2005). Pellets are mainly imported into Sweden from Canada, the Baltic Countries and Finland and exported to Denmark (Ericsson and Nilsson 2004). The Swedish import of pellets amounted to 300 000 tonnes and the export to 20 000 tonnes in 2004 (PIR 2005).

2.2.2 Production of wood pellets

When choosing a site for pellet production, access to raw material, existing fodder pellet production plants, distance to customers and the possibility of utilising surplus energy are important factors. It has been suggested that pellet production should be integrated with a pulp mill, sawmill or a combined heat and power plant using biofuels (Wahlund *et al.* 2002, Vidlund 2004, Wolf *et al.* 2005).

A flow sheet for pellet production in Sweden is presented in Figure 5. The raw materials must be correctly stored before production to avoid mould growth and anaerobic decomposition leading to methane emissions (Pier and Kelly 1997). There are also emissions of terpenes, mainly monoterpenes and sesquiterpenes, during storing (Rupar and Sanati 2005).

The first step in the production is the drying of sawdust, in order to reduce the moisture content from 50-55 % to 8-12 %, which requires a lot of energy (Ståhl 2005). Terpenes, mainly monoterpenes and sesquiterpenes, are emitted during the drying process (Granström 2003, 2005, Rupar and Sanati 2003, Ståhl *et al.* 2004). Dry shavings are mixed with the dried sawdust. The mixture is ground and sometimes a binding agent, such as potato starch, is added. This additive is relatively uncommon, but may lead to more stable pellets compared to those bound by the natural lignin in the wood.

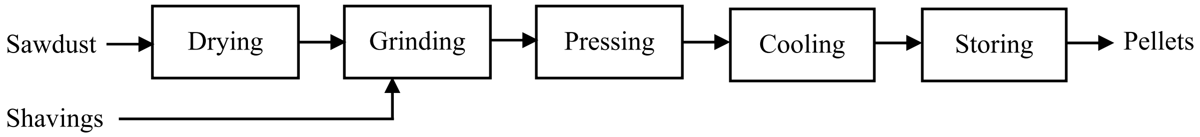

Figure 5: Flow sheet for the production of wood pellets from sawdust and/or shavings.

After grinding, the raw material is pressed through cylindrical holes in a pellet matrix. Figure 6 presents a schematic illustration of a flat pellet matrix. However, a cylindrical shape is more common. Friction leads to a rise in temperature to over 100ºC. The pellet strings are cut with a knife or automatically broken. Terpenes remaining after drying of the raw material are almost totally released during pressing (Granström 2005).

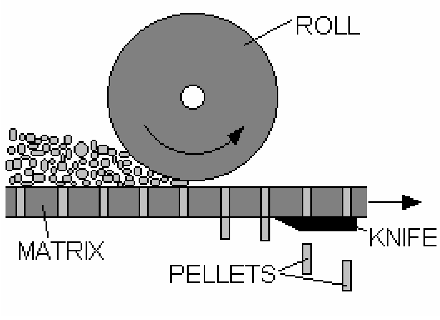

Figure 6: Flat pellet production matrix (Olsson 2002).

The pellets are left to cool before sieving, storing and transporting to the customer. High levels of hexanal and carbon monoxide have been determined from both large-scale and small-scale storing of wood pellets (Svedberg *et al.* 2004). Storage of pellets for longer periods has a negative effect on durability (Lehtikangas 2000). The working environment at pellet production plants has been studied, and exposure to wood dust was found to be high, while exposure to monoterpenes was relatively low (Edman *et al.* 2003).

From a life cycle perspective, approximately 80 % of the primary fuel input (including 5 % crude oil and 95 % wood) ends up in the pellets, whereas 13 % is consumed during pelletising and 3 % during forestry work (Gustavsson and Karlsson 2002, Karlsson 2003). Less than 1 % is used for transport of the raw material and the finished pellets.

2.2.3 Physical and chemical properties of softwood pellets

There is a Swedish Standard for fuel pellets (SS 18 71 20) and a European-wide standard (CEN) is under development. A number of different European standards have been compared in previous studies (Fiedler 2004, Obernberger and Thek 2004). Some Swedish pellet producers plan to label their pellets with the FSC brand (Forest Stewardship Council), certifying that they are products of environmentally sustainable forestry.

The Nordic Ecolabelling Board also has criteria for biofuel pellets (Nordic Ecolabelling Board 2005). The first wood pellets labelled by the Swan appeared on the Swedish market during the autumn 2005. Chemical and physical criteria for biopellets labelled by the Swan are presented in Table 2.

Table 2: Physical and chemical criteria for biopellets ecolabelled by the Swan (Nordic Ecolabelling Board 2005).

Physical/chemical properties	Limit value
Diameter (Ø, mm)	$\leq 6^{a} / \leq 8^{b}$
Length (mm)	$\leq 5\times Ø$
Bulk density (kg m^{-3})	630-700 ^{c} / 700-780 ^{d}
Fine fraction (<3.15 mm, % w/w)	≤ 2
Mechanical durability (% w/w)	≥ 97.5
Energy density (MJ kg^{-1})	≥ 16.9
Moisture content (% w/w)	≤ 9
Ash content of dry matter (% w/w)	≤ 0.5
Ash melting (°C)	$\geq 1\,300^{e} / \geq 1\,400^{f}$
Total sulphur content (% w/w)	≤ 0.04
Chlorine content (% w/w)	≤ 0.02
Nitrogen content (% w/w)	≤ 0.3

[a] Grade I for stoves, [b] Grade II for burners and boilers, [c] Grade a, [d] Grade b, [e] Initial temperature, [f] High temperature

The ash contains both mineral nutrients and other inorganic biomass materials as well as material that has contaminated the fuel during harvesting, transport and storage. The burning appliance must be cleared of ash, once a week in the case of older appliances and twice a year for more modern ones. The most common method of ash disposal is to spread them in the garden as a mineral nutrient fertiliser, which leads to a rise in the pH level (Vinterbäck 2000). Roughly 65 % of all pellet users spread their ashes in the garden, either with or without previous composting.

In the long term, modern forestry may deprive the soil of nutrients. When using pellets in large-scale combustion plants it is important to keep the ash free from contaminants in order to be able to return it to the forest ecosystem. Experiments have been conducted on returning pelletised ash from biofuel combustion to the forests (Lundborg 1998, Mahmoudkhani 2005). A problem with ash returning is that the ash may also contain small amounts of heavy metals, which could cause long-term environmental effects.

2.2.4 Combustion appliances for softwood pellets

Pellets can be burnt in residential burners, stoves and boilers (Figure 7). An old wood or oil boiler can be replaced by a pellet boiler or converted to pellet combustion by the installation of a pellet burner. A pellet stove is a suitable heating addition to, for example electric heating, district heating or a heat pump. Most pellets used in Swedish residences are burnt in burners installed in old wood or oil boilers. Generally, the combustion efficiency will be higher and the emissions lower if the boiler is new and suitable for the pellet burner (Löfgren and Arkelöv 2004). A combination of pellet and solar heating is very beneficial (Fiedler *et al.* 2006, Persson *et al.* 2005).

Figure 7: Pellet burner (left, Gordic Environment AB 2005), stove (middle, Calimax GmbH 2005) and boiler (right, Baxi AB 2005).

Generally, residential pellet combustion appliances are constructed for automatic feed of the fuel into the combustion chamber and automatic regulation of the effect (load) by means of a thermostat. When changing between different pellet qualities, it is important to adjust the burning appliance in order to prevent inefficient combustion. New automatic pellet boilers with significantly lower emissions are being introduced to the market (Löfgren 2005). Gas sensors and automatic combustion modulation are other new approaches for lower emissions (Eskilsson *et al.* 2004). Existing pellet combustion appliance technology and emission limits in Sweden, Austria and Germany have been presented (Fiedler 2004).

The Nordic Ecolabelling Board also has criteria for pellet burners, boilers and stoves (Nordic Ecolabelling Board 2004a, 2004b). The criteria include; e.g. combustion efficiency, emissions to air, heating system design, material requirements, packaging, installation and operation instructions. The emission limits include organic gaseous carbon (OGC), carbon monoxide and particulate matter, which are presented in Table 3.

Table 3: Present emission limits (mg m^{-3} dry gas) for pellet combustion appliances (OGC = organic gaseous carbon, Nordic Ecolabelling Board 2004a, 2004b).

	OGC	Carbon monoxide	Particles
Pellet boilers (measured at 10 % O_2)			
- The Swan (<100 kW, major heat source)	70	1 000	70
Pellet stoves (measured at 13 % O_2)			
- The Swan (Heat accumulation)	180	2 500	3 [a]
- The Swan (No heat accumulation)	55	1 250	< 10 [a, b]

[a] (g kg^{-1} fuel), [b] Average value, < 20 for each individual test

A large difference when comparing the emission limits to those of wood combustion appliances is that the emission limits for automatically fed appliances, such as pellet burners and boilers, are stricter. At present, four models of pellet stoves carry the Swan label.

The P-mark is a quality label developed by the SP Swedish National Testing and Research Institute. For pellet appliances, it has been developed together with combustion appliance manufacturers and the relevant authorities (SP 1999, 2000). It is based on emissions, efficiency, precautions against back-firing and other technical aspects. At present, 19 pellet burners, 6 boilers and 6 stoves are P-marked. The emission limits are generally somewhat higher than those of the Swan, and the limits for burners and boilers do not include particulate matter.

2.2.5 Pellet research in Europe

In order to further develop and promote pellets, a key issue is to compile and disseminate important research findings. As a part of the "www.EnergyCentre.info/Pellets" and "Pellets for Europe" projects, information on European pellet research and development was gathered by means of a questionnaire survey on past and current research and development activities (Olsson and Vinterbäck 2005a, 2005b).

There are currently more than 110 research groups and 250 scientists in Europe actively dealing with pellet related issues (Figure 8). This number has increased considerably over the past ten years. The early interest of the Nordic countries, and particularly Sweden, in pellet research is today reflected in a large number of research groups.

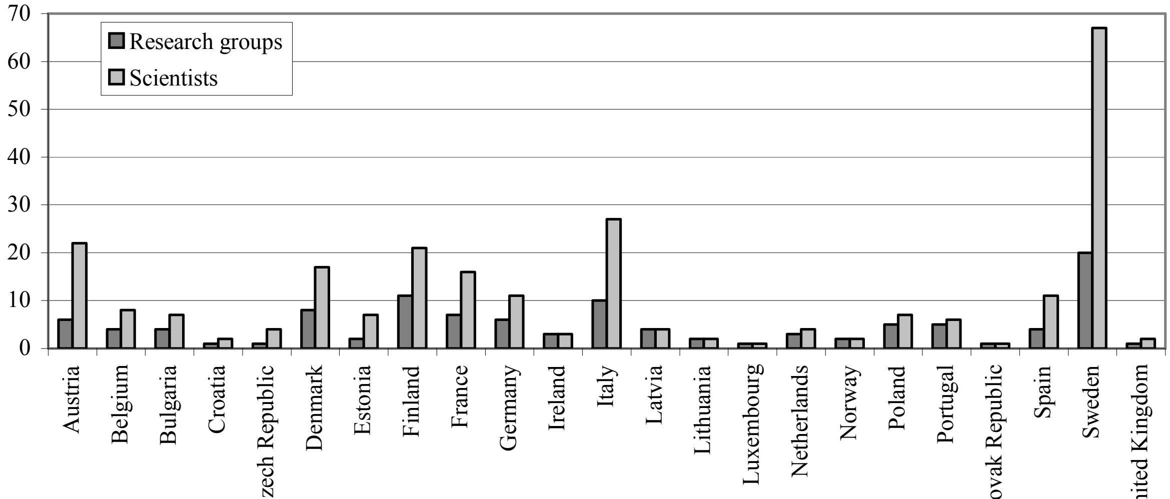

Figure 8: Number of European research groups and scientists involved in pellet research (Olsson and Vinterbäck 2005b).

2.2.6 Pellet research in Sweden

Pellet research in Sweden was included in the presentation of European pellet research and development (Olsson and Vinterbäck 2005a, 2005b). In Sweden there are currently more than 20 research groups working on pellet related issues. The total number of scientists involved is over 60. The research performed covers many different aspects of pellets, ranging from raw materials and production to combustion and emissions. Research groups represented are located at universities, institutes, private companies and hospitals.

A Swedish research network was initiated in 2001 and information is spread among the researchers and to the industry by research newsletters, network meetings and workshops. The researcher groups who contributed to the presentation of European pellet research are presented below, together with examples of publications in international journals within the pellet area.

Emissions of terpenes during drying and pelletising of biofuels, together with systems analyses, have been studied at Environmental and Energy Systems, Karlstad University (Granström 2003, 2005, Ståhl 2005, Ståhl *et al.* 2004). At Technology and Design, Växjö University, organic emissions, mainly terpenes, from the drying and storing of biofuels and self-ignition in stored biofuels are focused on (Rupar and Sanati 2003, 2005). Gaseous emissions from large- and small-scale storage of wood pellets have been further studied at Occupational and Environmental Medicine, Sundsvall Hospital (Svedberg *et al.* 2004).

Exposure to monoterpenes, wood dust and resin acids together with the health effects of industrial wood pellet production are being studied at Occupational and Environmental Medicine at Örebro University Hospital (Edman *et al.* 2003). The working environment at pellet production facilities has also been studied by the IVL Swedish Environmental Research Institute.

The main focus of the pellet research at Biomass Technology and Energy, SLU Swedish University of Agricultural Sciences has been new raw materials for pellets (Hadders and Olsson 1997, Lestander and Rhén 2005, Paulrud *et al.* 2002, Paulrud and Nilsson 2001, Paulrud *et al.* 2001). At Silviculture, research covers basic pelletising, raw material characterisation and systems analysis (Lestander and Rhén 2005).

At the SP Swedish National Testing and Research Institute, emissions from residential pellet burning, standardisation of pellet burning equipment and pellets from new raw materials are focused on (Eskilsson *et al.* 2004, Hansson *et al.* 2000, Hansson *et al.* 2004, Johansson 2002, 2005, Johansson *et al.* 2004, Johansson *et al.* 2003, Martinsson 2003, Rönnbäck *et al.* 2005, SP 1999, 2000). A great del of the research takes place in close cooperation with Energy Technology, Chalmers University of Technology, where combustion aspects are the main focus of pellet research (Hansson *et al.* 2000, Hansson *et al.* 2004, Johansson 2002, Johansson *et al.* 2004, Johansson *et al.* 2003, Larfeldt *et al.* 2000a, Larfeldt *et al.* 2000b, Thunman and Leckner 2002).

Pellet research at Energy Technology and Thermal Process Chemistry (ETPC), Umeå University, focuses on ash related problems, slagging, new raw materials, emission characterisation, aerosol formation, fundamental ash transformation chemistry, technical development and the health effects of exposure to emissions (Boman 2005, Boman *et al.* 2004, Boman *et al.* 2003b, Boman *et al.* 2005, Erlich *et al.* 2005, Öhman *et al.* 2004a, Öhman *et al.* 2004b). At the Energy Technology Centre in Piteå (ETC), raw material, pellet quality, feeding systems, combustion, emissions, problems and opportunities with ashes and slag are in focus (Hedman 2005, Wiinikka 2005, Wiinikka and Gebart 2004a, 2004b, 2005a, 2005b, Öhman *et al.* 2004a, Öhman *et al.* 2002).

At TPS Termiska Processer AB, Research (R&D), the combustion and gasification of biomass is studied. High temperature air and steam gasification of biomass, especially wood pellets, have been further studied at Energy and Furnace Technology, KTH Royal Institute of Technology (Lucas *et al.* 2004).

At Environmental and Energy System Studies, Lund Institute of Technology, the socio-economic aspects of pellet use are studied. At Bioenergy, SLU Swedish University of Agricultural Sciences, system studies of biofuels have been conducted (Bohlin *et al.* 1998, Hillring and Vinterbäck 1998, Hillring and Vinterbäck 1999, Lehtikangas 2000, 2001, Vinterbäck 2000). System studies of pellets and solar heating in residences is presently taking place at the Solar Energy Research Centre, Högskolan Dalarna (Fiedler 2004, Fiedler *et al.* 2006, Henning 2004, Persson 2004, Persson *et al.* 2005).

At Ecotechnology, Mid Sweden University, the design, analysis and implementation of resource- and cost-efficient energy systems with low environmental impact is in focus (Gustavsson and Karlsson 2002, Gustavsson and Mahapatra 2005, Karlsson 2003) with particular emphasis on the diffusion of small-scale pellet heating systems in the Swedish residential sector (Gustavsson and Mahapatra 2005). System aspects such as energy savings, carbon dioxide emissions and the economy of integrated pellet production systems have been investigated at Energy processes, KTH Royal Institute of Technology (Wahlund *et al.* 2002, 2004, Vidlund 2004). Pellet production integrated with a pulp mill has been studied in cooperation with the Department of Mechanical Engineering, Linköping University and the Department of Energy and Environment, Chalmers University of technology (Wolf *et al.* 2005).

2.3 New raw materials for pellets

The increased demand for wood pellets may lead to a future shortage of the present raw materials, sawdust and shavings. If the price and demand continue to rise, alternative raw materials for pellet production or for direct combustion in adapted pellet appliances will be considered. Examples of such future raw material sources are; logging residues, peat, energy crops, farming residues, sewage sludge and the organic fraction of household waste. A study of materials available for future production of fuel pellets in Sweden suggested forest fuels, such as thinning material and cull tree, in a short-term perspective and energy crops and lignin in a long-term perspective (Martinsson 2003).

To date, studies have been carried out on e.g. pellets (or briquettes) produced from bark (Hansson *et al.* 2004, Lehtikangas 2000, 2001, Obernberger and Thek 2004, Öhman *et al.* 2004a), logging residues (Lehtikangas 2000, 2001, Öhman *et al.* 2004a), reed canary grass (Hadders and Olsson 1997, Paulrud *et al.* 2001), lignin from production of ethanol using wood (Öhman *et al.* 2002), sugar cane bagasse (Erlich *et al.* 2005), almond residue (González *et al.* 2005), tomato residue, olive stones, cardoon (González *et al.* 2004), Miscanthus Giganteus (de Jong *et al.* 2003), lignite (Heschel *et al.* 1999), hay (Vierle *et al.* 1999), palm fibre and palm nut shell (Husain *et al.* 2002).

The emissions of specific organic compounds from the combustion of alternative pellet fuels must be thoroughly studied before they can be considered for the residential market. Not only do they have different technical burning characteristics, such as higher ash content, a greater tendency towards sintering and lower energy content, but they also contain more pollutants and mineral nutrients. This could give rise to uncontrolled emissions of compounds that are hazardous to health and the environment.

2.3.1 Oats, wheat straw and peat

Oats are an example of a fuel that can be directly combusted in adapted residential pellet appliances, whereas wheat straw and peat are examples of new raw materials for pellet production (Figure 9). These fuels were selected for studies of organic compounds in the emissions from combustion (Section 3.1.3 and 4.2, **VII**, **VIII**).

Figure 9: Oats, wheat straw pellets and peat/wood pellets.

The availability of the selected fuels is good. Oats are a very common cereal in Sweden and annual production in 2004 amounted to 900 000 tonnes (FAO 2004). Oats grown in Sweden are mainly used as animal feed, and only about 2 % are used for human consumption and industrial purposes (Åman 1987). World oat production in 2004 was 26 million tonnes (FAO 2004). Approximately 95 % of the global oat production is used as animal feed (Haard *et al.* 1999).

The potential for wheat straw in 2000 amounted to 1.7 million tonnes in Sweden and 44 million tonnes in Europe (Pellets for Europe 2005). The world potential for residues from wheat residues (straw, stalk and shell) was 684 million tonnes in 1983 (corresponding to 2.7 PWh, Werther *et al.* 2000).

Peat amounts to 25 % of the land area of Sweden, with an annual regrowth of about 20 million m^3 and an annual energy use of 3.5 million m^3 in 2005 (corresponding to approximately 3.5 TWh, Swedish Peat Producers Association 2005). The corresponding world figure was 3 % of the land area while the production of peat for energy use amounted to 70 million m^3 (Swedish Peat Producers Association 2005).

Oats have been suggested as the most suitable cereal for combustion due to a somewhat higher heat value and ash melting temperature compared to other cereals (Hadders *et al.* 2001). The combustion of oats and other cereal crops in suitable residential boilers has been shown to result in low emissions of organic gaseous carbon (OGC) and carbon monoxide (Löfgren 2001, Löfgren and Windestål 2001, Olsson *et al.* 2004a, Rönnbäck *et al.* 2005). Pellet burners for straw pellets are also available on the Swedish market and it has proven possible to combust wheat straw pellets in adapted residential boilers with low emissions of carbon monoxide and nitrogen oxides and relatively low emissions of sulphur dioxide (Fløjgaard Kristensen *et al.* 1999).

Combustion of oats, wheat straw pellets and peat/wood pellets differs in many ways from the combustion of softwood pellets and could lead to problems other than the emission of organic compounds. A high ash content compared to wood pellets makes automatic removal of the ash from the combustion appliance necessary.

According to a previous study, the use of straw pellets for residential heating is not recommended, as the present small-scale pellet furnaces are neither designed nor suitable for this kind of fuel (Obernberger and Thek 2004). A suggestion is to use straw pellets in medium and large-scale plants, due to the greater robustness and more sophisticated combustion technology of such systems. Straw pellets have been used for a long time in large-scale combustion plants in, for example, Denmark. Nevertheless, both residential straw pellet and oat combustion appliances are available on the market in Sweden, Germany, Denmark, Austria and other countries. Peat-containing pellets are at present not used for residential heating in Sweden.

2.3.2 Ecological aspects of pellets from new raw materials

The ecological and ecotoxicological aspects are important when discussing the potential role of pellets in a sustainable biofuel system. The general conclusion is that wood pellets should be reserved for residential heating whereas other, more contaminated, biomass waste should be burnt in large-scale combustion plants with flue-gas purification (Figure 10, **IV**, Olsson 2002, Olsson and Kjällstrand 2004).

Wood pellets are made from wood shavings and sawdust. These raw materials are by-products of sawmills and the timber industry and are clean and homogeneous, with low emissions to air during combustion (**I**, **II**, **IV**, **V**) and a low content of mineral nutrients. Wood pellets are therefore suitable for residential heating. Replacing large-scale coal combustion with wood pellets has, however, been found to have the highest potential for carbon dioxide reduction in Sweden (Wahlund *et al.* 2004).

