CHALMERS

Wood pellets as low-emitting residential biofuel

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THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

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Cover: Maria Olsson presenting information on wood pellets in Los Angeles, 2002
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ABSTRACT

Softwood pellet fuel is increasingly used as a residential fuel in Sweden, mainly replacing petroleum oil and firewood. Today, the annual small-scale use of wood pellets amounts to more than 145 000 tonnes. The increased use is supported by environmental and ecotoxicological arguments in favour of reserving pellets of pure trunk wood for residential use. Pellets of other biomass and waste should be burnt in large-scale combustion plants with flue-gas purification.

Even though wood pellet fuel is an environmentally advantageous residential biofuel with low emissions to air, it is very important to examine the emissions. This includes both assessing the compound composition of the smoke and finding methods for minimising the emission of environmental and health hazardous compounds. The organic content of the smoke from the combustion of wood pellets was therefore analysed by gas chromatography and mass spectrometry as the main analytical method.

Softwood pellets from three different Swedish manufacturers were burnt in laboratory experiments, and the organic components of the smoke were analysed. The experiments were designed to simulate incomplete combustion in a pellet burner or a pellet stove. It was clear that the combustion conditions greatly affected the content of the smoke, but also that different pellet brands gave rise to similar emissions. The organic substances found during flaming combustion of pellets were mainly 2-methoxyphenols with antioxidant properties. Benzene was, however, predominant during glowing combustion.

Chimney emissions were studied for residential burners, stoves and a boiler. The smoke samples were collected in the chimney outlet during normal operation of the burning appliance. Organic compounds in the smoke were studied in combination with other smoke characteristics. Phenolic antioxidants were present in the smoke from the pellet stoves and the boiler, but almost absent in smoke from the pellet burners. The carcinogenic hydrocarbon benzene was also emitted, and benzene was the major aromatic compound in the smoke samples from the pellet burners. The results emphasise the importance of measuring not only the total amount of emitted organic carbon (OGC), but also the specific organic substances emitted during the combustion phases.

The emissions from wood pellet embers were more thoroughly analysed and compared to those from glowing charcoal and birchwood embers. The remainders of wood pellets after flaming burning have characteristics resembling those of glowing charcoal. Benzene was the predominant aromatic compound emitted, whereas methane, ethene and ethyne were prominent among the volatile hydrocarbons.

Keywords: pellets, softwood, burner, stove, boiler, benzene, methoxyphenol

Träpellets som lågemitterande småskaligt biobränsle

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Kemisk Miljövetenskap

Chalmers

SAMMANFATTNING

Barrträdspellets från sågspån och hyvelspån är ett biobränsle som i ökande takt ersätter olja och ved på den svenska villamarknaden. Av ekologiska och ekotoxikologiska skäl bör pellets av ren stamved reserveras för småskalig användning, medan pellets av mer kontaminerade råmaterial lämpligen eldas i storskaliga förbränningsanläggningar med rökgasrening. Idag används årligen mer än 145 000 ton pellets som villabränsle.

Pellets är ett från miljösynpunkt mycket lämpligt villabränsle med låga utsläpp. Trots detta är det viktigt att studera dessa, både för att analysera sammansättningen av olika föreningar i röken och för att hitta metoder för att ytterligare minska utsläppen av miljö- och hälsofarliga ämnen. Därför analyserades miljö- och hälsomässigt intressanta organiska ämnen i röken från förbränning av träpellets. Främst användes gaskromatografi och masspektrometri.

Barrträdspellets från tre olika svenska tillverkare eldades i laboratorieskala och rökgasernas organiska innehåll studerades. Analyserna utformades för att efterlikna ofullständig förbränning i en pelletsbrännare eller kamin. Det framkom tydligt att innehållet i röken i stor utsträckning påverkades av förbränningsförhållandena, men också att pellets från de olika tillverkarna gav upphov till likartade emissioner. Vid flammande förbränning av pellets emitterades huvudsakligen 2-metoxifenoler med antioxidanteffekt, medan röken från glödande förbränning dominerades av bensen.

Skorstensrök analyserades från några pelletsbrännare, kaminer och en panna. Vid dessa försök togs rökgasprover i skorstensmynningen under normala förbränningsförhållanden. De organiska ämnena i röken studerades tillsammans med andra parametrar. Fenoliska antioxidanter fanns i röken från kaminerna och pannan, tillsammans med det cancerogena kolvätet bensen. Bensen dominerade i röken från pelletsbrännare. Resultaten understryker vikten av att inte enbart mäta totalhalten av organiskt kol (OGC) utan även vilka specifika ämnen som emitteras under olika förbränningsfaser.