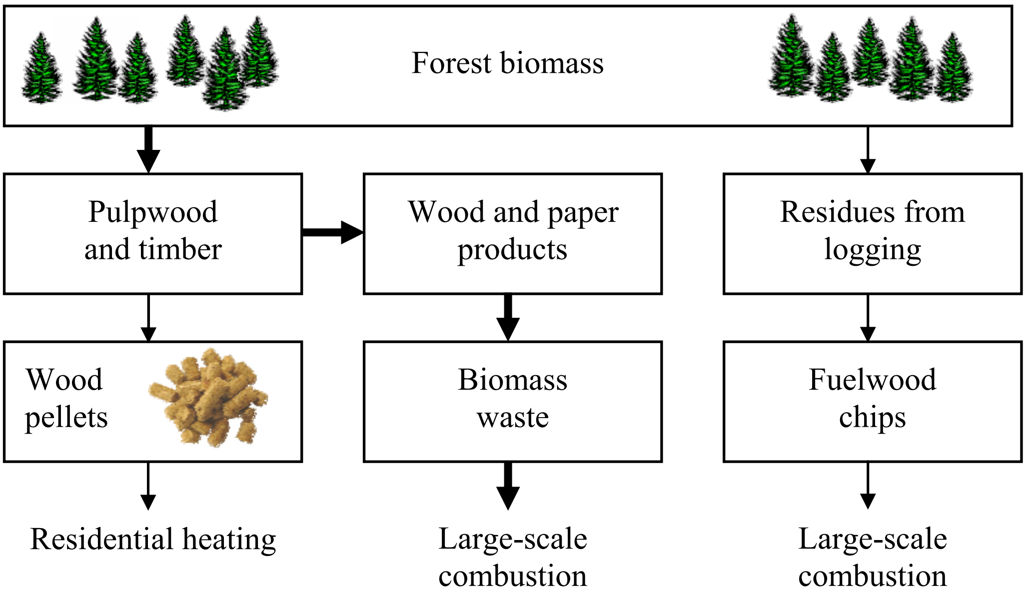

Figure 10: Sustainable use of biofuels from different sources in terms of biomass resources and environmental pollution (**IV**, Olsson 2002, Olsson and Kjällstrand 2004).

Biomass waste consisting of wood, paper and other biomass materials is a potentially useful biofuel, available in vast quantities. New waste regulations and higher deposition taxes will lead to a decrease in the amount being deposited on dumps. If the quantity of biomass waste burnt were to increase, the amount of forest biofuel used can be reduced and thus the impact on the forest ecosystem. Biomass waste is a complex fuel with hazardous chemical additives and contaminants (Launhardt *et al.* 1998). It must therefore be handled in large-scale combustion plants with rigorously controlled combustion and advanced flue gas purification.

Logging residues comprise twigs and foliage that can be collected as biofuels when timber for wood and pulp is taken out of the forest. Logging residues contain most of the mineral nutrients of the trees (Olsson *et al.* 1996) and removal of these nutrients from the forest affects productivity (Kimmins 1976), increases soil acidification (Olsson *et al.* 1996) and leads to an unsustainable cation balance (Lundborg 1997). The mineral nutrients are a problem during the combustion of the biofuels, giving rise to higher emissions of nitrogen oxides as well as more ash. Chopped logging residues can be pelletised with good results (Lehtikangas 2001), but are more suitable for large combustion plants with flue gas purification, due to the high content of mineral nutrients. The ecological disturbances in the forest can possibly be resolved by returning the ashes to the forest ecosystem.

3 Methods for smoke studies

The organic content of the smoke from the combustion of the selected fuels was studied both on a laboratory scale and in residential appliances. Various combinations of gas chromatographic columns and detectors were used for the analyses.

The emissions of organic compounds (≥ 6C) from incomplete flaming and glowing burning of softwood pellets were studied in laboratory experiments (**I**). Pellets from three different manufacturers were compared. The experiments were designed to simulate incomplete combustion in a pellet burner or stove. In an additional study, the emissions of organic compounds (≤ 7C) from five sequential combustion stages were determined on a laboratory scale for softwood pellets (**II**). Comparisons have been made with the results from a study of the emissions of organic compounds from glowing charcoal and pellet embers (**III**).

An extended laboratory scale study of organic compounds in smoke from these five sequential combustion stages was made for oats (**VII**), straw pellets and peat/wood pellets (**VIII**) and the emissions were compared to those from softwood pellets (**VII**, **VIII**).

Organic compounds (≥ 6C) were determined in the emissions from residential pellet burning appliances (**IV**, **V**). The smoke was sampled in the chimney outlets during normal operation of the appliances. In addition, the emissions of organic compounds from combustion in an ecolabelled residential wood boiler were studied (**V**, **VI**).

3.1 Laboratory studies

Incomplete combustion on a laboratory scale was studied, due to the fact that it reflects the chemical composition of the fuel and indicates the compounds that might be emitted during, for example, start-ups and temporary disturbances. In laboratory studies, it is also relatively easy to observe and control the combustion and achieve reproducible results. The results from laboratory studies can be confirmed by measurements on residential appliances.

3.1.1 Softwood pellets

The emissions of organic compounds (≥ 6C) were studied for incomplete flaming and glowing burning of softwood pellets in laboratory experiments (**I**).

Table 4: Overview of the different softwood pellets studied.

	Producer	Raw material
Pellets A	AB Forssjö Bruk	Sawdust and some shavings, mixed pine and spruce
Pellets B	Bioenergi in Luleå AB	Pine sawdust and some spruce
Pellets C	Mellanskogs Bränsle AB	Unspecified mixture of pine and spruce shavings, 1 % potato starch as binding agent

Softwood pellet samples from three different Swedish manufacturers were used (Table 4). The pellet samples chosen (Pellets A, Pellets B and Pellets C) represent different mixtures of sawdust and shavings, tree species and binding agents. The pellets studied were all 8 mm in diameter.

Flaming burning experiments were intended to resemble incomplete combustion in a pellet stove or burner, whereas glowing burning experiments were intended to simulate the combustion characteristics of a burner or stove at low effect or during shut down. During the experiments, six pellets were set aflame or completely burnt in a ceramic pot. For the flaming burning experiments, five additional pellets were subsequently added in order to simulate the automatic feed of pellets in residential combustion appliances. The smoke was collected on Tenax adsorbent (Figure 11).

Figure 11: Photo and schematic illustration of the combustion and sampling during studies of organic compounds (≥ 6C) on a laboratory scale (**I**).

Additionally, the emissions of organic compounds (≤ 7C) from five sequential combustion stages; initial smouldering, early flaming, late flaming, after-flame smouldering and final glowing, were determined for Pellets A on a laboratory scale (**II**).

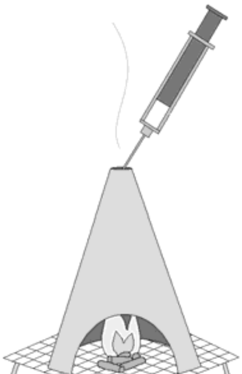

Figure 12: Sampling procedure during studies of organic compounds (≤ 7C) from five sequential combustion stages on a laboratory scale (**II**).

In this study, the pellets were placed on a steel net covered by an aluminium cone (Figure 12). Three pellets were set aflame from below using a butane torch, and three additional pellets were subsequently added. Samples were collected inside the top of the cone, using a gas-tight syringe.

3.1.2 Charcoal

The emissions of organic compounds from fully burnt out, glowing pellet embers (Pellets A) were further examined and compared to those of glowing birchwood embers and a few different types of charcoal (**III**). The fuel (15-60 g) was set on fire and burnt freely on a steel net. After the flaming ceased, they were further heated to a uniform glowing state. The smoke was concentrated and sampled using both a gas-tight syringe and Tenax adsorbent.

3.1.3 Oats, straw pellets and peat/wood pellets

The emissions of organic compounds from the five sequential combustion stages for oats (**VII**), straw pellets and peat/wood pellets (**VIII**) on a laboratory scale were determined and compared to those of softwood pellets (**VII**, **VIII**). Information on the different fuels studied is presented in Table 5.

Table 5: Overview of the different fuels studied.

	Producer	Raw material
Oats	-	Belinda, common fodder oat, grown in the Västra Götaland Region, Sweden
Straw pellets	Energi E2 A/S, Denmark	Wheat straw grown in Sealand, Denmark
Peat/wood pellets	Mebio AB, Sweden	35 % peat and 65 % softwood sawdust, unspecified mixture of pine and spruce
Softwood pellets	BrikettEnergi AB, Sweden	Unspecified mixture of sawdust and shavings of pine and spruce

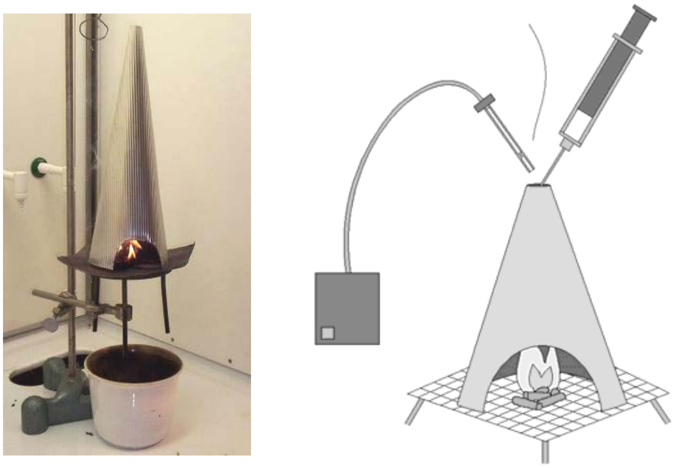

Figure 13: Photo of the combustion equipment used in the laboratory tests and a schematic illustration of the simultaneous sampling of carbon dioxide, carbon monoxide and organic compounds (≤ 7C) (gas-tight syringe, right) and organic compounds (≥ 6C) (Tenax adsorbent with pump, left), respectively (**VII**, **VIII**).

Seven pellets or a small amount of oats were placed on a steel net covered by an aluminium cone (Figure 13). The fuels were set aflame and two different types of samples were simultaneously collected inside the top of the cone, using a gas-tight syringe and Tenax adsorbent. The glass-liner containing Tenax adsorbent was cooled above the surface of liquid nitrogen just before sampling, in order to prevent break-through of volatile organic compounds, e.g. benzene, due to the relatively high sampling temperatures.

3.2 Measurements on residential appliances

Chimney sampling allows data from real, although not always perfectly installed, appliances. It is only possible to measure the actual emissions to the atmosphere in the chimney outlet. Sampling closer to the combustion chamber may also include compounds that normally condense onto the walls of the chimney, forming soot and tar, which are ultimately removed by the chimney-sweep.

3.2.1 Softwood pellet combustion appliances

In order to estimate the emissions from small-scale softwood pellet burning in Sweden, smoke samples were collected from the chimney outlets of a number of different burning appliances (**IV**, Olsson 2002).

The appliances studied, four different burners, two pellet stoves and one pellet boiler, were all intended for normal residential heating (Table 6, Figure 14). Softwood pellets of 8 mm diameter were used for the burners and the boiler and 6 mm softwood pellets were combusted in the stoves. Organic compounds (≥ 6C) in the chimney smoke were sampled on Tenax adsorbent. Smoke was also collected in Teldar bags for subsequent laboratory analyses of carbon dioxide, carbon monoxide and methane. Burner C, Stove A and Boiler A were studied at both high and low effect.

Table 6: Overview of the residential pellet combustion appliances studied.

	Producer Boiler (for burners)	Effect (kW)	Location
Burner A	Sahlins EcoTec A3 Albin Kombi 952, 1996	25	Small block of flats
Burner B	Sahlins EcoTec B1 Arimax 360 Bio	50	Burner manufacturer
Burner C	PellX P20 CTC combination boiler, 1971	20	Single family residence
Burner D	Janfire Flex-a CTC combination boiler, 1982	23	Single family residence
Stove A	Calimax Sandor	7	Boiler manufacturer
Stove B	Austroflamm Integra	11	Consultant’s laboratory
Boiler A	Baxi Multiheat	25	Boiler manufacturer

Samples were taken at the top of the chimney of all studied appliances, with one exception; the smoke from Stove B was sampled in a sampling pipe from the flue gas channel. Smoke was collected in Tedlar bags for laboratory assessment of carbon monoxide, carbon dioxide and methane simultaneously to the sampling of organic compounds (≥ 6C) on Tenax adsorbent. The temperature and flue gas flux were measured in the chimney outlet together with the oxygen, carbon monoxide, carbon dioxide and nitrogen oxide content of the smoke using direct recording instruments.

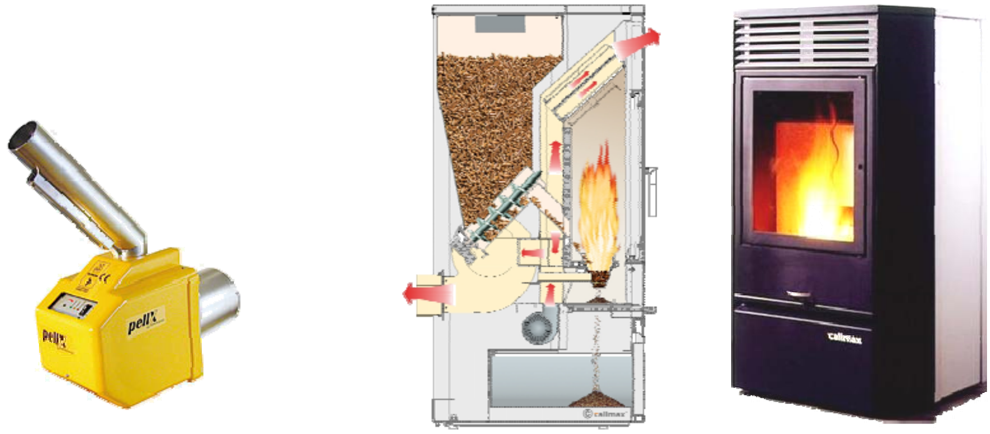

Figure 14: Pellet Burner C (picture, left, Gordic Environment AB 2005) and pellet Stove A (cross-section and picture, right, Calimax GmbH 2005).

3.2.2 Firewood combustion appliances

Organic compounds in chimney smoke from wood combustion in a modern ecolabelled residential boiler were studied (**VI**).

The wood boiler studied was a Baxi Solo Innova (30 kW), installed on the premises of the Swedish boiler distributor Baxi AB, Falköping, Sweden (Figure 15). The boiler was connected to a large hot water storage tank and intended for heating and hot-water production. The Baxi Solo Innova wood boiler was manufactured in 2001 and is ecolabelled.

Figure 15: Cross-section of the Baxi Solo Innova wood boiler (Baxi AB 2005).

The boiler was loaded with 10-40 kg of dry birchwood on four different sampling occasions. When using the largest volume, the burning period exceeded five hours. Smoke was sampled at the top of the chimney outlet using Tenax adsorbent (organic compounds, ≥ 6C) and Tedlar bags (carbon dioxide, carbon monoxide and organic compounds, ≤ 6C), for subsequent gas chromatographic analysis.

In order to compare the emissions of organic compounds from the ecolabelled wood boiler with more old-fashioned wood burning, an old wood stove was studied (**V**, Kjällstrand 2002). The wood stove was a 1981 EB-Pannan (20 kW) fireplace like boiler, which was connected to a hot water storage tank and installed in a single family residence in Ulricehamn, Sweden. Spruce logs, supplemented by some birch logs were used. Samples were taken during the flaming combustion phase.

3.3 Analytical data

Various combinations of gas chromatographic columns and detectors were used for the analyses (Figure 16).

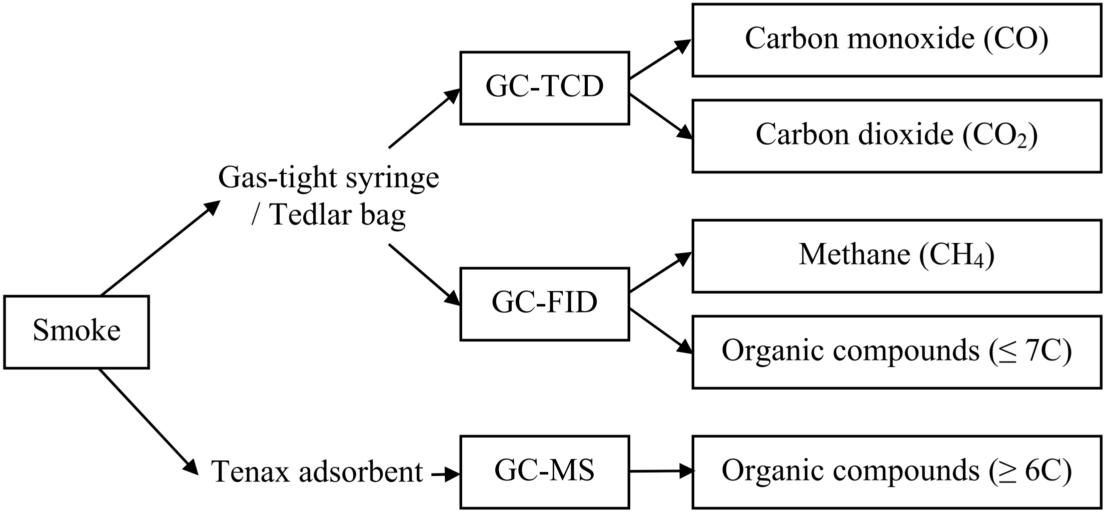

Figure 16: Analytical methods used for sampling and assessment of different compounds and compound groups.

3.3.1 Carbon monoxide and carbon dioxide (GC-TCD)

Carbon monoxide and carbon dioxide were assessed using a gas chromatograph with a thermal conductivity detector (GC-TCD, **II**, **III**, **IV**, **V**, **VI**, **VII**, **VIII**). A more detailed description of the analytical method is given in **II**.

Smoke samples were collected in 50 or 100 ml gas-tight glass syringes. The samples from residential appliances were transported and stored in Tedlar bags for subsequent analysis. Samples were injected in gas sampling loops. Carbon monoxide was separated on a molecular sieve column and carbon dioxide on a porous polymer column.

The concentrations were determined from peak areas in the chromatograms. The response factors of carbon dioxide and carbon monoxide for the thermal conductivity detector were determined by injecting pure gases.

The thermal conductivity detector records changes in the thermal conductivity of the incoming gas. Concentrations >10 ppm of the gases could be detected by the analytical system. The precision of the GC-TCD analyses is estimated to be 2 % for compounds at high concentrations (>1 000 ppm).

3.3.2 Organic compounds (≤ 7C) (GC-FID)

The organic compounds (≤ 7C) emitted were determined using a gas chromatograph with a flame ionisation detector (GC-FID, **II**, **III**, **VI**, **VII**, **VIII**). This system was previously used to study smoke from biomass combustion (Barrefors and Petersson 1995a, 1995b) and for vehicle emissions in urban air (Löfgren and Petersson 1992). A more detailed description of the analytical method is given in **II** and **VI**.

Smoke samples were collected in 50 or 100 ml gas-tight glass syringes (Figure 13, right). The samples from residential appliances were transported and stored in Tedlar bags for subsequent analysis. Samples were injected through a gas sampling loop (about 3 ml). An aluminium oxide column was used and a temperature gradient was applied for the separation (from –20ºC to 200ºC). The column used allows selective determination of volatile hydrocarbons (≤ 7C) and furans, while it irreversibly retains polar volatile compounds.

Identification was based on comparison with previous studies (Barrefors *et al.* 1996, Barrefors and Petersson 1995b). The response factor for hydrocarbons was determined by either injecting propane (**II**, **VII**, **VIII**), a reference gas mixture containing benzene and methylbenzene (**VI**) or a mixture of different hydrocarbons (**III**, according to Löfgren *et al.* 1991). The response factor was set equal (1.0) for all hydrocarbons. The relative response for furan was set to 0.6 in accordance with results of a previous study using the same analytical equipment (Barrefors *et al.* 1996).

In two earlier studies (**IV**, **VI**), methane was determined using a molecular sieve column and a flame ionisation detector. The concentrations were determined from the peak areas in the chromatograms. The flame ionisation detector was calibrated by injecting pure methane.

The flame ionisation detector is widely used for organic substances and has a high sensitivity and uniform response to hydrocarbons (Jorgensen *et al.* 1990). Compounds are ionised in the hydrogen flame and the ion current through the flame is measured. The response of a substance is generally proportional to the mass of carbon content in the sample. The presence of hetero atoms such as oxygen, nitrogen and halogens in the molecule decreases the relative response.

A large study of the relative response factors of 14 different GC-FID systems and 30 different hydrocarbons was presented (Slemr *et al.* 2004). All steps from sampling to detection were included and large differences in relative response between different systems were revealed. The reason for these large differences was ascribed to the construction and operating conditions of the different detectors used, inadequate peak area measurements and loss of hydrocarbons during preconcentration and desorption. However, when detector response alone was considered, the relative sensitivity was shown to be in the same range for most alkanes, and 5-15 % higher for ethene, ethyne, benzene and methylbenzene (Dietz 1967). The ethyne deviation was larger in another study (Sternberg *et al.* 1962).

According to the literature, benzene has a 15 % higher relative response factor than propane (Dietz 1967, Sternberg *et al.* 1962). Therefore, the choice of benzene as a reference gas overestimates the concentrations of other compounds, whereas the relative response of propane is more similar to the majority of hydrocarbons. The use of the same response factor for all hydrocarbons and with propane as reference gas slightly overestimates the concentrations of ethene and ethyne. The relative response factor 0.6 used for the determination of furan is very close to values calculated on the basis of previous studies (Jorgensen *et al.* 1990, Sternberg *et al.* 1962).

The precision of the GC-FID analyses is estimated to be 10 % for compounds at high concentrations (>1 ppm) and for the sampling volume used. However, combustion fluctuations give the major contribution to concentration variations. In this study, the focus has mainly been on the proportions of different compounds, and generally average values of several samples and their standard deviations are presented.

3.3.3 Organic compounds (≥ 6C) (GC-MS)

Organic compounds (≥ 6C) in the emissions were assessed using gas chromatography in combination with mass spectrometry (GC-MS, **I**, **III**, **IV**, **V**, **VI**, **VII**, **VIII**). This analytical method has previously produced satisfactory results in the assessment of organic compounds (≥ 6C) from the combustion of wood and other biomass (Kjällstrand and Petersson 2000, 2001a, 2001b, 2001c, Kjällstrand *et al.* 1998, 2000). A more detailed description of the analytical method is given in **I**.

Compounds present at very low concentrations have to be concentrated before the analysis. A way of simultaneously sampling and concentrating as well as storing both air borne and particle borne organic compounds (≥ 6C) is adsorption on Tenax. During sampling, smoke was pumped through a glass liner (0.8 mm × 30 mm) filled with Tenax adsorbent for 20 s - 10 min (Figure 17 and Figure 13, left). The total sampling volume was between 1 and 40 ml in the various studies.