Emissionerna från glödrester av pellets studerades närmare och jämfördes med de från glödande grillkol och björkvedsglödrester. Förbränningsegenskaperna för helt utbrända träpellets eller vedstycken liknar i mycket dem för glödande grillkol. Bensen var den dominerande aromatiska föreningen i röken, medan metan, eten och etyn var de viktigaste flyktiga kolvätena.

Nyckelord: pellets, barrträd, brännare, kamin, panna, bensen, metoxifenol

LIST OF PUBLICATIONS

This work is based on the following articles, appended in the thesis:

I. **Oxidative pyrolysis of integral softwood pellets**
Olsson M, Kjällstrand J and Petersson G (2002)
Journal of Analytical and Applied Pyrolysis, *in press*

II. **Specific chimney emissions and biofuel characteristics of softwood pellets for residential heating in Sweden**
Olsson M, Kjällstrand J and Petersson G (2002)
Manuscript accepted for publication in Biomass and Bioenergy

III. **Benzene emitted from glowing charcoal**
Olsson M and Petersson G (2002)
Manuscript submitted to The Science of the Total Environment

Some information in the thesis originates from:

IV. **Wood pellets as small-scale biofuel**
(Report written in Swedish: Träpellets som småskaligt biobränsle)
Olsson M (2001)
Report for the Swedish Energy Agency

Results relating to the thesis are also presented in:

V. **Emissions from burning of softwood pellets**
Olsson M and Kjällstrand J (2002)
Article for the 1st world pellets conference “Pellets 2002” in Stockholm, September 2002

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1. INTRODUCTION

Wood pellet fuel is increasingly used as residential biofuel in Sweden and has mainly replaced petroleum oil and firewood as an environmentally well adapted biomass fuel. Due to the increased residential installation of pellet burners, stoves and boilers, it is important to study the emissions of different compounds. The environmental aspects and health impacts of the emissions have to be evaluated and compared to emissions from the fuel previously used in the residences.

When considering the effects on health and the environment, it is very important to study not only the total emissions, but also the composition of different compounds in the smoke. A previously overlooked aspect of the emissions has been the organic compounds studied in this thesis. They are all emitted in varying amounts from different kinds of combustion and have different effects and properties.

Furthermore, it is important that the information and research results reach the pellet industry. When it is clear how different burning appliances and combustion conditions influence emissions of different compounds, it will be possible to minimise the emissions of compounds with negative effects on health and the environment.

2. WOOD PELLETS

Processing of biomass fuels may give rise to many advantages, for example relatively low costs, low moisture content and convenient use and transport. The properties of wood pellets differ a great deal from the properties of firewood. This is mainly due to the homogeneity and low moisture content of wood pellets, which is achieved by drying and pressing the sawdust and shavings. Wood pellet fuel offers many advantages and is therefore rapidly replacing petroleum oil and firewood for residential heating in Sweden.

2.1 PROCESSED BIOMASS FUELS

There are three kinds of processed biomass fuels; pellets, briquettes and powder. Despite the fact that briquettes have lower production costs, pellet fuel is the most suitable reformulated biofuel for small-scale use, as the easiest fuel to transport and feed into burners.

The high moisture content of unprocessed biomass is normally a drawback, leading to high transport costs and microbial degeneration during handling and storage. The variations in moisture content also give rise to an uneven combustion with unnecessary emissions and lower efficiency. Drying and compressing biofuels to pellets give a higher energy density and better combustion properties. The storage properties of wood pellets with low moisture content are favourable (Lehtikangas 2000). Pellets are also more convenient to transport (Hillring and Vinterbäck 1998). The processing costs are offset by lower transport and storage costs due to the higher energy density. Another advantage of pellets compared to unprocessed biomass fuels is convenience to the customer. Pellets can be automatically fed into the burner, does not need splitting and have a lower ash content. There are, however, some drawbacks, as pellets are more expensive and the fine fraction may disturb the combustion and the feed of the pellets into the burner.

Pellets also have several advantages compared to fossil oil. Wood pellet fuel is a renewable fuel that does not provide any net contribution of to the greenhouse effect. The burning of 5 m^3 of oil releases 13.8 tonnes of carbon dioxide into the atmosphere. Thus, the change from fossil fuels to biofuels is a significant way to decrease the Swedish carbon dioxide emissions (Bohlin *et al.* 1998). One way to encourage this change is through a carbon dioxide tax (Hillring 2000). Furthermore, wood pellet fuel is cheaper than petroleum oil and electricity and has a more stable price development. No major increase is expected in the price of wood fuels in Sweden, since both the domestic supply and the possibilities for importing biofuels are large (Carlson 2002). The price for oil has increased by 70 percent since 1995 and electricity by 13 percent (**IV**). However, it is difficult to compare the environmental impact of a change from electricity to pellets as it depends on how the saved electricity is produced. As pellets are a native fuel, they provide employment opportunities in Sweden. Some drawbacks compared to petroleum oil are the need for larger storage facilities, regular control and removal of ashes.