When sampling with adsorbent cartridges, it is important to be aware of the risk of breakthrough of the most volatile compounds. Decomposition of and reactions between compounds adsorbed by the Tenax adsorbent at high temperatures and in the presence of nitrogen oxides must also be considered. Generally, the sampling temperature was 30-100ºC, the higher values referring to pellet Burner C. In some of the later studies (**VII**, **VIII**) the sampling temperatures were higher. The glass-liner containing Tenax adsorbent was therefore cooled in the fumes just above the surface of liquid nitrogen before sampling in order to prevent break-through of e.g. benzene and decomposition of sampled compounds.

Figure 17: Sampling in the chimney pipe.

The compounds sampled were thermally desorbed by placing the glass liner containing the Tenax adsorbent in the injector of the gas chromatograph and raising the temperature to 220ºC (Figure 18). A medium polar capillary column was used and a temperature gradient was applied for the separation (from –50ºC to 250ºC). The mass spectrometer used was an ion trap instrument and electron impact ionisation was selected.

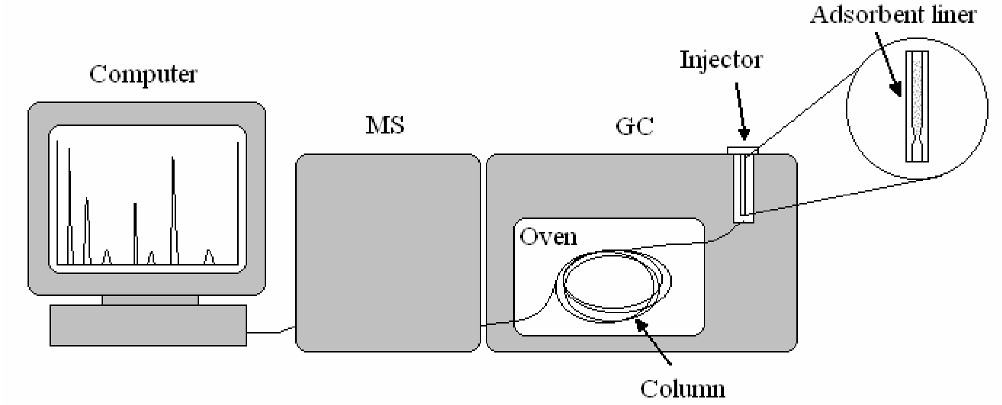

Figure 18: The gas chromatograph – mass spectrometer system with the Tenax filled adsorbent liner.

The organic compounds were identified from their mass spectra, relative retention times and by comparison with data from previous studies (Kjällstrand and Petersson 2001c, Kjällstrand *et al.* 1998) and from the NIST library. Selective ion monitoring allows the identification of compounds present in low concentrations, such as polycyclic aromatic hydrocarbons, among higher concentrations of other compounds (Figure 19).

Quantitative proportions of the compounds studied were determined from integrated peak areas either directly through total ion current monitoring (**I**, **IV**, **V**, **VI**) or recalculated to total ion concentrations using NIST library data and single ion monitoring (**VII**, **VIII**). No NIST data were available for the $SyCH_3$, $SyCH_2CH_3$, $SyCH=CH_2$ and $SyCH=CHCH_3$ syringols. Ion proportions from peaks in previous studies (Kjällstrand and Petersson 2001a) were used for the recalculations. Retention times for the studied compounds are presented in Table 7 together with specific ion and data from NIST library or from previous studies used for the recalculations.

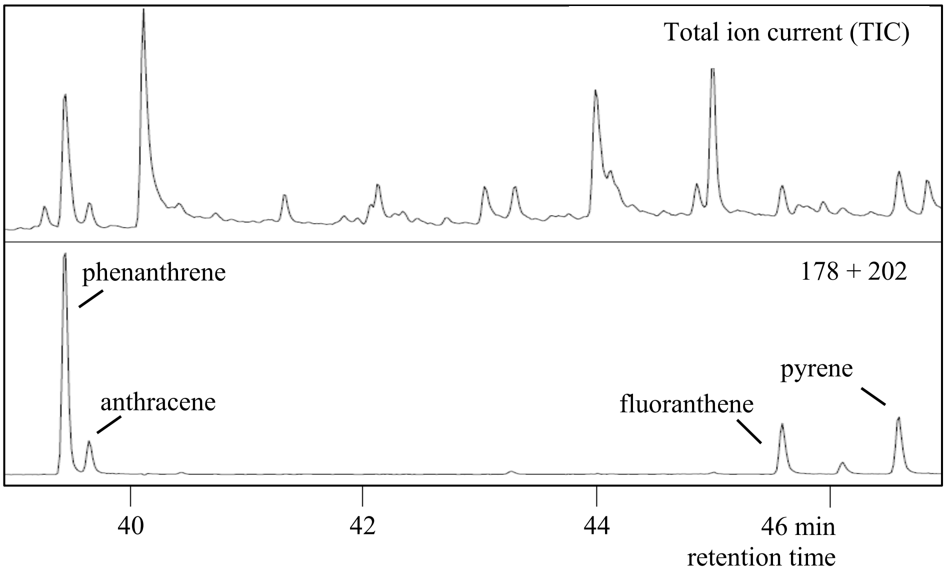

Figure 19: Smoke sample from the flaming combustion phase of the ecolabelled residential wood boiler (**VI**). The upper chromatogram shows the total ion current, while the lower chromatogram illustrates the selective ion monitoring of phenanthrene/anthracene (178) and fluoranthene/pyrene (202).

Table 7: Approximate retention time, specific ion and data from NIST library or from previous studies used for the recalculation from single ion current to total ion current (TIC) for the studied compounds.

Compound	Retention (min)	Specific ion	% specific ion of TIC
Benzene	8	78	43 [a]
2,5-Dimethylfuran	9	95	13 [a]
Methylbenzene	10	91	34 [a]
2-Furaldehyde	14	95	25 [a]
Benzofuran	17	118	28 [a]
Phenol	21	94	39 [a]
GuH (guaiacol)	21	109	31 [a]
Naphthalene	23	128	53 [a]
$GuCH_3$	24	123	23 [a]
$GuCH_2CH_3$	27	137	29 [a]
$GuCH{=}CH_2$	28	150	17 [a]
5-Hydroxymethyl-2-furaldehyde	29	97	24 [a]
SyH (syringol)	30	154	12 [a]
$GuCH{=}CHCH_3$ (*E*)	32	164	16 [a]
$SyCH_3$	32	168	24 [b]
GuCHO	32	151	20 [a]
$SyCH_2CH_3$	34	167	25 [b]
$SyCH{=}CH_2$	35	180	28 [b]
$SyCH{=}CHCH_3$ (*E*)	36	194	17 [b]
1,6-Anhydroglucose	38	60	28 [a]
SyCHO	39	182	22 [a]
GuCH=CHCHO	41	178	11 [a]

[a] From the NIST library, [b] From peaks in previous studies (Kjällstrand and Petersson 2001a)

Absolute mass spectrometer response was determined in two different ways. In **I**, **III**, **IV** and **V**, reference gas mixtures containing methylbenzene were used (also benzene in **III**). In **VI**, **VII** and **VIII**, the analyses of benzene by both GC-MS and GC-FID were used for the intercalibration between these two systems. The GC-FID was calibrated using benzene/methylbenzene or propane reference gases (Section 3.3.2). In the case of the combustion of oats (**VII**), the benzene concentrations during the final glowing stage were below the detection limit, thus the average response of 1,6-anhydroglucose from the other four combustion stages of oats was used.

The mass spectrometer is a highly sensitive detector that allows identification of different compounds through their specific mass fragmentation spectra. The relative response of a molecule depends on its total ionisation cross section (Q, Fitch and Sauter 1983). An estimate of the cross section of a molecule can be calculated as:

$$Q = 0.082 + \Sigma\,(a_i\, n_i)$$

where a_i is the atomic cross section (Table 8) and n_i the number of constituent atoms (Fitch and Sauter 1983).

Table 8: Selected atomic cross sections (Fitch and Sauter 1983).

Atom	a_i
C	1.43
H	0.73
O	1.10

Quantitative weight factors (Q/M) are obtained by dividing the molecule's relative cross section by its molecular mass (M). The relative cross section, the molecular mass and the relative response of selected compounds are reported in Table 9 together with the relative response normalised to benzene.

Relative response was set equal for all studied compounds. In the studies where benzene was used for intercalibration between the GC-FID and the GC-MS system (**VI**, **VII**, **VIII**), benzene is the natural choice of reference compound. Benzene also has a more average relative response than methylbenzene used in the earlier studies (**I**, **IV**, **V**). According to Table 9, the use of both benzene and methylbenzene as reference compounds overestimates the concentrations of other organic compounds studied (≥ 6C) by 5-30 % (Fitch and Sauter 1983).

The precision of the analyses by Tenax sampling and GC-MS is estimated to be 30-50 % for compounds at high concentrations (>0.1 ppm) and for sampling volumes >10 ml. However, combustion fluctuations give the major contribution to concentration variations. In this study, the focus has mainly been on the proportions of different compounds, and generally average values of several samples and their standard deviations are presented.

Table 9: Relative cross section (Q), molecular mass (M) and relative response (Q/M) of selected compounds together with their relative response normalised to benzene (Fitch and Sauter 1983).

Compound	Q	M	Q/M	Normalised to benzene
Methylbenzene	15.9	92	0.17	1.04
Benzene	13.0	78	0.17	1.00
Naphthalene	20.2	128	0.16	0.94
Phenanthrene	27.4	178	0.15	0.92
Pyrene	30.3	202	0.15	0.90
Phenol	14.1	94	0.15	0.90
Guaiacol (GuH)	18.1	124	0.15	0.87
Benzofuran	17.0	118	0.14	0.86
Syringol (SyH)	22.1	154	0.14	0.86
Vanillin (GuCHO)	20.7	152	0.14	0.81
1,6-Anhydroglucose	21.5	162	0.13	0.79
2-Furaldehyde	12.4	96	0.13	0.77

3.3.4 Further smoke characteristics (direct recording instruments)

The flue gas flux was measured using a Testo 445 instrument from Nordtec Instruments AB while the smoke temperature was measured with a Testo 925 or a Testo 300M instrument.

Compounds present at high concentrations in the smoke, such as carbon dioxide, carbon monoxide, nitrogen oxides and oxygen can be analysed with direct recording instruments. However, such instruments are only available for a limited number of compounds. The Testo 300M direct recording instrument was also used for carbon monoxide and carbon dioxide in the studies of residential appliances. Moreover, the same instrument was used for oxygen and nitrogen oxides. It was calibrated by Nordtec Instruments AB before use.

4 Emissions from laboratory studies

Incomplete combustion was studied, as it indicates the compounds that may be emitted at high concentrations during start-up and disturbances of residential pellet combustion appliances. During these periods, the emissions can be larger than normally and have a different chemical composition. The studies were made on a laboratory scale, and thus it was relatively easy to observe and control the combustion and to achieve reproducible results.

The results from laboratory studies were confirmed by measurements on residential appliances (Section 5). Pellet burning in residential appliances mainly comprises flaming, shorter periods of glowing and very little smouldering combustion. The temperatures are higher than those in laboratory experiments and combustion is almost complete.

The results presented refer to analyses of the emissions of organic compounds (≥ 6C) from the flaming and glowing of softwood pellets on a laboratory scale (**I**, Olsson and Kjällstrand 2004), as well as the emissions of organic compounds (≤ 7C) from five sequential combustion stages of softwood pellets (**II**). Furthermore, wood pellet ember emissions were more thoroughly analysed and compared to the combustion characteristics of different types of glowing charcoal and birchwood ember (**III**). The results presented also include analyses of the emissions of organic compounds from five sequential combustion stages of oats (**VII**), straw pellets and peat/wood pellets (**VIII**).

4.1 Combustion of softwood pellets

Softwood pellets give rise to very low emissions of organic compounds to air during combustion. The reason for this is not only the low water content and uniform shape. The thermal conductivity of solid wood is low (Larfeldt *et al.* 2000a, Larfeldt *et al.* 2000b), but wood pellets are more porous than solid wood since they consist of small compressed sawdust particles, which leads to a more rapid gas diffusion and heat transfer (Hansson *et al.* 2000). This results in improved combustion characteristics and decreased emissions to air in comparison with firewood and other solid biofuels.

4.1.1 Organic compounds (≥ 6C) from the combustion of softwood pellets

Organic compounds (≥ 6C) in the emissions from glowing and flaming laboratory burning of softwood pellets from three different manufacturers (Pellets A, Pellets B and Pellets C) were studied (**I**, Olsson and Kjällstrand 2004). The combustion conditions had a significant effect on the contents of the smoke, whereas the different pellet brands gave rise to similar emissions.

During flaming burning, a few pellets were burnt in a ceramic pot with a flame temperature of up to 800ºC. The pellets mainly emitted 2-methoxyphenols (Figure 20) with a guaiacyl (Gu) structure, originating from the lignin of the fuel. The total concentration of the six most prominent of these guaiacyl derivatives was 0.1-1 mg m^{-3} for all studied pellet brands. The assessed compounds shown in Figure 20 were related to this sum for each pellet brand. The single most predominant compound was methylguaiacol ($GuCH_3$). The chromatographic separation of the compounds released during flaming burning is shown in Figure 21.

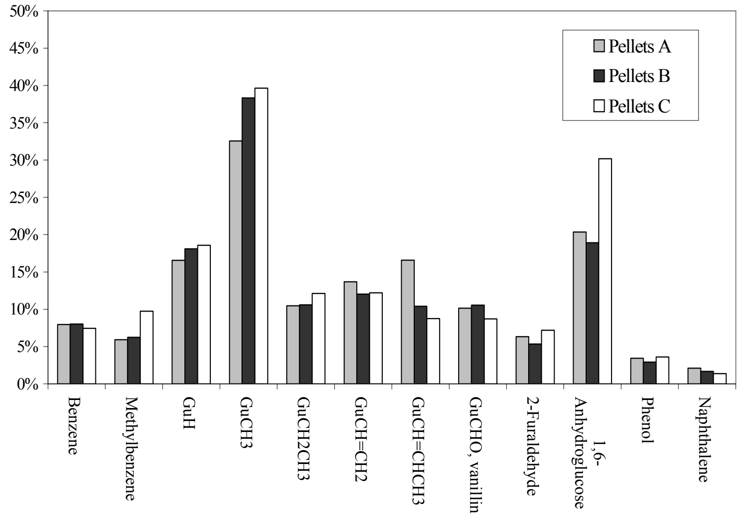

Figure 20: Relative proportions of major organic compounds (≥ 6C) in smoke from flaming burning of softwood pellets from three different manufacturers (Pellets A, Pellets B and Pellets C). The sum of all guaiacyl derivatives (Gu = 4-hydroxy-3-methoxyphenyl) was set to 100 % for each pellet brand (Olsson and Kjällstrand 2004).

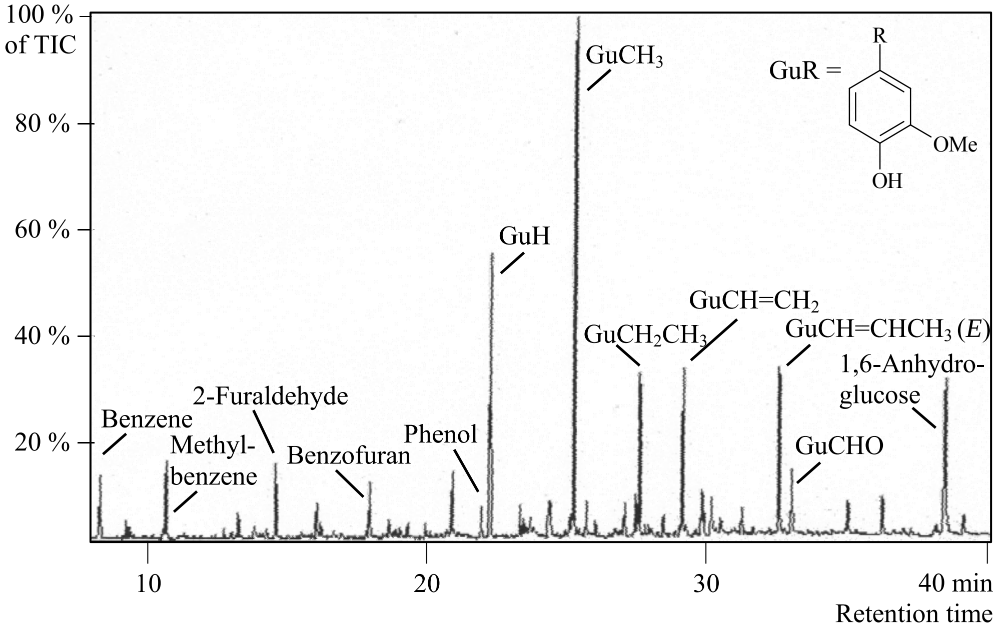

Figure 21: Section of total ion current (TIC) chromatogram illustrating the separation of organic compounds (≥ 6C) emitted during flaming burning of Pellets A. Separation on a medium polar gas chromatographic column and detection by mass spectrometry (Olsson 2002).

The most prominent polysaccharide derived compound from flaming burning of pellets was 1,6-anhydroglucose. The higher concentration of this compound in Pellets C may be due to the use of potato starch as a binding agent. Another polysaccharide derived compound found from flaming burning was 2-furaldehyde.

Benzene (0.01-0.1 mg m^{-3}) and methylbenzene were the major aromatic hydrocarbons emitted from flaming burning of pellets. The formation of naphthalene and other hazardous polycyclic aromatic hydrocarbons was low.

After the flaming period, the pellets glowed with a surface temperature below 400ºC. The predominant organic compound (≥ 6C) from glowing burning was benzene (0.01-0.3 mg m^{-3} for all studied pellet brands, Figure 22, Figure 23). The relative ratio between benzene and methylbenzene was much higher than during the flaming burning stage and from flaming burning of firewood in a stove (Barrefors and Petersson 1995b, Kjällstrand and Petersson 2001c). The concentrations of naphthalene and phenanthrene, as well as other polycyclic aromatic hydrocarbons were, as expected, low due to the low combustion temperature (Alén *et al.* 1996, Hauk *et al.* 1994).

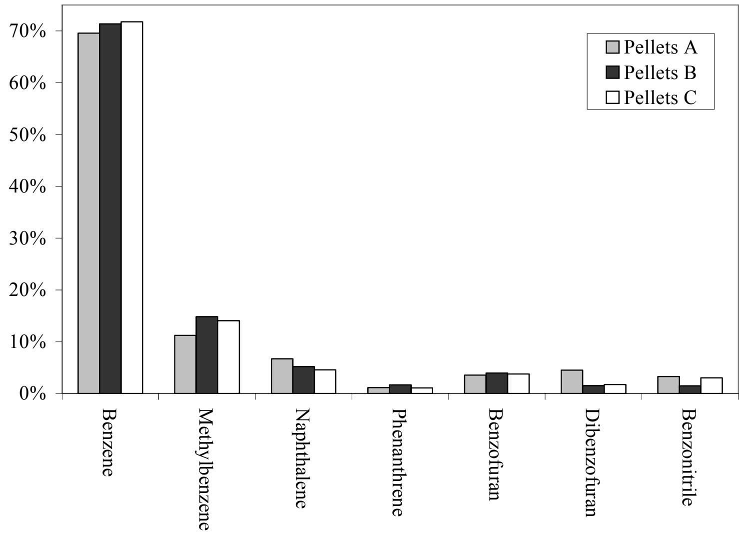

Figure 22: Relative proportions of major organic compounds (≥ 6C) in smoke from glowing burning of softwood pellets from three different manufacturers (Pellets A, Pellets B and Pellets C). The sum of the selected compounds was set to 100 % for each pellet brand (Olsson and Kjällstrand 2004).

Primary combustion products from the wood lignin and cellulose, such as guaiacyl derivatives and 1,6-anhydroglucose were absent in the smoke from glowing pellets. Formation of these compounds seems to have occurred almost exclusively during the flaming burning stage. This absence of primary combustion products is a great difference when comparing glowing pellets to glowing firewood (Kjällstrand and Petersson 2001c), which can be explained by the more rapid gas and heat transfer in the porous pellet (Hansson *et al.* 2000, Larfeldt *et al.* 2000a, Larfeldt *et al.* 2000b).

The large proportion of the carcinogenic benzene in the emissions from glowing burning makes it essential to consider the emissions from this stage, in spite of the fact that the total concentrations of organic compounds are larger during the flaming stage.

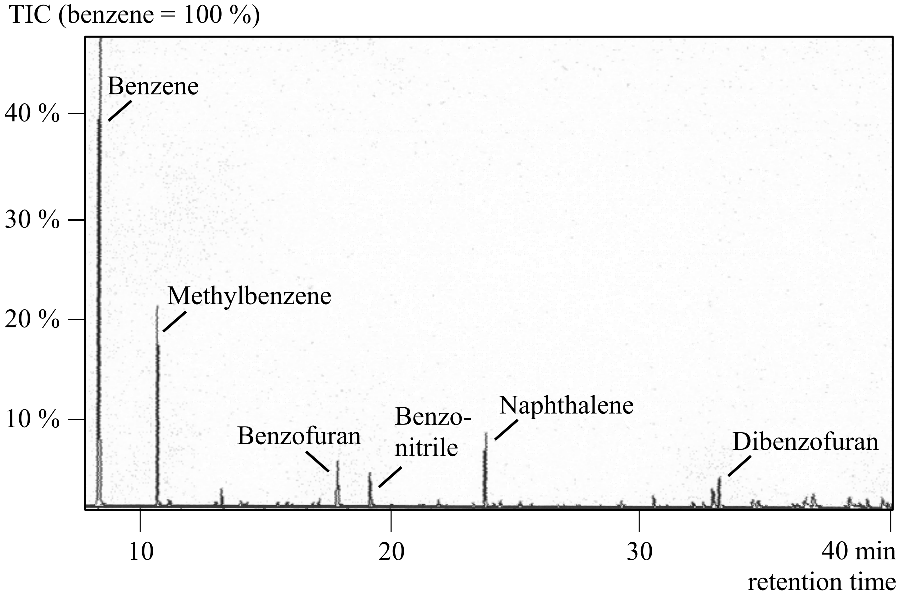

Figure 23: Section of total ion current (TIC) chromatogram illustrating the separation of organic compounds (≥ 6C) emitted from glowing burning of Pellets A. Separation on a medium polar gas chromatographic column and detection by mass spectrometry (Olsson 2002).

In another study (**III**), the emissions of organic compounds from softwood pellet embers (also of Pellets A) were investigated in greater detail and compared to those from glowing Swedish charcoal and glowing birchwood embers. The compound composition of the emissions from the glowing burning of softwood pellets (**I**) largely resemble that of softwood pellet embers and glowing charcoal (Figure 24, Figure 25, **III**).