2.2 PELLETS IN SWEDEN

As a background to this thesis, the production and use of fuel pellets were investigated (**IV**, **II**). This was done in order to describe the situation on the Swedish pellet market. Some conclusions were made based on this survey.

At present, there are more than 20 production sites for wood pellets in Sweden (Figure 2.1), with an annual total production of 700 000 tonnes. The produced pellets consist of softwood sawdust and softwood shavings, and in some cases an additive. Sweden has sufficient raw material to produce 3 million tonnes of wood pellets annually. If this is not sufficient, there are plenty of sawdust and shavings available in the Baltic States and in Russia.

Swedish wood pellet production began at the beginning of the 1980s with an annual production of 45 000 tonnes (**IV**) and has increased dramatically ever since (Figure 2.2).

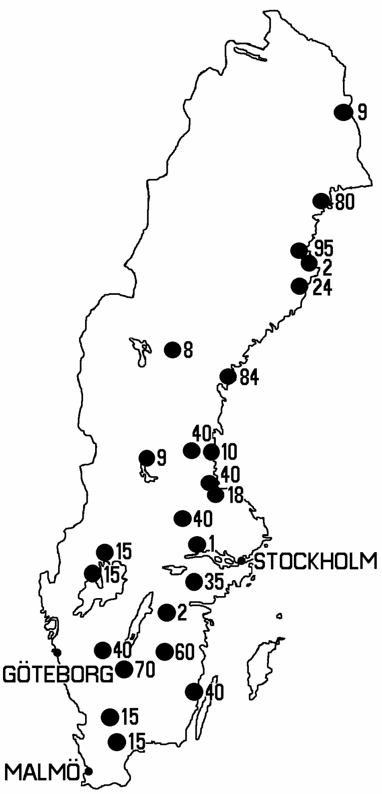

Figure 2.1: Production of wood pellets in Sweden (in thousands of tonnes, **IV***)*

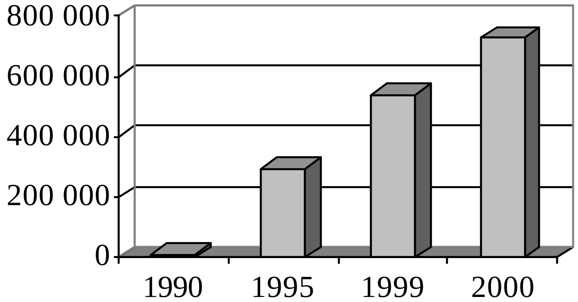

*Figure 2.2: Total Swedish wood pellet production in 1990, 1995, 1999 and 2000 in tonnes (***IV***, Vinterbäck 2000c)*

At present, the Swedish wood pellet production amounts to 700 000 tonnes per annum. The production capacity is about 1.5 million tonnes. The total Swedish production of wood pellets would be sufficient to heat 300 000 homes, but the major proportion is still burnt in large-scale heating plants.

However, approximately 20 percent is used for residential heating, and this use has increased by 30-35 percent yearly (**IV**). According to the latest information from pellet producers, residential use amounts to 145 000 tonnes annually, for use in about 25 000 burners and 8 000 stoves (Figure 2.3). During the 1995-96 season, this figure was 17 000 tonnes (Hillring and Vinterbäck 1998). In the year 2000, more than 6 000 pellet burners were installed. There are great possibilities for an even further increase in the shift to wood pellets (Carlson 2002).

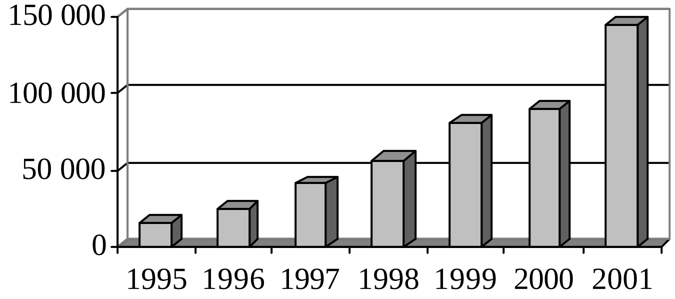

Figure 2.3: Residential use of wood pellets in Sweden 1995-2001 in tonnes (Vinterbäck 2000c, **IV***)*

Most of the residential heating appliances for pellets have replaced wood stoves. The reasons for the change from firewood to pellets are convenience, mainly due to the automatic feed, and the fact that pellet fuel is a cheap alternative. Today, the number of oil burners being replaced by pellet burners is increasing. This is due to pellets being an environmentally friendly alternative and oil being relatively expensive. The price of pellets for a small-scale customer is approximately 0.40 SEK/kWh.

Sweden is not the only country where the production and use of wood pellet fuel is significant. Pellets have been used for residential heating for 15 years in the US, and there are more than 70 producers (Vinterbäck and Roos 2000). Unlike the Swedish market, the

American market has always been dominated by the use of pellets in stoves. This is because the residential heating using electricity or oil is convenient and rather cheap. The pellet stove is used as a complement during the winter. In Europe there is significant production and use in for example Denmark, Austria, Italy and the Netherlands.

2.3 PRODUCTION OF PELLETS

Pellets are at present produced from softwood sawdust and shavings at more than 20 production sites all over Sweden (**IV**). In order to produce pellets as economically as possible and in the most environmentally friendly way, the location of the production site is very important. When choosing where to produce pellets, access to cheap raw material, preferably close to a saw mill, and already existing fodder pellets production plant are factors often considered. Furthermore, the possibilities to use surplus energy and the distance to customers are important.

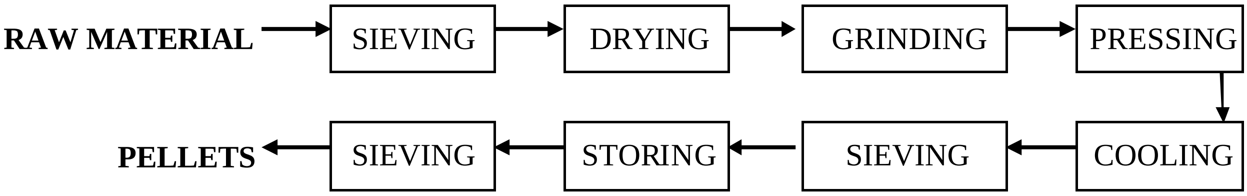

Figure 2.4: Flow sheet for the production of pellets from sawdust and shavings

Figure 2.4 shows a flow sheet for pellet production in Sweden. The raw materials must be correctly stored to avoid mould growth and anaerobic decomposition with methane emissions (Pier and Kelly 1997). The first step in the production is the drying of moist sawdust from 50-55 percent moisture content to 8-12 percent, which usually requires a lot of energy. It also leads to emissions of terpenes and other hydrocarbons (Granström 2002). Dry shavings are mixed with the dried sawdust. The mixture is ground and a binding agent is sometimes added. The use of binding agent is not necessary, but may give more stable pellets compared to the binding of the natural wood lignin. The binding agent may be Wafolin S or potato starch. Wafolin S contains hydrocarbons and calcium lignosulphonathe, which gives an unwanted increase in the formation of sulphur dioxide during combustion. Potato starch is a better alternative as it does not contain sulphur and is easier to handle.

After the grinding, the raw material is pressed through cylindrical holes in a pellet matrix (Figure 2.5). The friction gives a temperature rise to above 100°C. The pellet strings are cut off with a knife or automatically broken. The pellets are left to cool before sieving, storing and transporting to the customer.

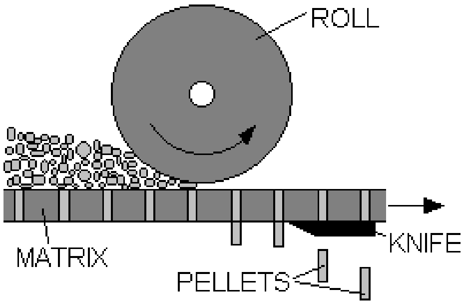

Figure 2.5: Pellet production matrix

2.4 PHYSICAL AND CHEMICAL PROPERTIES

Some of the properties of wood pellets are shown in Table 2.1 below. These are regulated by the Swedish Standard (SS 18 71 20) for fuel pellets.

*Table 2.1: General summary of physical and chemical data for pellets made from pure trunk-wood sawdust (***IV***)*

Density	550-700	kg/m^3
Diameter	5-12	mm
Lower heat value	17.0-17.9	MJ/kg
	4.7-5.0	MWh/ton
Moisture content	6-10	weight percent
Ash content	0.3-0.8	weight percent of dry substance
Sulphur content	0.01-0.02	weight percent of dry substance
Nitrogen content	approximately 0.05	weight percent of dry substance
Fine fraction	varying	

Usually, pellets have a density of 600-700 kg/m^3. Thus 3 m^3 of pellets have the same energy content as 1 m^3 of petroleum oil. The most common pellet diameters for residential use are 6 and 8 mm. The length of the pellets is normally 5-50 mm. It is important to adjust the burning appliance when changing pellets to avoid inefficient combustion.