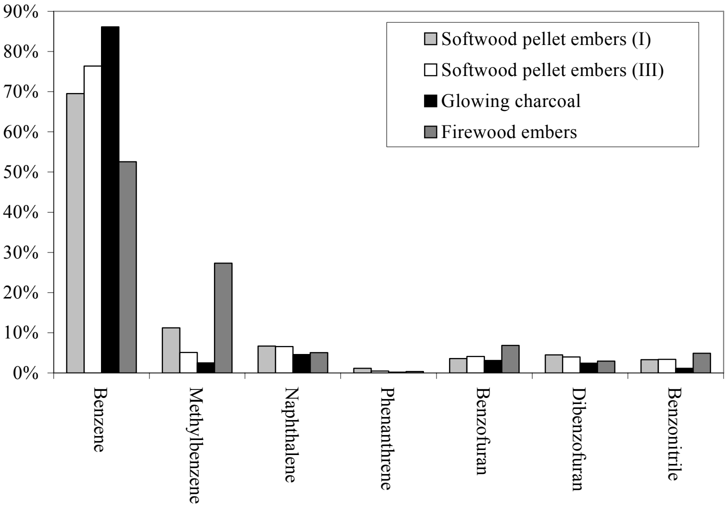

Figure 24: Comparison of relative proportions of major organic compounds (≥ 6C) in smoke from embers of Pellets A in two different studies (**I, III**), glowing charcoal and firewood embers (**III**). The sum for each fuel was set to 100 %.

Benzene was the predominant organic compound (≥ 6C) emitted during glowing burning of all studied fuels (Figure 24, **I**, **III**). The relative ratio between methylbenzene and benzene was lower from glowing remains of solid firewood, than from the other fuels, which is in accordance with a previous study of the glowing phase of birchwood combustion in a stove (Barrefors and Petersson 1995b).

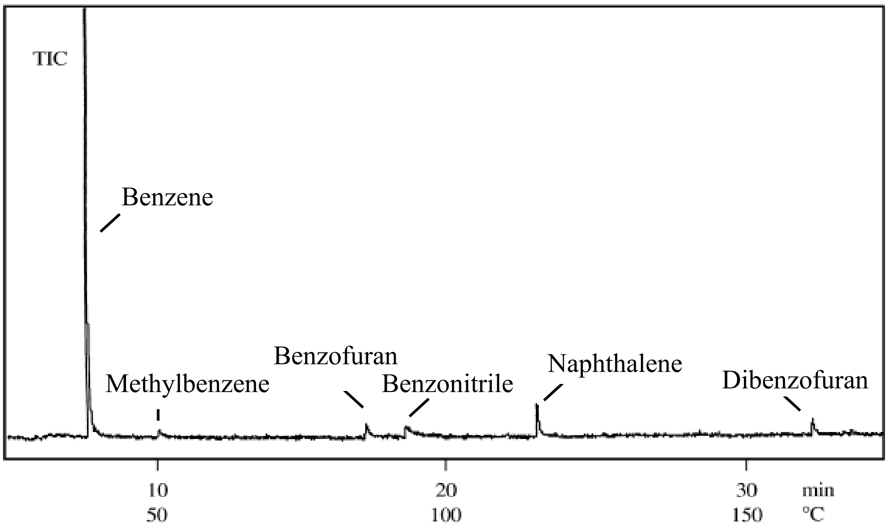

Figure 25: Section of total ion current (TIC) chromatogram showing benzene and aromatic compounds released from glowing Swedish charcoal. Separation on a medium polar gas chromatographic column and detection by mass spectrometry (**III**).

4.1.2 Organic compounds (≤ 7C) from the combustion of softwood pellets

The emissions of organic compounds (≤ 7C) from five sequential combustion stages; initial smouldering, early flaming, late flaming, after-flame smouldering and final glowing (Figure 26), were determined on a laboratory scale for Pellets A (**II**). Large differences in the proportions of specific organic compounds from the different combustion stages were found.

Figure 26: Initial smouldering, early flaming, late flaming, after-flame smouldering and final glowing of softwood pellets.

In Figure 27, concentrations of carbon dioxide, carbon monoxide, methane and the sum of other assessed organic compounds (≤ 7C) (Other OC) are reported for the different stages of laboratory burning of softwood pellets. Chromatograms from the five combustion stages are presented in Figure 28 and illustrate the varying composition of the smoke during the different stages.

The concentrations of organic compounds (≤ 7C) were high during the short initial smouldering stage. The main compounds emitted were methane, furan and ethene. Initial smouldering reflects pyrolysis of the original softwood, and high proportions of furan-related compounds, such as furan, 2-methylfuran and 2,5-dimethylfuran, were released. The furan-related compounds originate from cellulose and other polysaccharides. The concentrations of furan-related compounds were negligible in smoke from the other combustion stages.

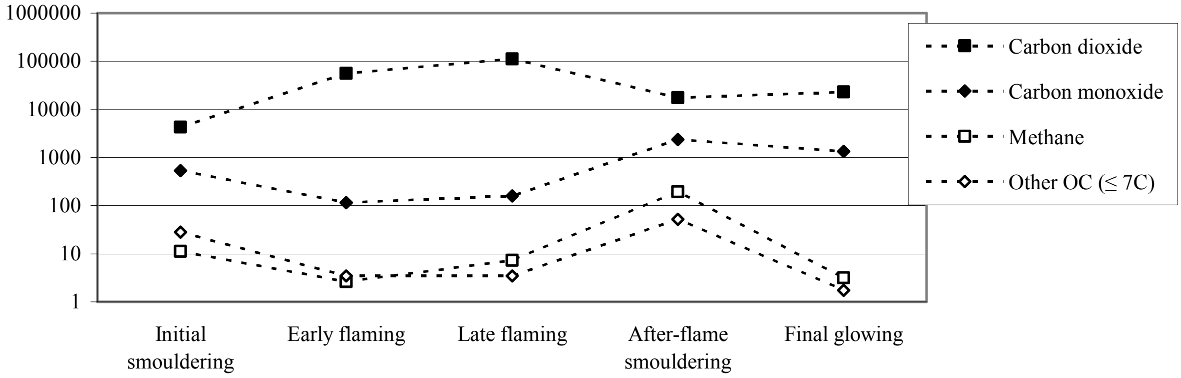

Figure 27: Concentrations (mg m^{-3}, logarithmic scale) of carbon dioxide, carbon monoxide, methane and the sum of other assessed organic compounds (≤ 7C) (Other OC) from different stages of laboratory burning of softwood pellets (Pellets A).

Combustion during the early and late flaming stages was very efficient, with high concentrations of carbon dioxide, together with low concentrations of carbon monoxide and organic compounds (≤ 7C). The temperature measured between the pellets was 400-500ºC during early flaming and around 500ºC during late flaming. The combustion efficiency, calculated as $[CO_2]/([CO_2]+[CO])$, was above 99 %, despite the fact that the samples were taken from a few pellets burning on a metal net under laboratory conditions. During the flaming stages, about 80 % of the dry biomass was combusted. The dominant organic compounds (≤ 7C) emitted were methane, ethene and ethyne. Previous studies of pinewood burnt in a fireplace showed similar proportions of organic compounds (≤ 7C), but the emissions from the fireplace were ten times higher in relation to carbon dioxide (McDonald *et al.* 2000, Schauer *et al.* 2001). Late flaming differed from early flaming in terms of higher proportions of alkanes.

The highest concentrations of organic compounds (≤ 7C), especially methane, ethane, ethene and benzene, were found during the short after-flame smouldering stage.

The emissions from final glowing of softwood pellets were even lower than from flaming burning and very different in composition, with only methane, ethyne and benzene as prominent compounds. The carbon monoxide emissions were, however, higher for glowing than for flaming combustion. The formation of ethyne and benzene may be explained by the charcoal-like character of the glowing pellets, with a high carbon content (more than 80 % compared to about 50 % in dry wood) and a low hydrogen/carbon ratio. Ethyne and benzene have high thermal stability and low reactivity towards oxygen radicals. Therefore, their relative proportions of the total amount of unsaturated volatile hydrocarbons from wood fuels increase with increasing combustion temperature (Barrefors and Petersson 1995b).

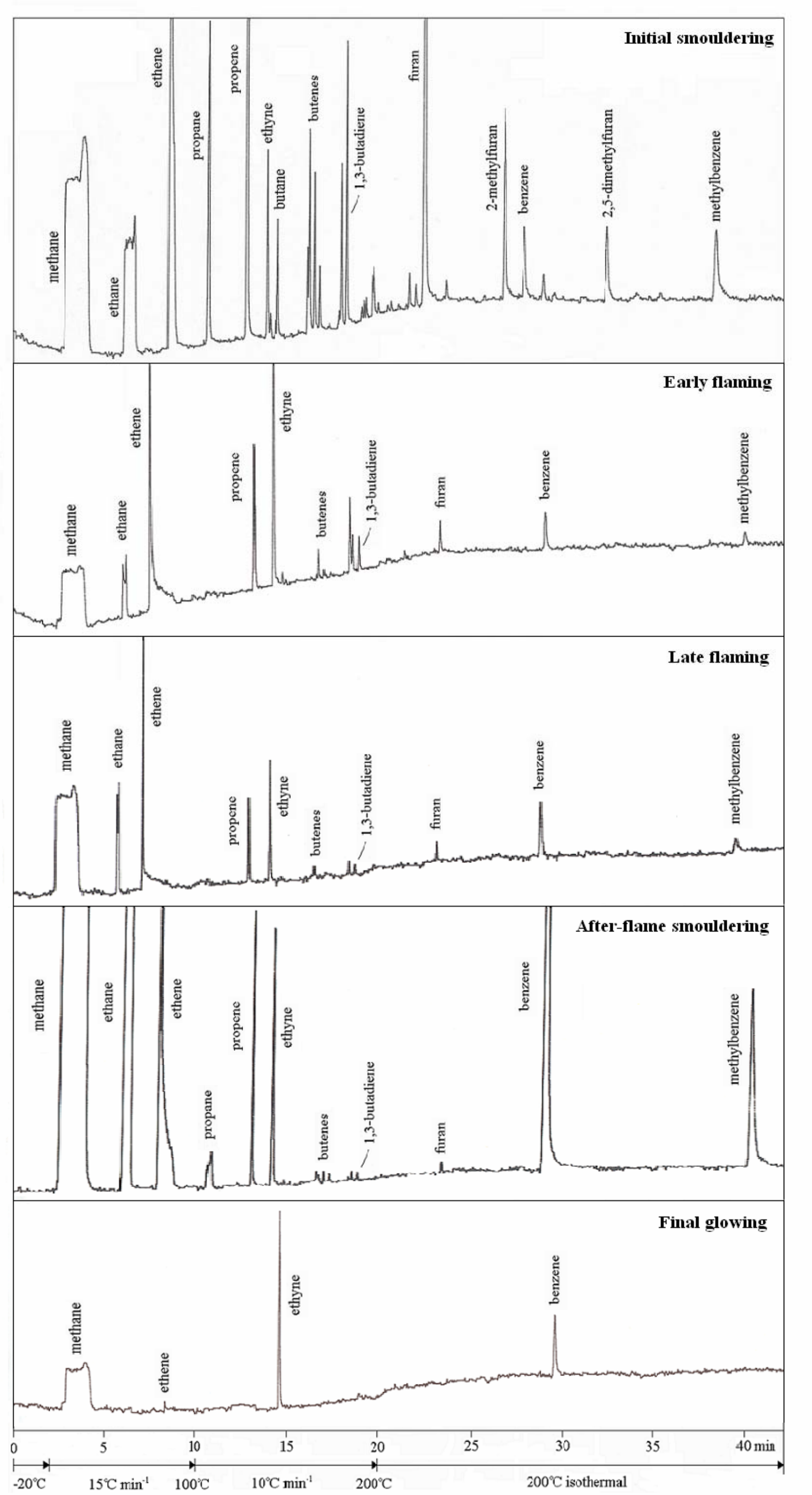

Figure 28: Organic compounds (≤ 7C) emitted from different stages of softwood pellet combustion on a laboratory scale. Separation on an aluminium oxide column and determination by flame ionisation detection (Olsson 2004a).

Generally, combustion during the early and late flaming stages was very efficient and only low emissions of organic compounds (≤ 7C) were determined. The emissions from initial and after-flame smouldering were much higher. The emissions from the different combustion stages should be considered when evaluating residential pellet burning appliances in terms of combustion technology and impact on health and the environment. Significant contributions from the initial and after-flame smouldering stages are likely to occur mainly as a result of improperly functioning pellet combustion appliances. Residential combustion appliances have automatic regulation of the effect by means of a thermostat. It is important that the design prevents unnecessary and slow fluctuations between the different combustion stages.

In another study (**III**), the emissions of organic compounds from softwood pellet embers (also of Pellets A) were investigated in greater detail and compared to those from glowing Swedish charcoal and glowing birchwood embers. In Table 10, concentrations of carbon dioxide, carbon monoxide and prominent organic compounds (≤ 7C) in smoke from pellet embers (glowing softwood pellets in **II**) are presented together with emission data on glowing charcoal, firewood embers and pellet embers (**III**). Note that the combustion conditions varied slightly in the different studies.

Table 10: Concentrations (mg m^{-3}) of carbon dioxide, carbon monoxide and prominent organic compounds (≤ 7C) in smoke from glowing softwood pellets (**II**). Comparison with pellet embers, glowing charcoal and firewood embers (**III**).

	Pellet embers [a]	Pellet embers [b]	Glowing charcoal [b]	Firewood embers [b]
CO_2	23 000	50 000	110 000	97 000
CO	1 300	4 700	11 000	14 000
Methane	3.1	6.7	40	470
Ethane	<0.03	<0.03	0.63	89
Ethene	0.03	0.29	0.58	39
Propene	<0.03	0.03	0.43	21
Ethyne	1.2	1.6	7.6	4.9
Benzene	0.52	1.1	2.7	12

[a] (**II**), [b] (**III**)

Methane, ethyne and benzene were predominant organic compounds in emissions from all of the studied fuels (**II**, **III**). The emissions from glowing charcoal were in general ten times higher than those from glowing pellet embers, leading to high exposure to health hazardous compounds, mainly for the cook preparing food over glowing charcoal.

During the final glowing stage (**II**), the pellets were more completely charred and emitted lower amounts of all the compounds in Table 10 than the glowing charcoal and pellet embers (**III**). The results for glowing remains of solid firewood were quite different, with specific hydrocarbons in proportions similar to those from flaming firewood (Barrefors and Petersson 1995b). This can be explained by lower gas diffusion and heat transfer in solid wood compared to pellets (Hansson *et al.* 2000, Larfeldt *et al.* 2000a, Larfeldt *et al.* 2000b).

4.2 Combustion of oats, straw pellets and peat/wood pellets

Organic compounds (both ≤ 7C and ≥ 6C) in the emissions from combustion of oats (**VII**), straw pellets and peat/wood pellets (**VIII**) were determined and compared to those of softwood pellets (**VII**, **VIII**). The peat/wood pellets contained 35 % peat and 65 % softwood. The emissions were measured during five sequential combustion stages; initial smouldering, early flaming, late flaming, after-flame smouldering and final glowing (Figure 29). The emissions of organic compounds differed greatly, depending both on the combustion conditions and the chemical structure of the fuels.

Figure 29: Initial smouldering, early flaming, late flaming, after-flame smouldering and final glowing of oats (top row), wheat straw pellets (middle row) and peat/wood pellets (bottom row, **VII**, **VIII**).

The combustion started with initial smouldering, when moisture evaporated and volatile compounds were released. During early flaming, the temperature was 400-450ºC (measured between the pellets or grains of oats) and a considerable amount of the virgin fuel was still visible. At the late flaming stage, there was no virgin fuel visible, only charred surfaces. In the case of oats, the temperature decreased during this stage, whereas for all the pellets studied the temperature increased slightly to 450-500ºC. The duration of both the early and the late flaming stage was 1-2 min. When flaming ceases, the short after-flame smouldering stage was entered. No major temperature decrease took place in the case of the studied pellets. For oats, on the other hand, the temperature decreased dramatically. Following the after-flame smouldering stage, the final glowing stage began. The duration of this stage was very short for oats, whereas it lasted for up to 20 min for the studied pellets, during which the temperature slowly decreased.

During the burning of oats, only about 57 % of the fuel was combusted. In contrast, more than 98 % of the straw, peat/wood and wood pellets were burnt (ashes excluded).

Due to inefficient combustion, the total concentrations of organic compounds (Figure 30) from initial smouldering were high in comparison with those from the subsequent stages, especially for the peat/wood pellets. Generally, the emissions from early and late flaming of the studied fuels were low and the combustion efficiency high. However, during flaming burning, wood pellets burned even more efficiently and with lower emissions than the other fuels.

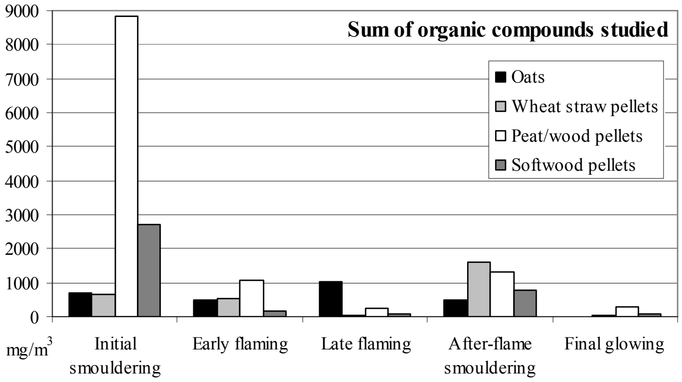

Figure 30: Concentrations (mg m^{-3}) of the studied organic compounds in the emissions from the five sequential combustion stages of the selected fuels (Olsson 2005b).

High concentrations of methoxyphenols (Figure 31) from the lignin of the fuels were emitted during the initial smouldering. This was especially pronounced for peat/wood pellets, probably due to more inefficient combustion.

Methoxyphenols with a guaiacyl structure, such as ethenylguaiacol, *trans*-propenylguaiacol and vanillin were most common in smoke from all of the studied fuels. In smoke from oats, wheat straw pellet and peat/wood pellet combustion, dimethoxyphenols with a syringyl structure were also present, especially syringol. For peat/wood pellets smoke, the guaiacols mainly originate from the softwood, whereas the lower amount of syringols (about 10 %) are considered to originate from other bog plants incorporated in the white moss.

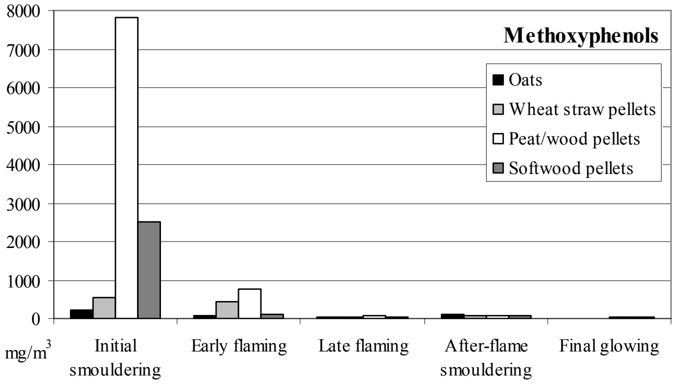

Figure 31: Concentrations (mg m^{-3}) of methoxyphenols in the emissions from the five sequential combustion stages of the selected fuels (Olsson 2005b).

The highest concentrations of 1,6-anhydroglucose (Figure 32) from the polysaccharides of the fuels were found from the combustion of oats, especially during late flaming.

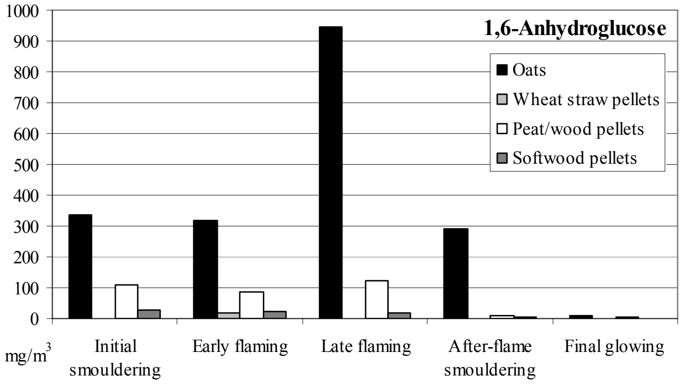

Figure 32: Concentrations (mg m^{-3}) of 1,6-anhydroglucose in the emissions from the five sequential combustion stages of the selected fuels (Olsson 2005b).

The concentrations of furan-related compounds (Figure 33), such as furan, 2,5-dimethylfuran, 2-furaldehyde, 5-hydroxymethyl-2-furaldehyde and benzofuran, were highest during initial smouldering of all the studied fuels, especially peat/wood pellets.

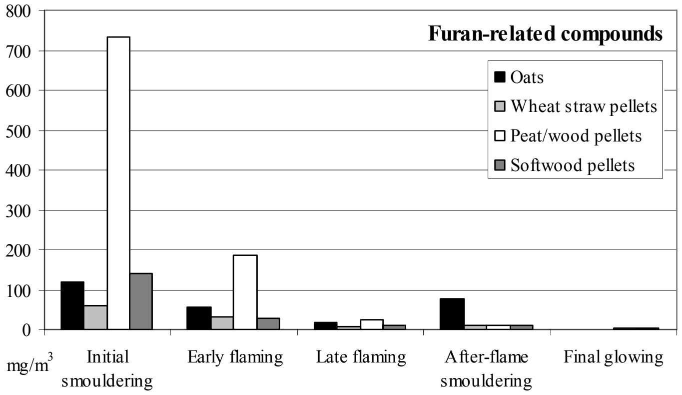

Figure 33: Concentrations (mg m^{-3}) of furan-related compounds in the emissions from the five sequential combustion stages of the selected fuels (Olsson 2005b).

Methane was the predominant greenhouse gas emitted from oats, wheat straw pellets and softwood pellets (Figure 34). Opinions differ as to whether peat should be considered a renewable fuel, a slowly renewable fuel or a fossil fuel. If it is considered a renewable fuel, the carbon dioxide emissions from combustion will not result in any net contribution to global warming. Only the methane emissions from the peat/wood pellets are included in Figure 34. The softwood content of the studied peat/wood pellets was 65 %.

Due to the high concentrations of methane, after-flame smouldering may be the stage during which all of the studied pellets give rise to the greatest global warming impact. This was most pronounced for wheat straw pellets. However, since methane was mainly formed during the short after-flame smouldering stage, the total emissions were low. The smoke from after-flame smouldering evolved during less than half a minute, compared to up to five minutes during flaming burning (both early and late). Very low methane emissions were observed during the after-flame smouldering of oats.

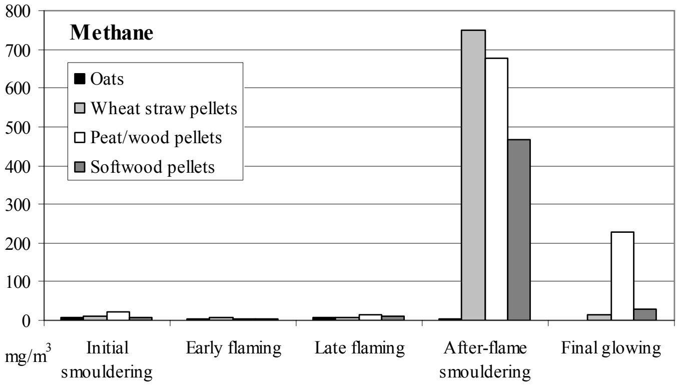

Figure 34: Concentrations (mg m^{-3}) of methane in the emissions from the five sequential combustion stages of the selected fuels (Olsson 2005b).

Some of the compounds studied are hazardous to health, such as ethene and propene (genotoxic), benzene (carcinogenic to humans), 1,3-butadiene (probably carcinogenic to humans), naphthalene, furan and benzofuran (possibly carcinogenic to humans, IARC 2004). The total concentrations of these compounds for the different combustion stages are presented in Figure 35.

In addition to high methane concentrations, high concentrations of health hazardous compounds were also found during after-flame smouldering of the studied pellets, but not the oats. The concentrations of the polycyclic aromatic hydrocarbons naphthalene and phenanthrene in smoke from the after-flame smouldering of straw pellets and the early flaming of peat/wood pellets were relatively high.

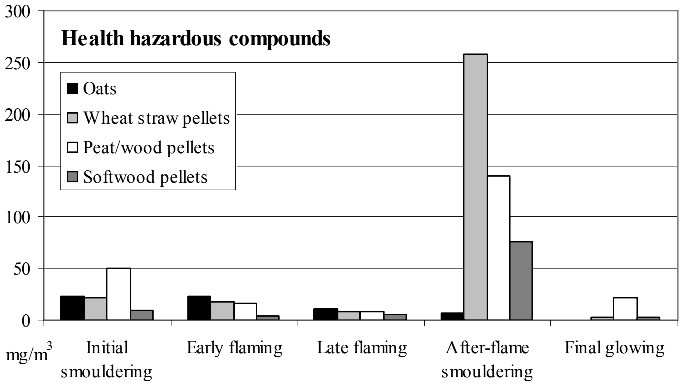

Figure 35: Concentrations (mg m^{-3}) of assessed health hazardous compounds in the emissions from the five sequential combustion stages of the selected fuels (Olsson 2005b).

Generally, the results from this laboratory study indicate that combustion of oats, wheat straw pellets and peat/wood pellets gives rise to relatively low emissions, almost as low as those from softwood pellets. The concentrations of certain carcinogenic compounds were, however, somewhat elevated. After-flame smouldering was the stage with the highest emissions of hazardous compounds, and it should therefore be avoided if possible.

5 Emissions from residential appliances

Wood pellets are an environmentally friendly replacement for firewood in traditional boilers and light fuel oil, with no carbon dioxide emissions contributing to global warming. It is important that the emissions of air pollutants from residential combustion appliances are low, especially in urban areas. The concentrations of specific organic compounds in the smoke from wood pellet appliances and an ecolabelled wood boiler were therefore determined.

Chimney sampling is a means of obtaining data from genuine, although not always perfectly installed, appliances. It is only possible to measure the actual emissions to the atmosphere in the chimney outlet. Sampling closer to the combustion chamber may include less volatile compounds that normally condense onto the walls of the chimney, forming soot and tar, which are eventually removed by the chimney-sweep.

The emissions from the combustion of softwood pellets in residential appliances were generally low. The emissions from the combustion of firewood in the studied ecolabelled boiler were in the same range as those from wood pellet combustion.

The results presented here refer to studies of organic compounds (≥ 6C) and other smoke characteristics in chimney smoke from pellet burners, stoves and boilers used for residential heating (**IV**, Olsson and Kjällstrand 2004). Results from measurements of organic compounds in chimney smoke from an ecolabelled residential wood boiler are also presented (**VI**). Further, the results from residential pellet and firewood combustion are compared (**V**).

5.1 Residential combustion appliances for softwood pellets

All samples from residential combustion appliances for softwood pellets were taken in the chimney outlet of appliances installed for heating purposes. It is important to emphasise that the results are not general emission data, but rather examples from individual cases which indicate the approximate emission levels. The emissions are not only related to the brand and design of the combustion appliance, but also to its installation, management and maintenance. In the case of pellet burners, the choice of boiler in which the burner is installed is of great importance as well.

5.1.1 Residential pellet burners

The emissions of organic compounds (≥ 6C) from four residential pellet burners; Burner A, B, C and D, were sampled and measured in the chimney outlet together with other smoke characteristics (**IV**, Olsson and Kjällstrand 2004). The four burners were all studied at maximum effect. In addition, Burner C was studied at half effect. All the studied burners were installed in combination boilers and fuelled with softwood pellets.

The concentrations of carbon dioxide, carbon monoxide, methane, benzene and phenanthrene in the emissions from pellet Burner A, C and D are presented in Table 11.

Table 11: A comparison of the concentrations of selected compounds in the emissions from different residential pellet burners (mg m^{-3}, **IV**, Olsson and Kjällstrand 2004).

	Burner A	Burner C		Burner D
	25 kW	20 kW	10 kW	23 kW
Carbon dioxide	61 000	110 000	39 000	120 000
Carbon monoxide	1 300	23	530	70
Methane	19	0.30	3.3	n.d. [a]
Benzene	11	0.010	0.46	0.021
Phenanthrene	1.4	0.0006	0.068	0.0090

[a] Not determined

Both the amount and the composition of the emitted organic compounds varied greatly between the different appliances and were also dependent on the effect. The concentrations of organic compounds measured in the chimneys of most of the burners studied were low, and since the compounds are emitted at roof level, there is little human exposure. The total concentrations of organic compounds from Burner C and D at maximum effect were very low. However, the concentrations from Burner C at half effect were noticeably higher. It is therefore important to consider the advisability of running the appliances at low effect and the length of time involved.

The highest concentrations of all organic compounds studied came from Burner A. This burner was an old model, installed in a boiler, where the flames cooled too quickly on the boiler walls. The concentration of benzene emitted from this burner was considerably larger than from any of the other appliances. The large variations in emissions from the different examples emphasise the importance of choosing the "best technology", with regard to the design of the burner and the combination of burner and boiler.

The relative proportions of prominent organic compounds ($\geq$ 6C) in the chimney smoke from Burner A are compared to the results from Burner B, a larger burner of the same brand (Figure 36, **IV**). It is obvious that the relative proportions did not vary much between the different samples, although the total amounts of the compounds vary in the range of 2-25 mg m^{-3}.

The major aromatic hydrocarbon assessed was benzene. The relative ratio of benzene to methylbenzene was even higher than in glowing laboratory burning of softwood pellets. The second most prominent organic compound ($\geq$ 6C) studied was naphthalene. Acenaphthylene, phenanthrene, fluoranthene and pyrene were other representatives of polycyclic aromatic hydrocarbons. Minor variations between the samples may be explained by the fact that the relative amount of polycyclic aromatic hydrocarbons formed increases with combustion temperature (Alén *et al.* 1996, Kjällstrand and Petersson 2001c).

The primary pyrolysis products 2-methoxyphenols and 1,6-anhydroglucose were not present in smoke from the studied pellet burners, probably due to relatively complete combustion at high temperature.

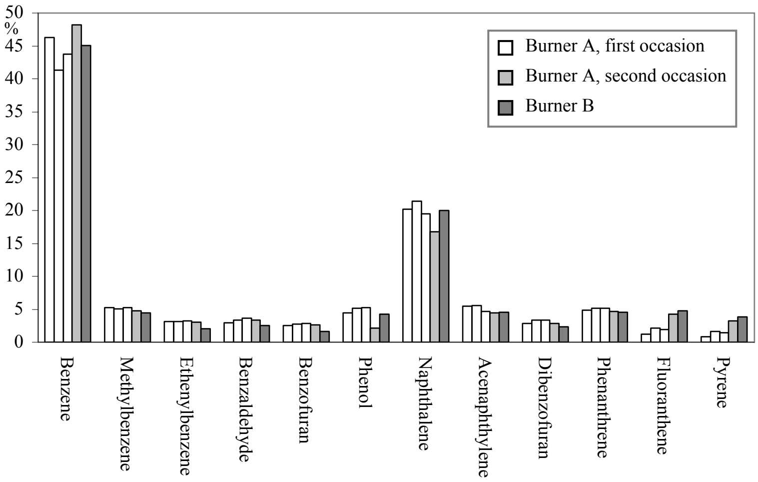

Figure 36: Relative proportions (%) of prominent organic compounds (≥ 6C) in chimney smoke from pellet Burner A and B (**IV**). The first three samples (white bars) were taken on the same occasion while the fourth (light grey bar) was taken from Burner A some weeks later. The fifth sample (dark grey bar) was taken from Burner B, a larger burner of the same brand.

The emissions of organic compounds (≤ 7C) from Burner C were also analysed (Figure 37, Olsson 2002). The most prominent alkenes emitted were ethene and propene. The dominant alkyne was ethyne. The results are similar to those from flaming softwood pellets, but with a lower proportion of methane and ethane of the organic compounds (≤ 7C) (**II**).

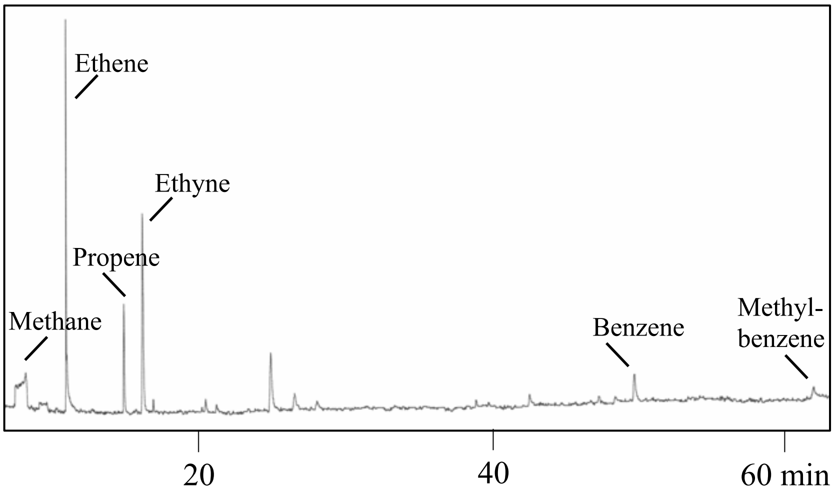

Figure 37: Chromatogram showing the major organic compounds (≤ 7C) emitted from Burner C at low effect. Separation on an aluminium oxide column and determination by flame ionisation detection (Olsson 2002).

5.1.2 Residential pellet stoves and boilers

The emissions of organic compounds (≥ 6C) from pellet Stove A and B and pellet Boiler A, were sampled and measured in the chimney outlets together with other smoke characteristics

(**IV**, Olsson and Kjällstrand 2004). Both the stove and the boiler were studied at maximum and low effect.

The concentrations of carbon dioxide, carbon monoxide, methane, benzene, phenanthrene and guaiacol in the emissions from Stove A and Boiler A are presented in Table 12 (**IV**, Olsson and Kjällstrand 2004). The emissions from Stove A, both high and low effect, resembled those from Boiler A at low effect.

Table 12: A comparison of the concentrations of selected compounds in the emissions from a stove and a boiler for residential use (mg m^{-3}, **IV**, Olsson and Kjällstrand 2004).

	Stove A		Boiler A	
	7 kW	4 kW	25 kW	8 kW
Carbon dioxide	57 000	39 000	110 000	32 000
Carbon monoxide	610	610	49	430
Methane	5.3	5.2	0.99	n.d. [a]
Benzene	0.57	0.60	0.084	0.47
Phenanthrene	0.012	0.034	0.080	0.018
Guaiacol	0.15	0.40	0.22	0.016

[a] Not determined for this effect

In Figure 38, the relative proportions of organic compounds (≥ 6C) from Stove A are compared to those from Stove B. The samples from Stove A have similar relative proportions of the prominent compounds, whereas the smoke from Stove B contains the same compounds but in different proportions.

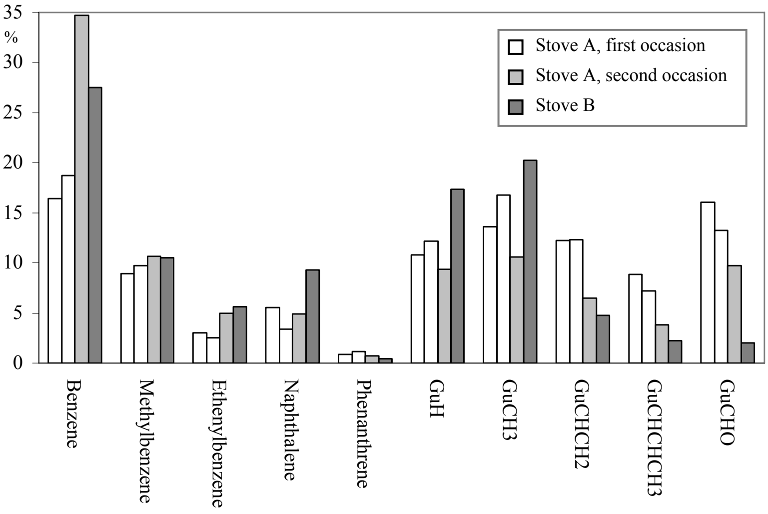

Figure 38: Relative proportions (%) of organic compounds (≥ 6C) in smoke from pellet Stove A and B (**IV**). The first two chimney samples (white bars) were from Stove A and taken on a single occasion, whereas the third sample (light grey bar) was taken a few weeks later. The fourth sample (dark grey bar) was from Stove B (Gu = 4-hydroxy-3-methoxyphenyl).

The predominant group of organic compounds (≥ 6C) in the smoke from the pellet stoves was methoxyphenols with a guaiacyl structure (Gu = 4-hydroxy-3-methoxyphenyl). These are primary pyrolysis products from the lignin of the wood and their presence in the smoke is probably due to a lower and less uniform combustion temperature and a shorter gas residence time compared to the pellet burners. The three most prominent methoxyphenols determined were methylguaiacol ($GuCH_3$), guaiacol (GuH) and vanillin (GuCHO).

Benzene was, as in the emissions from the burners, the most prominent aromatic hydrocarbon. The relative ratio of benzene to methylbenzene was lower than in the pellet burners and more similar to the proportions found in wood smoke (Barrefors and Petersson 1995b, Kjällstrand and Petersson 2001c, Schauer *et al.* 2001). The relative proportions of naphthalene and other polycyclic aromatic hydrocarbons were lower in the emissions from Stove A than from Burner A. Low emissions of polycyclic aromatic hydrocarbons from pellet stoves have previously been determined (Barnett *et al.* 1991).

The largest difference found when comparing the emissions from the pellet burners to those from the stove and the boiler was the large proportion of methoxyphenols and other primary pyrolysis products, such as 1,6-anhydroglucose. Comparisons of the results from the burners to those from the stoves and the boiler emphasise the importance of measuring not only the total amount of emitted organic gaseous carbon (OGC), but also the specific organic substances emitted during wood pellet combustion. The emissions of organic compounds from the studied Boiler A are probably higher than those from modern, highly efficient pellet boilers.

5.2 Ecolabelled residential firewood combustion

Organic compounds in chimney smoke from the combustion of firewood in a modern ecolabelled residential boiler were sampled and assessed at different times during the burning cycle (**VI**).

Concentrations of selected compounds in chimney smoke from the initial flaming and subsequent glowing phase of the combustion cycle are presented in Figure 39. The duration of the two combustion phases was approximately equal.

The concentrations of most compounds decreased over the combustion cycle. The transition into char combustion phase is considered to be reflected in the rapid decrease of the concentrations of methane and ethene 120 minutes into the burning cycle (Figure 39). The total emissions of organic compounds were very low at the end of the burning cycle and after 180 minutes, only glowing combustion occurred. The length of the phases obviously depends on the amount of firewood loaded.

The flaming burning phase resulted in higher concentrations of almost all compounds reported compared to the glowing phase. Methane constituted a large part of the emissions of organic compounds, with a calculated emission factor of <0.01-0.03 g kg^{-1} dry fuel. Other major organic compounds (≤ 7C) were ethene, ethyne and benzene.

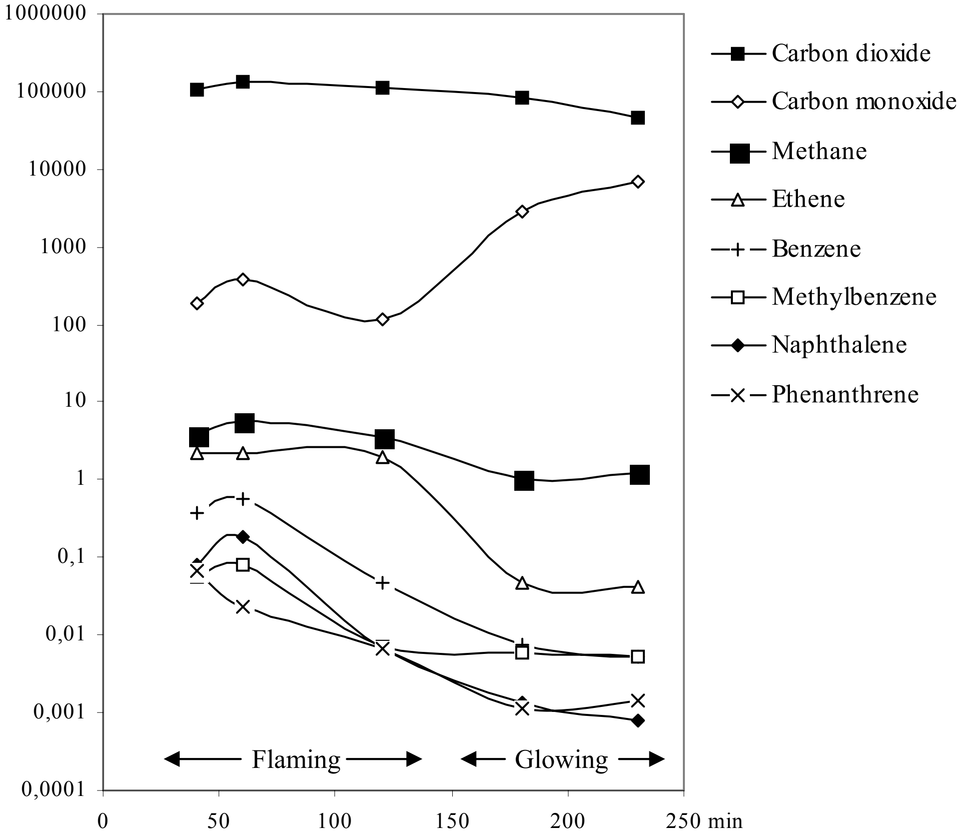

Figure 39: Concentrations of selected compounds in smoke from the studied wood boiler during a full burning cycle (mg m^{-3}, logarithmic scale, **VI**).

Carbon monoxide was the only compound in the smoke with a concentration that increased towards the later half of the combustion cycle. The organic compounds were mainly emitted during the flaming combustion phase, when the carbon monoxide concentration was relatively low, approximately 200 mg m^{-3}. The concentration of carbon monoxide increased to approximately 5 000 mg m^{-3} during the subsequent char combustion phase, while the emissions of other compounds decreased.

A chromatogram, showing the major organic compounds (≥ 6C) in the smoke from the flaming combustion phase, is presented in Figure 40.

Benzene, methylbenzene, naphthalene and dimethylbenzenes were the major organic compounds (≥ 6C) studied. The concentration of benzene was in the range 0.5 mg m^{-3} for flaming burning and 0.1 mg m^{-3} for glowing burning, which is very low. The concentrations of the selected polycyclic aromatic hydrocarbons were also low, except for naphthalene, which was the third most prominent organic compound (≥ 6C).

For many of the compounds studied, such as dimethylbenzenes and methylphenols, the concentrations relative to benzene were higher during the glowing combustion phase than in the flaming phase. In contrast, the relative concentrations of naphthalene and acenaphthylene from the flaming combustion phase were twice as high as in the glowing phase. The difference between the flaming and glowing phases was less evident for the other polycyclic aromatic hydrocarbons.

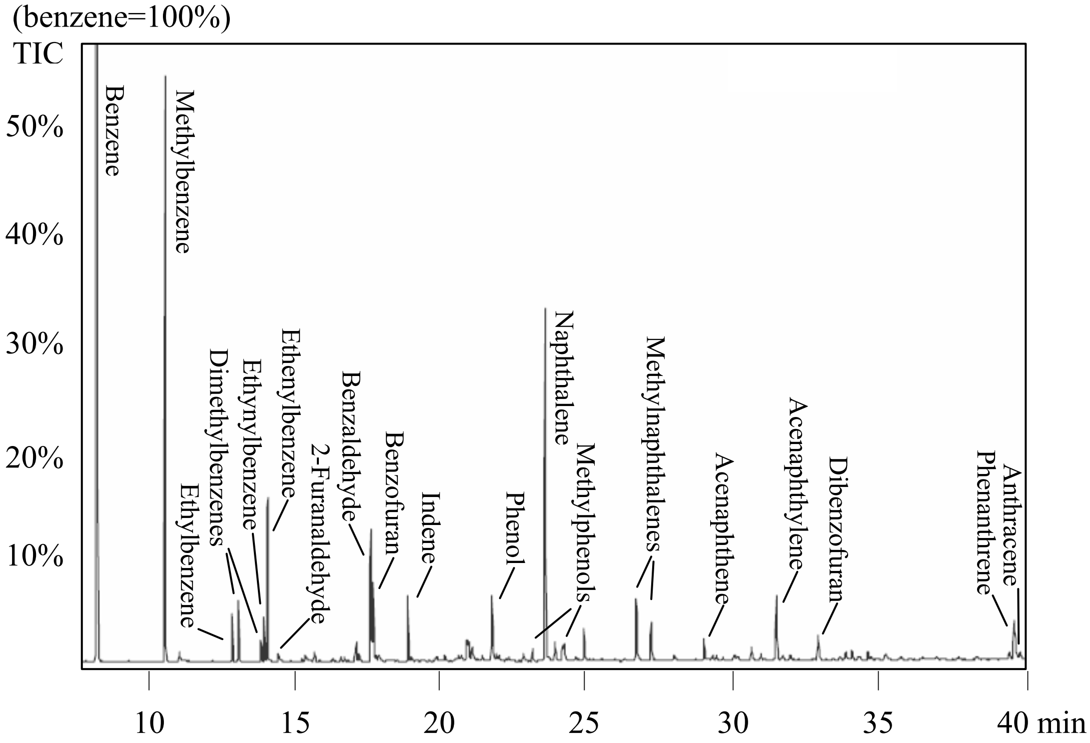

Figure 40: Section of the total ion current chromatogram illustrating major organic compounds (≥ 6C) as a percentage of the highest peak (benzene = 100%) of the flaming combustion phase of the ecolabelled wood boiler (40 min into the burning cycle). Separation on a medium polar gas chromatographic column and detection by mass spectrometry (**VI**).