The heat value of a fuel is defined as the amount of energy released during complete combustion in relation to the mass (**IV**). There are two different heat values: the lower heat value, which presumes that the evaporated water leaves with the smoke, and the higher heat value that includes the energy released when the evaporated water is condensed. The lower heat value corresponds better to reality and is thus more commonly used than the higher heat value. The heat value of wood pellets is quite stable, due to the relatively constant moisture content of about 8 percent, which is an advantage compared to other biomass fuels. The moisture content of dry firewood is approximately twice as high and more variable.

The ash content is defined as the amount of ashes divided by the amount of dry fuel. Normally, the ash content of wood pellets is 0.4-0.5 weight percent. This can be compared to the ash content of bark pellets, which is about 3.5 weight percent. The ash contains both inorganic materials from the biomass and material that has contaminated the fuel during harvest, transport and storage. The burning appliance must be cleared of ash, but not more often than once a week. The most common method of disposing of the ashes is to spread them in the garden as a supply of mineral nutrients, which leads to a raise in the pH level (Vinterbäck and Roos 2000). Roughly 65 percent of all pellet users spread the ashes in the garden, either with or without previous composting. The ashes contain most of the mineral nutrients originating from the wood (Table 2.2).

*Table 2.2: Summary of the content of mineral nutrients in wood pellet ashes (***IV***)*

	weight percent
Phosphorous	1
Potassium	6
Calcium	20
Magnesium	2.5

In the long term, modern forestry may deplete the soil of nutrients. When using pellets in large-scale combustion plants it is important to keep the ash free from contaminants in order be able to return it to the forest ecosystem. Experiments on returning pelletised ash to the forests have been made (Lundborg 1998). The ash may also contain small amounts of heavy metals, which could cause long-term environmental effects. This is important to take into consideration when discussing the potential of ash return.

The amount of fine fraction is important for combustion efficiency, especially in small-scale combustion appliances where it may interrupt the feed and cause incomplete combustion. The fine fraction is formed during the transport and handling of the pellets and must be sieved away before delivery to the customer. The formation of fine fraction may in some cases be prevented by the use of a binding agent.

3. METHODS FOR SMOKE STUDIES

Even though pellet fuel is an environmentally friendly residential fuel with low emissions to air, it is of great importance to examine the emissions from the burning of wood pellets, both in order to get a view of the different compounds in the smoke and their relative amounts and to reach an understanding of how to minimise the emissions of health and environmentally hazardous compounds in the smoke. The organic content of the flue gases from the combustion of wood pellets was therefore analysed.

Smoke from flaming and glowing pellets (**I**) was studied in laboratory experiments. Pellets from three different manufacturers were burnt in order to analyse the organic fraction of the flue gases with GC-MS. The experiments were designed to simulate incomplete combustion in a pellet burner or pellet stove.

Furthermore, chimney samples were taken from residential heating appliances (**II**).

The smoke was sampled in the chimney outlet during normal operation of the burning appliance. The organic content of the flue gases was analysed with GC-MS at the same time as other smoke characteristics were studied.

Furthermore, wood pellet ember emissions were more thoroughly analysed and compared to the combustion characteristics of different types of glowing charcoal (**III**). A comparison with birchwood ember was also made.

3.1 LABORATORY BURNING

Softwood pellets from three different Swedish manufacturers were burnt during the laboratory-scale experiments (**I**). The pellets used were all 8 mm in diameter. They were produced by AB Forssjö Bruk, Bioenergi i Luleå AB and Mellanskogs Bränsle AB and were chosen to represent different raw materials, tree species and binding agents. The pellets from AB Forssjö Bruk were mainly produced from sawdust, but to some extent also from shavings. The tree species used were mixed Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea Abies*). The pellets from Bioenergi i Luleå AB consisted of pine sawdust, with some addition of spruce.

Mellanskogs Bränsle AB produced their pellets from softwood shavings and used one percent of potato starch as a binding agent.

Flaming burning experiments were made to resemble incomplete combustion in a pellet stove or burner, whereas glowing burning experiments were made to simulate the combustion characteristics of a burner or stove on low effect or expiring. A few pellets were set aflame or completely burnt out in a ceramic pot. The smoke was collected on Tenax adsorbent (Figure 3.1) and analysed with gas chromatography coupled to mass spectrometry (**I**).