According to information from the boiler distributor, the combustion temperature is approximately 1 000ºC. This information is supported by low concentrations of polycyclic aromatic hydrocarbons, such as phenanthrene and pyrene, which indicate efficient combustion at a high temperature.

Methoxyphenols were practically absent in the smoke, whereas other primary pyrolysis products, such as 1,6-anhydroglucose and 2-furaldehyde, were identified at very low concentrations.

The concentrations of some compounds varied a great deal between different samples. This was expected, since the aim was to study the natural combustion cycle in a residential boiler, as opposed to attempting to control or modulate the combustion. The samples were also taken at different times during the relatively long flaming and glowing phases.

In conclusion, the combustion efficiency of the studied ecolabelled wood boiler was high and the emissions of compounds hazardous to health and the environment low. The studied ecolabelled wood boiler is therefore recommended as an environmentally sound residential heating option. To ensure optimal energy use, the boiler should be connected to a hot water storage tank.

5.3 Comparison of residential pellet and firewood combustion

The emissions from four selected residential combustion appliances were compared (**V**). Selected emission characteristics of a pellet burner (C), a pellet stove (A), an ecolabelled wood boiler and an old-fashioned wood stove are presented in Table 13 (**IV**, **V**, **VI**, Kjällstrand 2002).

Table 13: Concentrations of selected compounds (mg m^{-3}) determined in the chimney outlet of residential combustion appliances (- = below the detection limit, n.d. = not determined, **IV**, **V**, **VI**, Kjällstrand 2002).

Fuel	Pellets			Firewood	
Appliance	Burner C [a]		Stove A [a,b]	Ecolabelled boiler [c]	Wood stove [d]
Effect	20 kW	10 kW	7 kW	30 kW	20 kW
Carbon dioxide	110 000	39 000	57 000	120 000	120 000
Carbon monoxide	23	530	610	200	4 100
Methane	0.30	3.3	5.3	3.6	120
Benzene	0.01	0.46	0.57	0.50	13
Pyrene	-	0.02	-	0.05 [b]	0.35
Methoxyphenols	-	-	0.50	-	44
Comb. eff. (%) [e]	100	99	99	100	97
Benzene (mg h^{-1})	2	100	30	100	n.d.

[a] (**IV**), [b] Based on recalculations of previous results, [c] (**VI**), [d] (**V**, Kjällstrand 2002),
[e] Combustion efficiency, $[CO_2]/([CO_2]+[CO])$, calculated using data in mg m^{-3}

The concentrations of organic compounds emitted from the ecolabelled wood boiler were very low, in the same range as those from pellet Stove A, but higher than the emissions from pellet Burner C at high effect. The concentrations in the emissions from pellet Burner C at low effect were in the same range as those from the ecolabelled wood boiler. The concentrations from the firewood stove were much higher, as were concentrations of hazardous aromatic compounds from a previously studied firewood boiler developed in the 1970s (Kjällstrand and Petersson 2001c). A study of residential biomass combustion (Johansson *et al.* 2004) reported benzene emissions for modern wood boilers and pellet combustion appliances in the same range as those in Table 13. The benzene emissions for old-type wood boilers were reported to be about one hundred times higher (Johansson *et al.* 2004). The emissions of polycyclic aromatic hydrocarbons from old-type wood boilers were 30-100 times higher than those from modern wood boilers (Johansson *et al.* 2004, Launhardt *et al.* 1998). Additionally, the emissions of particulate matter have been found to be lower from modern wood boilers compared to older boilers (Johansson *et al.* 2004).

The emissions of the carcinogenic benzene from the studied wood pellet combustion appliances and the ecolabelled wood boiler may seem alarming in terms of health hazards. However, the hourly emissions of benzene from the pellet appliances and the ecolabelled wood boiler presented in Table 13 were well below the hourly emissions of benzene from an average vehicle (above 200 mg h^{-1}, Stemmler *et al.* 2005). Emissions at chimney level also result in lower human exposure compared to ground level emissions.

A large difference when comparing the firewood stove to the other combustion appliances was the high concentrations of methoxyphenols in the emissions. Pellet Stove A emitted lower concentrations of these primary pyrolysis products. Methoxyphenols dominated the emissions from a traditional tiled stove (Kjällstrand and Petersson 2001c).

In the 400-1 000ºC interval, the relative composition of compounds in the emissions from wood combustion changes strongly and continuously (Alén *et al.* 1996), with a decreasing structural relationship between products and wood components. In parallel, the total emissions of organic compounds, including volatile hydrocarbons decrease up to one hundred fold (Barrefors and Petersson 1995b).

Biomass burning with different combustion efficiencies was divided into three classes; incomplete, mid efficient and efficient, and the resulting emissions are schematically presented in Table 14.

Table 14: Characteristic smoke components emitted from biomass burning with different combustion efficiencies (**V**, Kjällstrand 2002).

Combustion	Example	Characteristic components
Incomplete (< 700ºC)	Meat curing chamber Smouldering forest fire Fire-place Tiled stove	Methoxyphenols and 1,6-anhydroglucose
Mid efficient (700-900ºC)	Conventional wood boiler	Benzene and polycyclic aromatic hydrocarbons
Efficient (> 900ºC)	Ecolabelled wood boiler Wood pellet burner	Low concentrations of benzene and polycyclic aromatic hydrocarbons

Incomplete combustion at relatively low temperatures in traditional appliances, such as wood stoves and open fireplaces, emits large amounts of organic compounds (Kjällstrand 2002). These are mainly primary decomposition products of the lignin, cellulose and hemicelluloses of the fuel and their total proportion decreases between 600ºC and 1 000ºC (Kjällstrand 2002). Relatively high concentrations of methoxyphenols with antioxidant properties were emitted from the firewood stove in Table 13.

The proportion of secondary combustion products, such as the health hazardous benzene and polycyclic aromatic hydrocarbons, increase with increasing combustion efficiency, as exemplified by the high concentrations of benzene and pyrene from the firewood stove in Table 13.

At even higher temperatures and more efficient combustion, methoxyphenols, polycyclic aromatic hydrocarbons and other organic compounds are almost completely combusted and the emissions of hazardous compounds are low. This is indicated by the very low concentrations in the emissions from pellet Burner C at high effect and from the ecolabelled wood boiler in Table 13. The total health and environmental impact of these new residential biomass combustion alternatives can therefore be considered as low.

In Figure 41, the relation between methoxyphenols and benzene are presented for smoke from appliances with increasing combustion efficiency (**V**, Kjällstrand 2002). Note that the total concentrations decrease with increasing combustion efficiency.

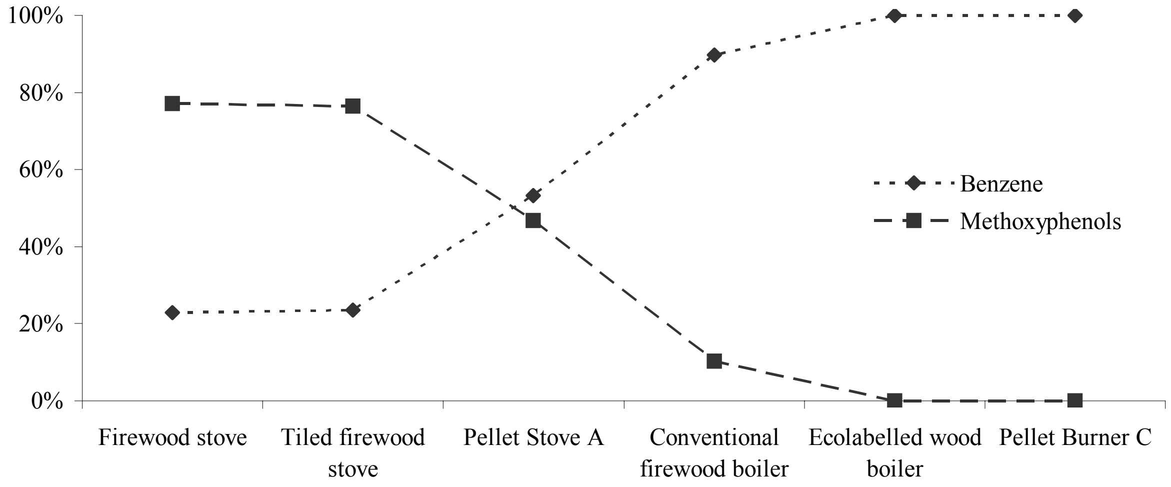

Figure 41: Relation between methoxyphenols and benzene sorted after increasing combustion efficiency for a firewood stove (**V**, Kjällstrand 2002), a tiled firewood stove and a conventional firewood boiler (Kjällstrand and Petersson 2001c), the ecolabelled wood boiler (**VI**), pellet Stove A and pellet Burner C (**IV**).

6 Specific compounds from biomass combustion

The emissions from the combustion of wood pellets in residential burners, stoves and boilers at high effect or from combustion in the ecolabelled wood boiler were generally low. However, at low effect, with poor maintenance as well as during ignition and temporary disturbances, the emissions can be higher and to a larger extent dependent on the chemical composition of the fuel.

Some of the compounds studied in the smoke have major effects on health and the environment. One example is methane, a greenhouse gas. Alkenes such as ethene and propene are rapidly photo-oxidant forming and genotoxic, whereas alkanes are photo-oxidant forming. There are also compounds with carcinogenic or suspected carcinogenic effects, such as benzene, 1,3-butadiene, naphthalene, furan and benzofuran (IARC 2004). In contrast, there are compounds with antioxidant effects in the smoke, such as the methoxyphenols.

6.1 Chemical composition of the studied fuels

The chemical composition of the smoke from incomplete combustion reflects that of the fuel. The chemical composition of the studied fuels (Figure 42); softwood pellets (**I**, **II**, **IV**, **V**, **VII**, **VIII**), birchwood (**V**, **VI**), oats (**VII**), wheat straw pellets (**VIII**) and peat/wood pellets (**VIII**), is schematically illustrated in Table 15.

Figure 42: Softwood pellets, oats, wheat straw pellets and peat/wood pellets.

Wood is mainly made up of cellulose, lignin and hemicelluloses (Sjöström 1981). An oat grain chiefly contains starch, hemicelluloses and protein (Salo and Kotilainen 1970, Åman 1987). Oats also contain a higher level of fat and ash-forming components than the other fuels studied. Wheat straw is mainly made up of cellulose, hemicelluloses and lignin (Theander and Åman 1978). Peat is formed from anaerobic decomposition of white moss (*Sphagnum*) and other bog plants. It is a heterogeneous fuel and the data presented in Table 15 are average values from several different studies on peat (Arpiainen and Lappi 1989, Hämäläinen and Albano 1992, Lappi and Fagernäs 1983). The peat/wood pellets studied were produced from 35 % peat and 65 % softwood sawdust and thus mainly contained cellulose, hemicelluloses and lignin.

Lignin is a heterogeneous polymer composed of *p*-hydroxyphenylpropane, guaiacylpropane and syringylpropane units (Adler 1977). All aspects of the lignin structure have not yet been elucidated (Ralph *et al.* 2004). In softwood lignin, the dominating phenylpropane unit is of the guaiacylpropane type. In hardwood lignin, both guaiacylpropane and syringylpropane units are present. Grass lignin contains all three units (Adler 1977). Mosses, such as the peat forming white moss, contains non-lignin polyphenols but no or only minor amounts of lignin (Adler 1977, Theander 1985). Plants incorporated in the moss contain different types of lignin (Van Smeerdijk and Boon 1987).

Table 15: Chemical composition (% w/w of dry material) of softwood (average of pine and spruce, Sjöström 1981), birchwood (Sjöström 1981), oats (grains and hulls, Salo and Kotilainen 1970, Åman 1987), wheat straw (Pessarakli *et al.* 2005, Theander and Åman 1978) and peat (Arpiainen and Lappi 1989, Hämäläinen and Albano 1992, Lappi and Fagernäs 1983).

	Softwood	Birchwood	Oats	Wheat straw	Peat
Lignin	28	22	7	20	6-40
Cellulose	41	41	9	24	0-20
Hemicelluloses	25	30	12	21	10-25
Starch	traces	traces	47	3	-
Protein	0.6 [a]	0.3 [a]	12	4	5-25
Humic acids	-	-	-	-	3-50
Residual components	5 [b]	7 [b]	13 [c]	28 [d]	rest [e]

[a] Calculated by multiplying the nitrogen content of the softwood pellets (0.1 % w/w, BrikettEnergi AB 2005) or birchwood (0.05 % w/w, Johansson *et al.* 2004) by 6.25 (Theander and Åman 1978, Åman 1987)

[b] Mainly extractives, other polysaccharides and ash

[c] Mainly fat, ash and low-molecular weight carbohydrates

[d] Mainly ash, low-molecular weight carbohydrates and waxes

[e] Mainly pectins, resins, waxes and ash

Cellulose is a long-chain, linear semi-crystalline polymer made up of about 10 000 D-glucose monomer units (Figure 46, Fengel and Wegener 1984, Simoneit *et al.* 1999).

Hemicelluloses are amorphous polysaccharides of 100-200 monomer units of hexoses (mainly glucose, mannose and galactose), pentoses (mainly xylose and arabinose) and small amounts of uronic acids (mainly 4-O-methylglucuronic acid, Alén *et al.* 1996, Simoneit *et al.* 1999, Sjöström 1981). The composition of the hemicelluloses differs among the various tree species (Simoneit *et al.* 1999). The main hemicellulose components are glucomannans and xylans (Alén *et al.* 1996). Glucomannans consist of a backbone of glucose and mannose (Sjöström 1981). Side groups of acetyl and galactose are present in softwood (Sjöström 1981). Xylans consist of a xylose backbone with side groups of 4-O-methylglucuronic acid in the case of hardwood (partly acetylated xylose backbone) and 4-O-methylglucuronic acid and arabinose in softwood (Sjöström 1981).

Starch is a semi-crystalline polymer ranging from a few hundred to several thousand repeating D-glucose monomer units and it can be either branched or linear. In contrast to cellulose with β-bonds, starch has α-bonds (Buléon *et al.* 1998).

6.2 Combustion processes

When wood fuel is heated, its moisture evaporates (Fiedler 2004, Kjällstrand 2002, Simoneit 2002). After the drying, the temperature of the fuel increases to 300-800ºC and the fuel is thermally decomposed forming volatile gases and carbonaceous char. Hemicelluloses decompose above 200-260ºC, cellulose above 240-350ºC and lignin not until 280-500ºC (Drysdale 1985, Kjällstrand 2002). When the ignition temperature of the volatile gases is attained, combustion starts. The volatile gases are mixed with air and burn at 500-900ºC. Primary pyrolysis products released from the fuel, such as methoxyphenols and 1,6-anhydroglucose are further combusted to secondary decomposition products in the flames. The heat released supplies energy for further gasification and char formation continues during the flaming combustion, until not enough combustible volatile gases are released. Thereafter, the smouldering process starts during which the char is gradually oxidised at 700-1 000ºC. About 80 % of the fuel is gasified through pyrolysis, whereas the char represent only 20 % of the fuel, but almost half of the total heat capacity (Drysdale 1985, Kjällstrand 2002). During the smouldering process, enough heat is produced to continue the char oxidation, as well as the release of further volatile gases. High temperatures (above 900ºC) and sufficient air supply, mixing and residence time are needed in order to attain maximum energy yield from the fuel.

6.3 Carbon dioxide, carbon monoxide and nitrogen oxides

Carbon dioxide and carbon monoxide were measured in almost all studies in order to investigate the combustion conditions and efficiencies and to be able to relate the emissions to those from other studies, fuels and appliances.

In view of global warming, biofuels are excellent options, since the plants take up as much carbon dioxide during their growth as is later released during combustion. Sustainable forestry with continual regrowth closes the carbon dioxide cycle. The carbon dioxide concentrations in the chimney outlets of the studied combustion appliances were generally 6-7 % at maximum and 2-3 % at low effect (**IV**, Olsson and Kjällstrand 2004).

High carbon monoxide emissions indicate imperfect combustion conditions and poor energy efficiency and are caused by inadequate mixing of air and combustible gases or too short residence time at sufficiently high temperature. The carbon monoxide emissions from pellet Burner C and D were low and varied between 20-60 ppm (**IV**, **V**, Olsson and Kjällstrand 2004). The corresponding figures were 500 ppm for pellet Stove A, 40 ppm for pellet Boiler A and 200 ppm for the ecolabelled wood boiler (**IV**, **V**, **VI**, Olsson and Kjällstrand 2004). The carbon monoxide emissions from the pellet appliances at low effect (pellet Boiler A, Burner C and D) were about ten times higher than those at high effect. The carbon monoxide emissions from pellet Burner A, an older model, were almost a hundred times higher than from the other burners at high effect.

Nitrogen oxides are formed during combustion, either from nitrogen in the air or in the fuel.

The nitrogen content of the fuel directly influences the formation of nitrogen oxides (Leckner and Karlsson 1993). Nitrogen oxides contribute to acidification, eutrophication and formation of ground-level ozone. Transports are the main source of emissions of nitrogen oxides (Swedish Environmental Protection Agency 2005). The emissions of nitrogen oxides from the studied pellet burning appliances were around 50 ppm or lower while those from the ecolabelled wood boiler were about 100 ppm. The emission of nitrogen oxides from a pellet burner in a previous study was about 100 ppm (Johansson 2002). The high content of nitrogen in peat (1-3 %, Hämäläinen and Albano 1992, Lappi and Fagernäs 1983) could lead to increased emissions of nitrogen oxides during combustion. Other nitrogen containing compounds, such as hydrogen isocyanate, hydrogen cyanide and ammonia are also formed during combustion of fuels containing nitrogen (Hansson *et al.* 2004).

6.4 Methane and global warming

Methane is one of the main organic compounds (≤ 7C) emitted from the combustion of materials containing carbon. Methane is not hazardous to health, but as it is a greenhouse gas with about 20 times higher global warming potential than carbon dioxide (100-year perspective, IPCC 2001), it is important to control the emissions.

Methane emissions decrease with increasing combustion efficiency, which results in large differences between various burning methods. Methane should therefore be one of the criteria for the ecolabelling of new residential biomass combustion appliances. Both the Swedish authorities and The Nordic Ecolabelling Board restrict the emissions of organic gaseous carbon (OGC), which is a non-specific parameter of which methane may constitute a large proportion (Table 1, Table 3, Nordic Ecolabelling Board 2004a, 2004b).

The methane emission factor (EF_{CH4}, g kg^{-1} dry fuel) represents the proportion of carbon released as methane during combustion and was estimated based on an average carbon content for dry wood of 45 % (Delmas 1994). The factor is calculated as:

$$EF_{CH_4} = \frac{([CH_4]_{plume} - [CH_4]_{ambient})}{[CO_2]} \times 0.45 \times 1000 \times \frac{M_{CH_4}}{M_C} \times \frac{[CO_2]}{([CO_2] + [CO])}$$

where 1.7 ppm was used for $[CH_4]_{ambient}$ and all concentrations were expressed in ppm (Yokelson *et al.* 1999).

Methane emission factors for the combustion appliances studied are presented in Table 16 together with literature data.

The concentrations of methane in the emissions from the pellet burners, stoves and boilers studied varied between 0.5-30 ppm (**IV**, **V**, Olsson and Kjällstrand 2004). The corresponding figure for the ecolabelled wood boiler was about 2 ppm (**VI**). These methane concentrations correspond to methane emission factors of <0.01-0.5 g methane per kg of dry fuel (Table 16).

This is accordance with results from a previous study of pellet burners and wood boilers (Johansson *et al.* 2004).

Table 16: Emissions of methane from different types of biomass burning (g kg^{-1} dry fuel).

Fuel	Appliance / burning	Methane emission factors
Pellets	Burner C (20 kW)	< 0.01[a]
Pellets	Boiler A	< 0.01[b]
Wood	Ecolabelled boiler	< 0.01 – 0.03 [c]
Pellets	Burner C (10 kW)	0.09 [a]
Pellets	Stove A (7 kW)	0.1 [b]
Pellets	Stove A (4 kW)	0.2 [b]
Pellets	Burner A	0.5 [a]
Wood	Residential combustion appliances	0.02 – 10 [d]
Wood	Traditional cooking stoves	0.5 – 10 [e]
Grassland	Fire	1 – 4 [f]
Forest	Fire	2 – 6 [f]

[a] (**IV**), [b] (Olsson and Kjällstrand 2004), [c] (**VI**), [d] (**V**, Johansson *et al.* 2004, Schauer *et al.* 2001), [e] (Bhattacharya *et al.* 2002, Ndiema *et al.* 1998), [f] (Ferek *et al.* 1998, Goode *et al.* 2000, Yokelson *et al.* 1999)

Small-scale burning of firewood in inefficient devices emits about 0.5-10 g methane per kg of dry fuel (Bhattacharya *et al.* 2002, Ndiema *et al.* 1998, Schauer *et al.* 2001). The burning of firewood and pellets in modern devices reduces the methane concentration in the smoke plume to the same levels as in ambient air.

With regard to carbon dioxide emissions, the use of biofuels from sustainable ecosystems with continual regrowth, such as Swedish forests, does not contribute to an increase in global warming. On the contrary, a change from fossil fuels to biofuels drastically reduces the greenhouse gas emissions. Despite the methane emissions, the studied pellet combustion appliances and the ecolabelled firewood boiler only contribute a few percent compared to the greenhouse effect arising from heating with fossil fuels (**IV**, **V**, **VI**, Olsson and Kjällstrand 2004). However, since there are large differences between biomass burning appliances, a relatively cheap and easy way to decrease the emissions of greenhouse gases from residential heating is to reduce the methane emissions.

6.5 Non-methane organic compounds (≤ 7C)

Organic compounds (≤ 7C) are formed from incomplete combustion. Alkenes such as ethene and propene are, due to their double-bonds, rapidly photo-oxidant forming and genotoxic (Törnqvist and Ehrenberg 1994) whereas alkanes can contribute to photo-oxidant formation. Ethene and propene are the most important ozone precursors in the smoke (Atkinson 1990). The emissions of alkenes from residential burning of softwood pellets or wood burning in the ecolabelled boiler are low (**VI**, Olsson 2002). Therefore, the contribution to photo-oxidant formation is also considered to be low. Furthermore, when the heat demand is high in the winter season, the light-induced formation of photo-oxidants is negligible.