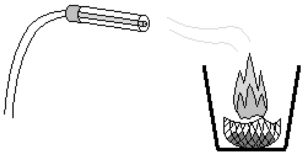

Figure 3.1: Sampling arrangement

3.2 RESIDENTIAL BURNING

In order to estimate the emissions from small-scale burning of pellets in Sweden, smoke samples were collected in the chimney outlets of a few different burning appliances (**II**). These were all intended for normal residential heating. Four different burners, two pellet stoves and one pellet boiler were examined. The softwood pellets were 8 mm for the burners and the boiler and 6 mm for the stoves. Smoke was sampled on Tenax adsorbent and analysed with gas chromatography and mass spectrometry.

The first pellet burner was used to heat a small block of flats in an organic farming village in Ubbhult, Härryda. The burner was an old model of Sahlins EcoTec A3 with a maximum effect of 25 kW. The burner was installed in a 1996 combination boiler for oil, wood and electricity (Albin Kombi 952). The pellets were fed continuously, 10-20 at a time. The results from the EcoTec A3 burner were confirmed by analyses from another burner of the same brand, a Sahlins EcoTec B1 of 30-50 kW. This burner was installed in an Arimax 360 Bio boiler used to heat parts of Sahlins EcoTec AB´s burner production factory in Skene. The second burner was a PellX P20 of 10-20 kW. This burner was installed in a 1971 CTC combination boiler for oil, wood and electricity in a residence in Annelund. The emissions from this burner were sampled with the burner on high effect and medium effect respectively. The third burner was a Janfire Flex-a, 23 kW installed in a residence in Åmål (Figure 3.2). The burner was installed in a 1982 CTC combination boiler for oil, wood and electricity.

Figure 3.2: Janfire Flex-a pellet burner

Figure 3.3: Calimax Sandor pellet stove

The first stove studied was a Calimax Sandor, 7 kW, used to heat a storage room at Baxi AB in Falköping (Figure 3.3). The pellets were fed continuously, one at a time. The results from the first stove were confirmed by the results from an Austroflamm Integra, 11 kW, pellet stove installed at the laboratory of Äfab AB in Lidköping. The boiler was a Baxi Multiheat 25 kW installed at Baxi AB in Falköping.

In order to sample the real emissions to air, the samples were taken in the chimney top of all the appliances. However, with one exception; the smoke from the Austroflamm Integra was sampled in a sampling pipe from the smoke channel. One of the great advantages of sampling in the chimney pipe is that compounds that condense naturally in the chimney pipe and are later on removed by the chimney sweep are not present in the samples.

In parallel to the sampling of semi-volatile organic compounds on Tenax adsorbent, smoke was collected in Tedlar bags for laboratory assessments of carbon monoxide, carbon dioxide and methane. 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.

3.3 GLOWING CHARCOAL

The emissions of volatile and semi-volatile compounds from fully burnt out, glowing pellet ember were examined (**III**). A few softwood pellets from AB Forssjö Bruk were 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 with both gas-tight syringes and Tenax adsorbent. The semi-volatile compounds in the smoke were analysed by GC-MS, whereas the more volatile compounds were separated on an aluminium oxide column and analysed with GC-FID. Carbon monoxide and carbon dioxide were analysed by gas chromatography and a hot wire detector.

The results were compared to those of glowing birchwood embers and glowing Swedish charcoal, which had been assessed in the same way. The charcoal was produced by Skogens Kol AB.

3.4 ANALYTICAL APPROACH

Compounds present in high concentrations in the smoke may be analysed with direct recording instruments. However, this kind of instrument is only available for a limited number of compounds as, for example, carbon dioxide and carbon monoxide. Smoke may also be collected in Tedlar bags, allowing the compounds to be analysed with more complicated equipment in the laboratory.

Compounds present in very low concentrations have to be concentrated during the sampling or before the analysis. A way of simultaneously sampling and concentrating semi-volatile organic compounds and particles is the adsorption on Tenax. Smoke was pumped through a glass liner filled with Tenax TA adsorbent (60-80 mesh, approximately 0.1 g) for 2-10 minutes and thus both the compounds in gaseous phase and in particle phase were collected (Figure 3.4). The total sampling volume was 10-40 ml.

Figure 3.4: Sampling in the chimney pipe

The analytical equipment used was a number of gas chromatographs with different specific columns and different detection methods for separation and analysis of a wide range of compounds with different characteristics.

3.5 CHROMATOGRAPHIC METHODS

Three different gas chromatographic systems with different detection methods were used for the analysis of the emissions.

The aromatic hydrocarbons in the emissions from burning and glowing pellets and charcoal were analysed using gas chromatography in combination with mass spectrometry (**I**, **II**, **III**). This analytical method has previously been used with good results to assess semi-volatile compounds (Kjällstrand *et al.* 1998).

The sampled compounds were thermally desorbed as the glass liner containing the Tenax adsorbent was placed inside the injector and the temperature was raised to 220°C. The colon used was a cyanopropylphenylsilicone (Rtx 1701). (For further details see **I** and Figure 3.5) The different compounds were identified by their specific mass spectra, their retention and the NIST library. A reference gas mixture from Scott Speciality Gases and the results from the GC-FID were used for the quantitative determinations.

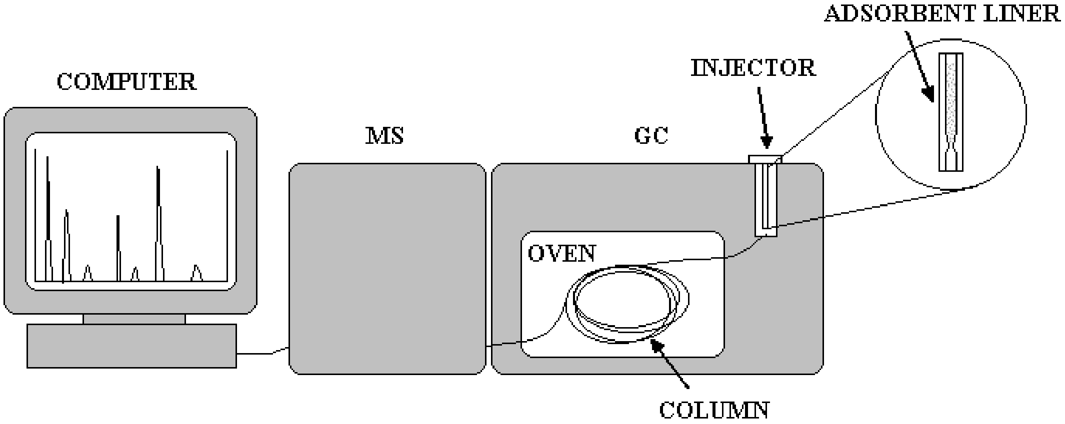

Figure 3.5: The gas chromatograph – mass spectrometer system

The volatile hydrocarbons emitted from pellet ember and glowing charcoal were analysed using gas chromatography with a selective column and flame ionisation detection (**III**). This system was previously used successfully to study the smoke from a wood stove (Barrefors and Petersson 1995) and for vehicle-polluted urban air (Löfgren and Petersson 1992). The column used was a PLOT aluminium oxide column (Al_2O_3 / KCl). (For more information see **III**) The reference gas mixture was used for the quantitative determinations. No corrections were made for the different responses of the various compounds.

In some cases methane was analysed with a molecular sieve (13X, 1.7 m × 3.2 mm) and flame ionisation detector (**II**).

Carbon monoxide and carbon dioxide were assessed using gas chromatography with a hot wire detector (**II**, **III**). Carbon monoxide was separated by a molecular sieve 13X and carbon dioxide by a HayeSep Q (60-80 mesh). A direct recording Testo 300M instrument from Nordtec Instruments AB was also used for carbon monoxide and carbon dioxide. This instrument was also used for oxygen and nitrogen oxides.

The flue gas flux and the smoke temperature were measured using a Testo 445 instrument from Nordtec Instruments AB and the Testo 300M respectively.

3.6 DETECTORS

The detector response is of great importance to achieve a correct quantification of the concentrations of different compounds. The assessment of different types of compounds may require different analytical methods. The same detection methods can not be used for all compounds but must be chosen to suit the most interesting or important compounds.

The mass spectrometer is a very sensitive detector that allows identification of the different compounds through their specific mass fragmentation spectra. This detector has been used for the quantification and detection of semi-volatile organic compounds. The dependence of the response of the mass spectrometer on chemical structure has been discussed (Kjällstrand 2002).

The thermal conductivity detector records changes in the thermal conductivity of the incoming gas. The detector can be used for all gases, but the sensitivity is quite low. This detector has been used to quantify carbon monoxide and carbon dioxide.