Some of the studied organic compounds (≤ 7C) are classified as carcinogenic to humans, such as benzene, others as probably carcinogenic to humans, such as 1,3-butadiene, while a third group is classified as possibly carcinogenic to humans, such as furan (IARC 2004). Ethene and propene are also significant in relation to health hazards (Törnqvist and Ehrenberg 1994). These compounds are emitted from the burning of solid biomass fuels (Barrefors and Petersson 1995a), but only in very small amounts from residential combustion of softwood pellets or wood burning in the ecolabelled boiler (**IV**, **V**, **VI**).

Volatile hydrocarbons have previously been studied in smoke from the combustion of wood pellets (Johansson *et al.* 2004), from the combustion of many different species of firewood in residential fireplaces and wood stoves (Barrefors and Petersson 1995b, Johansson *et al.* 2004, McDonald *et al.* 2000, Schauer *et al.* 2001) as well as from combustion of different types of forest plant materials (Barrefors and Petersson 1995a, Hays *et al.* 2002). Alkanes, alkenes and alkynes have also been studied in firewood smoke, cigarette smoke and car exhaust fumes (Barrefors and Petersson 1993, 1995b).

Acetic acid, formaldehyde and methanol are too polar to be determined with the column used for the GC-FID analyses but, in previous studies of smoke from incomplete burning, they have been determined at concentrations within a few percent of those of carbon monoxide (McKenzie *et al.* 1995, Yokelson *et al.* 1999).

6.6 Aromatic and polycyclic aromatic hydrocarbons

The relative proportion of benzene, naphthalene and many other polycyclic aromatic hydrocarbons increases with increasing combustion temperature, while the total concentrations of organic compounds decreases (Figure 43, Alén *et al.* 1996, Hauk *et al.* 1994, Kjällstrand and Petersson 2001c, McGrath *et al.* 2001).

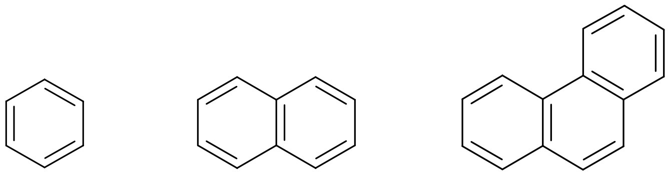

Figure 43: Benzene (left), naphthalene (middle) and phenanthrene (right).

6.6.1 Benzene

The carcinogenic benzene (Figure 43, left) is a major aromatic hydrocarbon from the incomplete combustion of wood and from car exhaust fumes (Barrefors and Petersson 1993, 1995b, IARC 2004). Earlier studies indicate that, compared to most other organic compounds, the proportion of benzene increases steadily with the combustion efficiency, although the total concentrations of compounds decreases (**V**, Kjällstrand 2002). The concentrations of benzene are typically higher than those of methylbenzene in wood smoke (**IV**, Barrefors and Petersson 1995b, Schauer *et al.* 2001). The relative ratio between benzene and methylbenzene increases with increasing combustion efficiency (Kjällstrand 2002). In contrast, the concentration of methylbenzene in urban air is approximately twice as high as that of benzene (Barrefors and Petersson 1992), which is the same relationship as for vehicle emissions.

Benzene was found in large proportions of organic compounds in the smoke from the studied pellet burners and the ecolabelled wood boiler (**IV**, **V**, **VI**) as well as in the smoke from the glowing combustion of softwood, wheat straw and peat/wood pellets (**I**, **II**, **VII**, **VIII**). Benzene was also present in lower proportions in the smoke from the studied pellet stoves and the pellet boiler (**IV**, **V**) as well as in the smoke from the other combustion stages of softwood pellets and the rest of the studied fuels (**I**, **II**, **VII**, **VIII**). Benzene was also the predominant aromatic compound emitted from glowing charcoal and pellet embers (**III**).

Benzene has previously been found at high concentrations in chimney smoke from a residential wood boiler (Kjällstrand and Petersson 2001c). It has also been studied in the emissions from residential wood pellet combustion (Johansson *et al.* 2004), from fireplace and wood stove combustion of many different species of firewood (Barrefors and Petersson 1995b, Johansson *et al.* 2004, McDonald *et al.* 2000, Schauer *et al.* 2001) and from the combustion of different forest plant materials (Barrefors and Petersson 1995a, Hays *et al.* 2002).

The high proportions of the carcinogenic benzene from the studied wood pellet combustion appliances and the ecolabelled wood boiler may seem alarming with respect to health hazards. It is, however, important to realise that the chimney concentrations were very low and that benzene is emitted at chimney level, resulting in low human exposure. The hourly benzene emissions measured were even lower than those from an average vehicle (Stemmler *et al.* 2005).

The main nitrogen-containing organic compound found in the smoke from glowing burning of wood pellets and from glowing charcoal was benzonitrile (**I**, **III**). The presence of this compound and its retention time was verified by injecting a sample of pure benzonitrile.

6.6.2 Polycyclic aromatic hydrocarbons

Many of the polycyclic aromatic hydrocarbons (PAHs) measured are toxic and carcinogenic and are formed in low concentrations during the combustion of organic material. The emissions of polycyclic aromatic hydrocarbons are strongly influenced by the combustion conditions (Alén *et al.* 1996, Hays *et al.* 2002, Jenkins *et al.* 1996, McGrath *et al.* 2001, Sharma and Hajaligol 2003). Polycyclic aromatic hydrocarbons are mainly formed at temperatures between 700 and 900ºC, and their total yield increases with temperature and residence time in the furnace within this interval (Alén *et al.* 1996, Hauk *et al.* 1994, Kjällstrand 2002, McGrath *et al.* 2001, Sharma and Hajaligol 2003). They are thermally decomposed at higher combustion temperatures (**IV**, **VI**, Kjällstrand 2002). The formation mechanisms of polycyclic aromatic hydrocarbons are not completely understood. At high temperatures, organic matter cracks to free radicals, which recombine and successively grow into larger polycyclic aromatic hydrocarbons (Sharma and Hajaligol 2003, Simoneit 2002).

The formation of polycyclic aromatic hydrocarbons is facilitated by the presence of lignin in the fuel (Edye and Richards 1991) and is the result of the thermal decomposition of methoxyphenols (Egsgaard and Larsen 2001, Hauk *et al.* 1994) and cellulose (McGrath *et al.* 2001).

Polycyclic aromatic hydrocarbons often condense on particulate matter. As a rule of thumb, polycyclic aromatic hydrocarbons with two to three rings occur mainly in the gas phase, four-ringed PAHs in both phases and five-ringed or larger PAHs in particle phase (Boström *et al.* 2002). Gas to particle phase PAH ratios of 1:1-3:1 have been measured in the combustion chambers of residential fireplaces and wood stoves (PAHs with less than three rings have been defined as present in the gas phase and larger PAHs as in the particle phase, McDonald *et al.* 2000).

Low concentrations of polycyclic aromatic hydrocarbons were found in the studies. The most prominent polycyclic aromatic hydrocarbons determined in smoke from softwood pellets, the ecolabelled wood boiler and glowing charcoal were naphthalene, phenanthrene, fluoranthene and pyrene (**I**, **III**, **IV**, **VI**). This is in accordance with previous results of a study on residential wood combustion (Kjällstrand and Petersson 2001c) and a study of a pellet stove (Boman *et al.* 2005). High concentrations of polycyclic aromatic hydrocarbons have previously been found in chimney smoke from a residential wood boiler designed in the 1970s (Kjällstrand and Petersson 2001c).

Emission factors of 700 µg PAH kg^{-1} of fuel combusted were found in a previous study of an old-type wood boiler (Johansson *et al.* 2004). Corresponding factors for a modern wood boiler and a pellet burner were 10-60 µg and 3-20 µg, respectively (Johansson *et al.* 2004). Another study of a pellet stove revealed emission factors of 0.05-0.7 µg PAH kg^{-1} wood pellets combusted at high and 0.4-2 µg at low effect (Boman *et al.* 2005).

Naphthalene is possibly carcinogenic (IARC 2004). The concentration of naphthalene in the emissions from wheat straw and peat/wood pellets was higher than from softwood pellets (**VIII**), especially during the after-flame smouldering of straw pellets and the early flaming of peat/wood pellets. The concentrations of phenanthrene were in the same range as naphthalene for the pellets and combustion stages studied. Cancer risk assessment of polycyclic aromatic hydrocarbons has previously been presented (Boström *et al.* 2002).

Many different polycyclic aromatic hydrocarbons have been studied in the emissions from the combustion of wood pellets (Barnett *et al.* 1991, Johansson *et al.* 2004), wood burning (Fine *et al.* 2001, 2002, 2004a, 2004b, Freeman and Cattell 1990, Jenkins *et al.* 1996, Johansson *et al.* 2004, Launhardt *et al.* 1998, McDonald *et al.* 2000, Purvis *et al.* 2000, Schauer *et al.* 2001), the combustion of different forest plant materials (Hays *et al.* 2002, Oros and Simoneit 2001a, 2001b), hardwood charcoal (Dyremark *et al.* 1995), from Asian cooking stoves burning wood fuels and sawdust briquettes (Oanh *et al.* 2005, Oanh *et al.* 2002), from the combustion of peat (Alsberg and Stenberg 1979, Kakareka *et al.* 2005, Muraleedharan *et al.* 2000) and pellets of wheat straw and other biogenic material (Vierle *et al.* 1999). Polycyclic aromatic hydrocarbons have also been found in grilled meat and many other foods (Kazerouni *et al.* 2001, Chen *et al.* 1997, Larsson *et al.* 1983, Rivera *et al.* 1996).

6.7 Methoxyphenols

Methoxyphenols are primary thermal degradation products originating from the lignin of the fuel (Amen-Chen *et al.* 2001, Faix *et al.* 1990, Kjällstrand 2002, Kjällstrand and Petersson 2001b, McKenzie *et al.* 1995, Oros and Simoneit 2001a, Simoneit 2002).

Lignin is the most thermally stable component in wood (Alén *et al.* 1996, Amen-Chen *et al.* 2001, Drysdale 1985). The methoxyphenols are formed in large proportions during pyrolysis of the lignin at 400-700ºC, through radical chain reactions, leading to cleavage of the α- and β-alkyl-aryl ether bonds (Alén *et al.* 1996, Amen-Chen *et al.* 2001, Faix *et al.* 1988, Kjällstrand 2002, Steinbeiss *et al.* 2006). The concentrations of methoxyphenols decrease with increasing combustion efficiency (Kjällstrand 2002, Kjällstrand and Petersson 2001c). At 600ºC, the methoxyphenols start to decompose to, for example, phenol (Alén *et al.* 1996). At even higher temperatures, 800-1 000ºC, polycyclic aromatic hydrocarbons are formed and the concentrations of methoxyphenols are almost negligible (Alén *et al.* 1996). Almost all methoxyphenols are thermally decomposed at the high combustion temperatures in modern wood boilers (**VI**, Amen-Chen *et al.* 2001).

Increasing combustion temperatures also degrade reactive side-chains, leaving guaiacol and methylguaiacol as the thermally most stable guaiacyl derivatives (**I**, Amen-Chen *et al.* 2001, Kjällstrand 2002, Kjällstrand and Petersson 2001b). During choked burning of softwood at low temperature (Kjällstrand *et al.* 2000), the proportions of methoxyphenols with large side chains are relatively high, whereas in smoke from more efficient combustion, guaiacol and methylguaiacol are the predominant methoxyphenols (**I**, **IV**, Hawthorne *et al.* 1989).

In smoke from the combustion of softwood pellets (**I**, **IV**, **VII**, **VIII**), the methoxyphenols with a guaiacyl structure (Gu = 4-hydroxi-3-methoxyphenyl, Figure 44, left) were predominant. In smoke from fuels such as hardwood, oats, wheat straw and peat, with a different lignin structure, both guaiacyl derivatives and dimethoxyphenols with a syringyl structure (Sy = 4-hydroxy-3,5-dimethoxyphenyl, Figure 44, right) were present (**VII**, **VIII**, Kjällstrand 2002). The guaiacyl/syringyl ratio for birchwood is about one (Adler 1977), whereas the ratio for wheat straw lignin has been found to be slightly over one (Rodríguez *et al.* 1997). Hardwood pellets were not studied. Previous research on hardwood combustion indicate that hardwood pellets would give rise to more syringyl than guaiacyl derivatives (Hawthorne *et al.* 1989, Kjällstrand 2002, Kjällstrand *et al.* 2000, Kleen and Gellerstedt 1991).

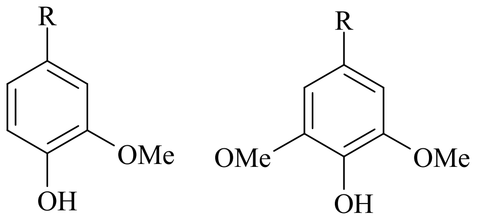

Figure 44: Guaiacyl structure (Gu, left) and syringyl structure (Sy, right).

The methoxyphenols have antioxidative qualities (Barclay *et al.* 1997, Kjällstrand 2002, Kjällstrand and Petersson 2001b, Ogata *et al.* 1997), which means that they may be able to protect cells in the body from attacks of free radicals. The antioxidant properties of the methoxyphenols have been thoroughly described in previous studies (Barclay *et al.* 1997, Kjällstrand 2002, Kjällstrand and Petersson 2001b). The antioxidant effect depends on the strength of the resonance stabilisation of the formed phenoxyl radical. Methoxyphenols with long alkyl or alkenyl side-chains have stronger antioxidant effects than guaiacol and vanillin (Kjällstrand 2002, Kjällstrand and Petersson 2001b). This is especially pronounced for side-chains with double bonds in conjugation with the aromatic structure, such as ethenylguaiacol and *trans*-propenylguaiacol, due to an even more stable resonance stabilisation (Kjällstrand 2002, Kjällstrand and Petersson 2001b). The syringyl derivatives have stronger antioxidant properties than their guaiacyl analogues (Kjällstrand 2002, Kjällstrand and Petersson 2001b).

The presence of antioxidants may render smoke from incomplete burning of firewood and wood pellets less hazardous than previously believed, as the methoxyphenols may partly counteract the negative health effects of hazardous compounds in the smoke (Kjällstrand 2002, Kjällstrand and Petersson 2001b). Methoxyphenols have been found in urine both after exposure to wood smoke and after consumption of smoked foods, which shows that they can be taken up both orally and through inhalation (Dills *et al.* 2001).

Guaiacyl derivatives were found in high concentrations in the smoke from incomplete flaming burning of pellets (**I**) and from the initial smouldering of softwood pellets, wheat straw pellets, peat/wood pellets and oats (**VII**, **VIII**). Syringyl derivatives were also present in the smoke from wheat straw, peat/wood and oats (**VII**, **VIII**). Lower concentrations of methoxyphenols have been found in smoke from pellet stoves and boilers, but not in emissions from pellet burners (**IV**, **VII**) or from the ecolabelled wood boiler (**VI**).

The most prominent methoxyphenols in smoke from incomplete burning of softwood pellets (Figure 45) were guaiacol, methylguaiacol, ethylguaiacol, ethenylguaiacol, *trans*-propenylguaiacol, vanillin and coniferaldehyde (**I**, **VII**, **VIII**).

High concentrations of methoxyphenols have, in earlier studies, been found in smoke from the combustion of firewood in a traditional tiled stove (Kjällstrand and Petersson 2001c). High concentrations of methoxyphenols have been identified in alder smoke from meat curing, where it both preserves and adds flavour to the food (Kjällstrand and Petersson

2001a). Syringyl compounds were prominent in laboratory and chimney emissions from incomplete burning of hardwood (Kjällstrand and Petersson 2001b, 2001c, Kjällstrand *et al.* 1998).

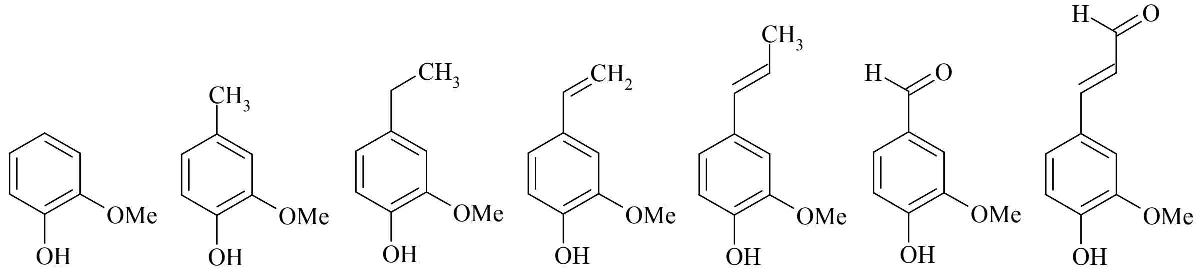

Figure 45: Guaiacol, methylguaiacol, ethylguaiacol, ethenylguaiacol, *trans*-propenylguaiacol, vanillin and coniferaldehyde.

Furthermore, methoxyphenols have been studied in emissions from fireplace and wood stove combustion of a number of different tree species (Fine *et al.* 2001, 2002, 2004a, 2004b, Hawthorne *et al.* 1989, Hawthorne *et al.* 1988, McDonald *et al.* 2000, Nolte *et al.* 2001, Rodrigues *et al.* 1999, Schauer *et al.* 2001), from smouldering combustion of wood (Edye and Richards 1991), charred rye grass residues (González-Vila *et al.* 2001) and from combustion of different forest plant materials (Hays *et al.* 2002, Kjällstrand *et al.* 2000, McKenzie *et al.* 1995, Oros and Simoneit 2001a, 2001b). Coniferyl alcohol ($GuCH=CHCH_2OH$) constituted a large proportion of the methoxyphenols from choked newsprint burning (Kjällstrand and Petersson 2000). Methoxyphenols have also been found in studies of forage (including alfalfa hay, red clover hay, peanut hulls and wheat straw, Reeves and Francis 1997), wheat straw (Hernández *et al.* 2001, Rodríguez *et al.* 1997) and peat (Van Smeerdijk and Boon 1987).

The most volatile methoxyphenols, such as guaiacol and methylguaiacol, are mainly present in the gaseous phase (Hays *et al.* 2002, McKenzie *et al.* 1995, Schauer *et al.* 2001), while most of the other methoxyphenols are mainly condensed on particulate matter at ambient temperatures (Hawthorne *et al.* 1989, Kjällstrand 2002, Simoneit 2002). During combustion of different forest plant materials and residential wood combustion in fireplaces, gas- to particle phase ratios of 2:1-4:1 have been reported for the methoxyphenols (Hays *et al.* 2002). Guaiacol and methylguaiacol were dominant in the gas phase and coniferaldehyde and acetovanillone in the particle phase (Hays *et al.* 2002).

Methoxyphenols have been suggested as useful tracers for atmospheric wood smoke pollution (Hawthorne *et al.* 1988, Hawthorne *et al.* 1992, Simoneit 2002). Guaiacyl derivatives could be used as general tracers and syringyl derivatives as a complement to differentiate between hardwood and softwood combustion (Hawthorne *et al.* 1989, Hawthorne *et al.* 1988, Simoneit 2002).

Phenol is a pyrolysis product originating from both lignin and hemicelluloses (Faix *et al.* 1990, McDonald *et al.* 2000, McKenzie *et al.* 1995), and is formed at somewhat higher combustion temperatures than the methoxyphenols (Alén *et al.* 1996). Phenol has been found in the smoke from softwood pellets and the other studied fuels (**I**, **VII**, **VIII**), in the smoke from pellet Burner A (**IV**) as well as the ecolabelled wood boiler (**VI**). In previous studies phenol has been determined from a tiled firewood stove and a residential wood boiler (Kjällstrand and Petersson 2001c). Methylphenols are also present in the smoke and arise from more efficient combustion than the methoxyphenols (Alén *et al.* 1996).

6.8 1,6-Anhydroglucose and furan-related compounds

1,6-anhydroglucose and furan-related compounds are primary pyrolysis products of the polysaccharides of the fuel (mainly cellulose, hemicelluloses and starch).

6.8.1 1,6-Anhydroglucose

1,6-Anhydroglucose (1,6-anhydro-β-D-glucopyranose, levoglucosan, Figure 46) is the main anhydrosugar from incomplete biomass combustion (Simoneit 2002, Simoneit *et al.* 1999). It originates from the polysaccharides of the fuel (Alén *et al.* 1996, Faix *et al.* 1991, Kleen and Gellerstedt 1991) and is mainly formed through cleavage of the β-1,4-glycosidic bonds of the cellulose via 1,4- and 1,2-anhydrides at temperatures above 300ºC (Figure 46, Alén *et al.* 1996, Lowary and Richards 1990, Simoneit 2002, Simoneit *et al.* 1999).

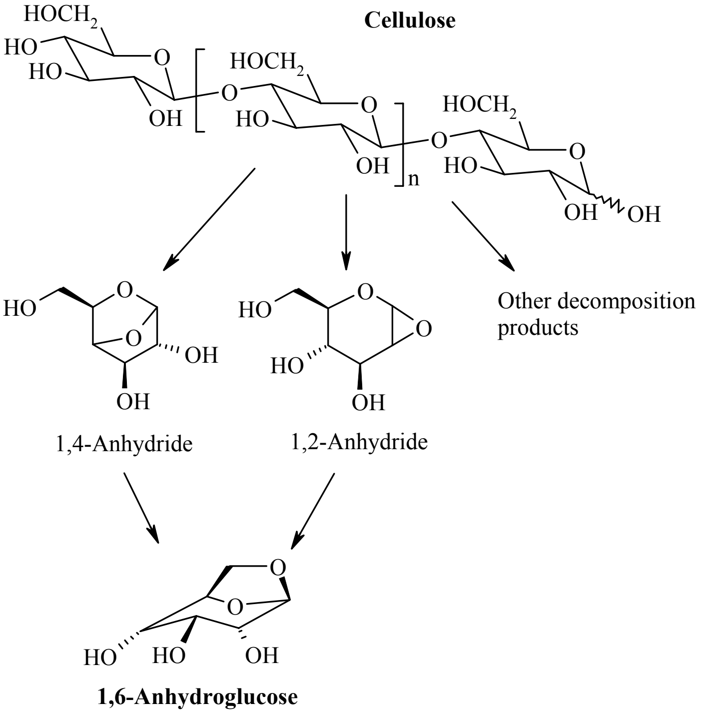

Figure 46: Formation of 1,6-anhydroglucose from burning of cellulose (Lowary and Richards 1990, Nolte *et al.* 2001, Simoneit 2002, Simoneit *et al.* 1999).

Hemicelluloses and starch generally exhibit a lower thermal stability than cellulose (Alén *et al.* 1996). 1,6-Anhydroglucose is similarly formed from glucose containing hemicelluloses at temperatures above 250ºC (Alén *et al.* 1996) and from starch above 220ºC (Bryce and

Greenwood 1963, Lowary and Richards 1991). 1,6-anhydro-β-D-mannopyranose and 1,6-anhydro-β-D-galactopyranose are also formed during the burning of hemicelluloses in a similar way to 1,6-anhydroglucose (Alén *et al.* 1996, Nolte *et al.* 2001, Simoneit 2002). 1,6-Anhydroglucose thermally decomposes at 800-1 000ºC (Alén *et al.* 1996).

1,6-Anhydroglucose is polar and has low volatility. Therefore it mainly appears in the smoke condensed on particulate matter, where it can contribute up to 30 % of the organic fraction (Fine *et al.* 2001, Hays *et al.* 2002, Schauer *et al.* 2001, Simoneit 2002, Simoneit *et al.* 1999). 1,6-Anhydroglucose is not associated with negative environmental or health effects (Kjällstrand 2002).

The anhydrosugar was found in large proportions in the smoke from flaming burning of wood pellets (**I**) and in very large proportions in smoke from late flaming of oats (**VII**) and peat/wood pellets (**VIII**). It was also found in the smoke from pellet Stove A and Boiler A.

In previous studies, 1,6-anhydroglucose has been found in high concentrations in alder smoke for industrial meat curing (Kjällstrand and Petersson 2001a), from the combustion of different forest plant materials (Hays *et al.* 2002, Kjällstrand *et al.* 2000, Oros and Simoneit 2001a, 2001b), from pyrolysis of wheat straw (Hernández *et al.* 2001), in emissions from the combustion of different tree species in campfires (Simoneit *et al.* 1999), fireplaces (Fine *et al.* 2001, 2002, 2004a, Nolte *et al.* 2001, Schauer *et al.* 2001), wood stoves (Fine *et al.* 2004b), a tiled wood stove and a wood boiler (Kjällstrand and Petersson 2001c).

The anhydrosugar has been suggested as a suitable molecular tracer for wood combustion, since it has a high atmospheric stability and is often emitted at such high concentrations that it can be detected at considerable distances from the combustion site (Fine *et al.* 2001, 2002, Nolte *et al.* 2001, Schauer *et al.* 2001, Simoneit 2002, Simoneit *et al.* 1999).

6.8.2 Furan-related compounds

Furan-related compounds such as furan, 2-methylfuran, 2,5-dimethylfuran, 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde (Figure 47) are decomposition products of polysaccharides (starch, cellulose and hemicelluloses, Alén *et al.* 1996, Bryce and Greenwood 1963, Faix *et al.* 1991, McDonald *et al.* 2000, McKenzie *et al.* 1995).

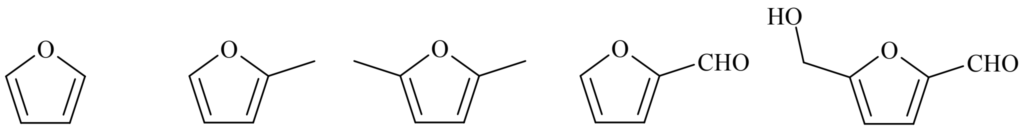

Figure 47: Furan, 2-methylfuran, 2,5-dimethylfuran, 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde.

The structures of the pentoses commonly found in hemicelluloses (xylose and arabinose) favour the formation of furans with substituents at the 2-position, such as 2-furaldehyde (McDonald *et al.* 2000, McKenzie *et al.* 1995). Furan-related compounds are formed from starch through degradation of α-D-glucopyranose (Bryce and Greenwood 1963, Kim *et al.* 1989). Furan concentrations decrease with more efficient combustion (Alén *et al.* 1996, Barrefors *et al.* 1996, McKenzie *et al.* 1995). Furan and benzofuran are possibly carcinogenic (IARC 2004).

Furan-related compounds have been studied in smoke from the combustion of softwood pellets (**I**, **II**). They have also been assessed in relatively large proportions in the smoke from initial smouldering of peat/wood pellets (**VIII**).

In previous studies, furan-related compounds have been found in alder smoke used for industrial meat curing (Kjällstrand and Petersson 2001a), from the combustion of different forest plant materials (McKenzie *et al.* 1995), from the combustion of birchwood on a laboratory scale (Barrefors *et al.* 1996) and in emissions from the combustion of different tree species in fireplaces (McDonald *et al.* 2000, Schauer *et al.* 2001) and wood stoves (McDonald *et al.* 2000).

Both benzofuran and dibenzofuran are furan-related compounds found in the different studies (Figure 48, **I**, **IV**, **VI**, **VII**, **VIII**).

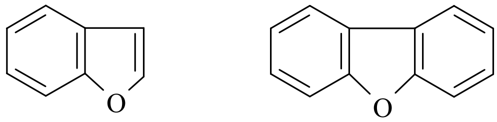

Figure 48: Benzofuran and dibenzofuran.

6.8.3 Dioxins

The generic term dioxins often includes both polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF). A high chlorine content of the fuel may lead to an increased risk of dioxin formation (Hedman 2005). The chlorine content of the studied softwood pellets was 0.01 % of the dry material (BrikettEnergi AB 2005). The corresponding figure was 0.05 % for oats (Olsson *et al.* 2004a), for wheat straw 0.1-0.6 % (Fløjgaard Kristensen *et al.* 1999, Obernberger and Thek 2004, Vierle *et al.* 1999) and for peat 0.003-0.03 % (Virtanen 1990).

In a previous study, the emission factor for dioxins was found to be very low for residential pellet burners, <0.01 ng WHO-TEQ PCDD/F kg^{-1} fuel (Johansson 2005), which was supported by a study of a residential pellet boiler (Hübner *et al.* 2005). Two other studies report higher dioxin emission factor from intermittent combustion in a residential pellet burner/boiler (Bergqvist *et al.* 2005, Hedman 2005). The dioxin emission factor for wood pellets in a small stoker boiler has been reported to be 0.2-0.5 ng I-TEQ kg^{-1} fuel (Lavric *et al.* 2004). Another study of the ecolabelled wood boiler showed particularly low emissions of PCDD/F and PCB (Hedman 2005). The WHO-TEQ value (World Health Organization) and the I-TEQ value (International, managed by U.S. Environmental Protection Agency) are calculated in almost the same way (Hedman 2005, Van den Berg *et al.* 1998).

The emissions of dioxins from the combustion of wheat straw pellets (Hedman 2005, Vierle *et al.* 1999) and peat pellets (Sinkkonen *et al.* 1995) have been studied. Higher amounts of dioxins have been found in the smoke from household waste and wood from demolished buildings than from natural wood (Launhardt *et al.* 1998, Schatowitz *et al.* 1994).

6.9 Particulate matter

The health effects of particulate matter are probably due to both their chemical composition and their size (Kjällstrand 2002). Particulate matter from biomass combustion includes both inorganic material, i.e. ash particles and organic material in the form of incompletely combusted solid material such as soot, tar and char (Johansson *et al.* 2004, Johansson *et al.* 2003, Wiinikka 2005).

It has been suggested that wood smoke particles consist of an elemental carbon core, coated with a liquid organic layer (McDow *et al.* 1996). The organic carbon fraction of particles from incomplete wood burning in residential fireplaces has been found to vary between 40-100 %, of which the elemental carbon fraction was 1-22 % (Fine *et al.* 2001, 2002, 2004a, 2004b, Schauer *et al.* 2001). Residential wood-smoke particles (<10 µm) primarily consist of a mixture of condensed organic compounds (Purvis *et al.* 2000). Most of the methoxyphenols, 1,6-anhydroglucose and polycyclic aromatic hydrocarbons are condensed on particulate matter at ambient temperatures (Fine *et al.* 2001, Hawthorne *et al.* 1989, Hays *et al.* 2002, Kjällstrand 2002, McDonald *et al.* 2000, Schauer *et al.* 2001, Simoneit 2002, Simoneit *et al.* 1999), probably in the liquid organic layer.

Incomplete combustion at low temperatures produces a large amount of particles with a high proportion of methoxyphenols and other primary pyrolysis products (Kjällstrand 2002, Kjällstrand and Petersson 2001a, 2001b). The amount of particles from mid efficient combustion is lower, but contains carcinogenic compounds (Kjällstrand and Petersson 2001c).

The organic fraction of the particles decreases with increased combustion efficiency (Johansson *et al.* 2003, Rau 1989). The carbon concentration in the fly ash of a well designed, automatically operated wood furnace may be below 1-10 % (Nussbaumer and Hasler 1999). The inorganic fraction of particulate matter from combustion in pellet burners and stoves mainly contain potassium sulphate and potassium chloride together with lower amounts of sodium and carbonate (Boman 2005, Johansson *et al.* 2003, Wiinikka 2005).

Most wood smoke particles are in the inhalable size range (Nolte *et al.* 2001). When the combustion efficiency is increased, the particle distribution shifts towards even smaller particles (Johansson *et al.* 2003, Purvis *et al.* 2000). The particle emissions from modern wood boilers, pellet stoves and pellet burners are dominated by particles <1 µm, with a major proportion of the particles in the 0.1-0.8 µm interval (Johansson *et al.* 2004, Johansson *et al.* 2003).

Particulate matter and organic compounds on particles from biomass combustion have been intensively studied (Fine *et al.* 2001, 2002, Hawthorne *et al.* 1989, Hawthorne *et al.* 1992, Hays *et al.* 2002, McDonald *et al.* 2000, Nolte *et al.* 2001, Oros and Simoneit 2001a, 2001b, Schauer *et al.* 2001). Total fine particle emission rates of 1-15 g kg^{-1} have been determined for fireplace and wood stove combustion (Fine *et al.* 2001, 2004a, 2004b, Johansson *et al.* 2004, McDonald *et al.* 2000, Purvis *et al.* 2000, Schauer *et al.* 2001). The emissions of particulate matter have been found to be lower from modern wood boilers compared to older boilers (Johansson *et al.* 2004, Johansson *et al.* 2003). The corresponding emission factor for modern wood boilers and pellet burners, boilers and stoves at full effect was <2 g kg^{-1}, with somewhat higher factors for the pellet appliances at low effect (Boman *et al.* 2005, Johansson *et al.* 2004). Another study reported emission factors from a wood pellet burner in the range of 0.2-0.3 g kg^{-1} (Wieser and Gaegauf 2001). Particulate matter is included in the criteria for the Nordic ecolabel the Swan, with a limit of 70 mg m^{-3} for wood and pellet boilers (Table 1, Table 3, Nordic Ecolabelling Board 2004b).

The chemical composition of particulate matter from traffic and wood smoke differs. A previous study of the health effects of particulate matter found a ten times higher life-time lung cancer risk for particulate matter from traffic than that due to wood combustion (Cupitt *et al.* 1994)), which may be explained by the methoxyphenol content. The life-time risk was five times lower from hardwood compared to softwood particulate matter. A more recent study of the particulate matter in wood smoke and diesel exhaust fumes did not confirm these results (Kubátová *et al.* 2004). A literature review concluded that there seem to be no reason to assume that the health effects of particulate matter from wood combustion are less adverse than those of particulate matter from other sources (Boman *et al.* 2003a).

6.10 Non-specific parameters for the evaluation of residential appliances

When studying residential combustion appliances, non-specific parameters, such as CO (carbon monoxide), THC (total hydrocarbons) and OGC (organic gaseous carbon), are generally used as indicators of inefficient combustion (Fiedler 2004).

It has previously been suggested that high carbon monoxide concentrations indicate high emissions of organic compounds (McKenzie *et al.* 1995). Carbon monoxide is also included in the criteria for the Nordic ecolabel the Swan, with limits of 1 000-2 000 mg m^{-3} (Table 1, Table 3, Nordic Ecolabelling Board 2004b). The studied combustion appliances were within this limit, except for pellet Burner A and the old-fashioned wood stove (**IV**, **V**, **VI**, Olsson and Kjällstrand 2004).

The results from final glowing of the different pellets studied on a laboratory scale (**II**, **VII**, **VIII**) show that carbon monoxide may not be a general parameter that is applicable to all types of combustion. Of the five sequential combustion stages studied, final glowing gave rise to the second highest concentrations of carbon monoxide, but very low concentrations of organic compounds including the carcinogenic benzene. The same conclusions could be drawn from the results from the ecolabelled wood boiler (**VI**). Organic compounds at the highest concentrations were emitted during the flaming combustion phase, when the concentration of carbon monoxide was relatively low. The concentration of carbon monoxide was higher during the glowing combustion phase, when the concentrations of organic compounds were lower.

OGC is also included in the criteria for the Nordic ecolabel the Swan, with a limit of 70 mg m^{-3} for pellet and wood boilers (Table 1, Table 3, Nordic Ecolabelling Board 2004b). When measuring the emissions as OGC, the difference in the response of various compounds is not considered. The amount of saturated hydrocarbons and compounds containing oxygen is therefore underestimated. Furthermore, it is not possible to arrive at specific conclusions on the environmental and health effects of the smoke exclusively on the basis of the OGC value without studying the concentrations of specific compounds.

The highest total concentration of organic compounds and consequently high OGC values, originates from smoke from initial smouldering of the different studied pellets (**II**, **VII**, **VIII**). However, the predominant compounds are primary pyrolysis products from the cellulose and lignin of the wood, such as 1,6-anhydroglucose and the antioxidant methoxyphenols. High OGC-values are therefore not necessarily linked to large emissions of organic compounds hazardous to health and the environment.

These non-specific emission parameters are therefore not sufficient for the evaluation of environmental and health effects of all types of residential biomass combustion. In addition, specific compound emissions need to be determined.

Future emission requirements for the ecolabelling of small-scale combustion appliances for wood logs and pellets should include methane, benzene and a representative polycyclic aromatic hydrocarbon (Olsson and Kjällstrand 2005). The emissions should be related to the concentration of carbon dioxide in order to eliminate dependence on dilution. The greenhouse gas methane should be included from a global environmental perspective. Since the concentration of methane in emissions from biomass burning decreases with improved combustion efficiency, high methane concentrations indicate poor energy management. Benzene and a polycyclic aromatic hydrocarbon should be included with regard to human health.

7 Conclusions

- The striving to replace fossil fuels with biofuels has led to an increased interest in new alternatives for residential heating and hot water production such as wood pellet combustion appliances and highly efficient wood boilers. The emission from these new alternatives can be significantly lower than those from traditional appliances (**IV**, **V**, **VI**).
- Wood pellets are an increasingly popular fuel and are replacing oil and firewood as a fuel for residential heating in Sweden. New raw materials for pellet production or for direct combustion in pellet appliances are of great interest.
- The emissions from the different stages of incomplete laboratory combustion of softwood pellets differ greatly. Flaming burning of wood pellets emits large amounts of methoxyphenols with an antioxidant effect, whereas glowing burning emits carcinogenic benzene and polycyclic aromatic hydrocarbons in low concentrations (**I**, **II**).
- Results from incomplete combustion of oats, wheat straw pellets and peat/wood pellets on a laboratory scale indicate that these fuels give rise to relatively low emissions of organic compounds during combustion, almost as low as those from softwood pellets (**VII**, **VIII**).
- Pellets made of pure wood shavings and sawdust should be reserved for the residential market since they give rise to low emissions of organic compounds and reduced ash formation during combustion and, moreover, have little ecological impact on forest ecosystems (**IV**, **VII**, **VIII**).
- The emissions of organic compounds and further combustion characteristics of other new raw materials for pellets must be thoroughly studied before introduction to the residential fuel market.
- The combustion of softwood pellets in residential pellet stoves and boilers gives rise to emissions of methoxyphenols together with aromatic hydrocarbons (**IV**, **V**).
- The combustion of wood pellets in residential pellet burners is more complete than combustion in pellet stoves and emits benzene and other aromatic hydrocarbons in low concentrations (**IV**, **V**).
- The large differences observed between emissions from different residential wood pellet appliances make it important to choose the best available appliance and to install and maintain it correctly (**IV**, **V**).
- The studied ecolabelled wood boiler has high combustion efficiency. The emissions of compounds hazardous to health and the environment are low and this boiler is therefore recommended as an environmentally sound option for residential firewood combustion (**VI**).
- With regard to the environment and human health, future emission requirements for the ecolabelling of residential combustion appliances for firewood and pellets should include methane and benzene as well as a representative polycyclic aromatic hydrocarbon. The concentrations should be related to carbon dioxide, in order to eliminate dependence on dilution (**VI**).

8 Future work

Studies of new raw materials for pellets other than oats, straw and peat would be important. Examples of new interesting opportunities are:

- Forest residues, for example, bark, logging residues, lignin from pulp mills or bio ethanol production.
- Energy crops, such as salix, reed canary grass, cardoon and Miscanthus Giganteus.
- Farming residues, for example, hay, sugar cane bagasse, almond residues, olive stones, tomato residues, palm fibre and palm nut shells.
- Other organic waste, such as sewage sludge and the organic fraction of household waste.

Measurements of the emissions of organic compounds from oats, straw pellet and peat/wood pellets in residential pellet combustion appliances should be conducted.

Additional compounds in the smoke, for example formic acid, acetic acid, higher molecular weight PAHs and dioxins should be determined. More elaborate studies of the nitrogen oxide emissions would also be of interest.

More in-depth studies and comparisons of emissions from suitable or unsuitable combinations of pellet burners and boilers installed in residences would be interesting to perform, either by studying a larger amount of different combinations or by studying a specific combination of burner and boiler in many different residences.

Measurements of organic compounds from combustion in cutting edge firewood and pellet boilers with, for example, gas sensors, flue gas condensation and catalytic converters should be performed.

9 Acknowledgements

First I would like to thank the Swedish bioenergy industry, the Swedish pellet researchers and all other bioenergy enthusiasts for sharing valuable information and for their interest in my research. The owners of the pellet and wood burning appliances evaluated and the producers of the pellets studied are especially acknowledged for their time and interest.

Special thanks to those who participated in the projects Pellets i Västra Götaland, EnergyCentre.Info/Pellets and Pellets for Europe, especially Mats Rydehell, Kent-Olof Söderqvist, Bengt-Erik Löfgren and Johan Vinterbäck for giving me an invaluable insight into the pellet business.

Thanks to all the members of the Swedish network for pellet researchers for participating and attending network meetings and for their efforts to increase the dissemination of the research results. Special thanks to Katja Hagström and Magnus Ståhl for their collaboration.

I appreciate the belief in me shown by the members of the Swedish Bioenergy Association (SVEBIO) when electing me as a board member, thus providing me with a perspective on the larger bioenergy aspects.

I gratefully acknowledge the financial support for research, conference participation and other bioenergy related projects from:
The Swedish Energy Agency
The Royal Swedish Academy of Agriculture and Forestry
The Västra Götaland Region
The Swedish Savings Bank Foundation
The VL Foundation
The Swedish Farmers´ Foundation for Agricultural Research
EU ALTENER
The Royal Society of Arts and Sciences in Göteborg
The Royal Swedish Academy of Sciences
The Nils Pihlblad Foundation
The Adlerbert Research Fund
The Funds for internationalisation of the PhD education at the Department of Chemical and Biological Engineering

I would like to express my gratitude to my supervisors Olle Ramnäs and Göran Petersson at Chemical Environmental Science and also my examiner Hans Theliander at Forest Products and Chemical Engineering.

Very special thanks to my research colleague Jennica Kjällstrand for valuable discussions and support, but especially for being such a good friend.

I would also like to thank my other research colleagues Magdalena Svanström, Morgan Fröling, Sara Mangs and Kristin Johansson for their support and cooperation and for tempting me into new research areas, resulting in somewhat unexpected publications (Johansson *et al.* 2005, Olsson *et al.* 2005).

Thanks to all those at Forest Products and Chemical Engineering and the Department of Chemical and Biological Engineering who have given me support and friendship, especially my most recent roommate, Johannes Bogren. Thanks to the students who participated in our environmental courses for making teaching such a pleasant and valuable experience.

Thanks to my family, relatives and friends for making my life happy.

Erik, special thanks for always being here for me.

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I

Oxidative pyrolysis of integral softwood pellets

Maria Olsson, Jennica Kjällstrand and Göran Petersson

Journal of Analytical and Applied Pyrolysis 2003, 67, 135-141

II

Specific volatile hydrocarbons in smoke from oxidative pyrolysis of softwood pellets

Maria Olsson, Olle Ramnäs and Göran Petersson

Journal of Analytical and Applied Pyrolysis, 2004, 71, 847-854

III

Benzene emitted from glowing charcoal

Maria Olsson and Göran Petersson

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IV

Specific chimney emissions and biofuel characteristics of softwood pellets for residential heating in Sweden

Maria Olsson, Jennica Kjällstrand and Göran Petersson

Biomass and Bioenergy 2003, 24, 51-57

V

Chimney emissions from small-scale burning of pellets and fuelwood - examples referring to different combustion appliances

Jennica Kjällstrand and Maria Olsson

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VI

Low emissions from wood burning in an ecolabelled residential boiler

Maria Olsson and Jennica Kjällstrand

Atmospheric Environment 2005, *in press*

VII

Emissions of organic compounds from the combustion of oats – a comparison with softwood pellets

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Manuscript submitted to Bioresource Technology 2005

VIII

Wheat straw and peat for fuel pellets – organic compounds from combustion

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Biomass and Bioenergy 2005, *in press*

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The change from fossil fuels to biofuels is important and the residential sector has a significant role to play. New alternatives for residential biomass combustion, such as wood pellets and very efficient wood boilers, have entered the market over the course of the past ten years. Softwood pellets are increasingly used as a residential fuel in Sweden, at present in more than 80 000 Swedish homes. Alternative fuels, such as oats, wheat straw and peat, are of great interest in view of the increasing use of and consequent demand for wood pellets.

The smoke from the combustion of biomass contains a large number of compounds, which may be hazardous to varying degrees. Although it is desirable to increase the use of biofuels, it is also important to protect the local environment and human health. Therefore, the concentrations of specific organic compounds, e.g. carcinogenic benzene and polycyclic aromatic hydrocarbons, and methoxyphenols with antioxidant effect, were measured in the smoke from softwood pellets and other new residential biomass combustion alternatives. The concentrations of organic compounds from the combustion of oats, wheat straw pellets and peat/wood pellets were almost as low as those from wood pellets.

The emissions measured in the chimney outlet of an ecolabelled wood boiler and pellet burners, stoves and boilers were generally low and these appliances can therefore be recommended as environmentally sound options for residential heating. Major differences between emissions from different pellet burning appliances make it important to choose the best available appliance and to install and maintain it correctly.