The flame ionisation detector is widely used for organic substances with high sensitivity to hydrocarbons. The recorded compounds are ionised in a hydrogen flame and the ion current through the flame is measured. The response of a substance in a flame ionisation detector is approximately proportional to its carbon content. The presence of hetero atoms (O, N, Cl etc) in the molecule decreases the relative response. This detector has been used for quantification of volatile hydrocarbons. The relative response of many different compounds has been more thoroughly evaluated by Jorgensen *et al.* 1990. This permits quantitative adjustments, but in this study all results are based on peak areas only.

When measuring the emissions by the general emission factor OGC (organic carbon), the difference in response of various compounds is not considered. Oxygen-containing compounds contribute less than hydrocarbons, and saturated hydrocarbons somewhat less than unsaturated hydrocarbons, relative to the real quantitative proportions. Thus OGC does not show the real amounts of emitted organic compounds. Furthermore, it is not possible to make specific conclusions on the effects of the smoke based only on the OGC value. In order to estimate the greenhouse effect, photo-oxidant formation potential or health hazards of the smoke, the specific compounds present in the smoke must be assessed.

4. RESULTS

The emissions from residential burning of wood pellets are generally low and pellets is a fuel environmentally well suited to replace petroleum oil and firewood. Even though the emissions are low, they should be measured, examined and, when possible, also decreased. During temporary disturbance and start-up, the emissions are larger, but have a different chemical composition. It is therefore important to acquire knowledge of the emissions from different types of combustion.

The results refer to analyses of the emissions from flaming pellets, glowing pellets (**I**, **V**) and glowing pellet embers and charcoal (**III**) sampled on a laboratory-scale. Furthermore, they refer to samples of chimney smoke taken from pellet burners, stoves and boilers used for residential heating (**II**, **V**).

4.1 LABORATORY BURNING

Smoke was analysed from glowing and flaming laboratory burning of wood pellets from three different manufacturers (**I**, **V**). It was clear that the combustion conditions largely affected the contents of the flue gases, but also that the different pellet brands gave rise to similar emissions. The organic compounds found during inefficient flaming combustion of pellets were mainly 2-methoxyphenols with antioxidant properties.

A few softwood pellets were burnt freely in a ceramic pot with flame temperatures of approximately 800°C. The pellets emitted 2-methoxyphenols with guaiacyl (Gu) structures as the major lignin originating compound group (Figure 4.1). The total concentration of the six most prominent of these compounds was 0.1-1 mg m^{-3}, and all assessed compounds were related to this sum. The single most predominant compound was 4-methyl-2-methoxyphenol ($GuCH_3$). The chromatographic separation of the compounds released during flaming burning is shown in Figure 4.2.

The most prominent cellulose originating compound from flaming pellets was 1,6-anhydroglucose. The higher emissions of this compound from softwood pellets produced by Mellanskogs Bränsle AB may be due to the use of potato starch as a binding agent. Another polysaccharide derived compound was 2-furaldehyde.

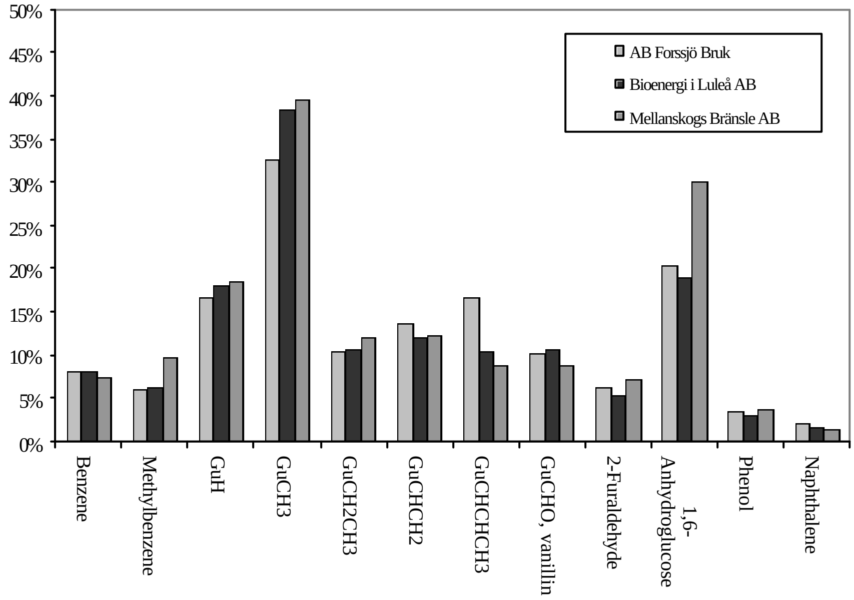

Figure 4.1: Relative proportions of components in smoke from flaming burning of softwood pellets from three different manufacturers (Gu = 4-hydroxy-3-methoxyphenyl)

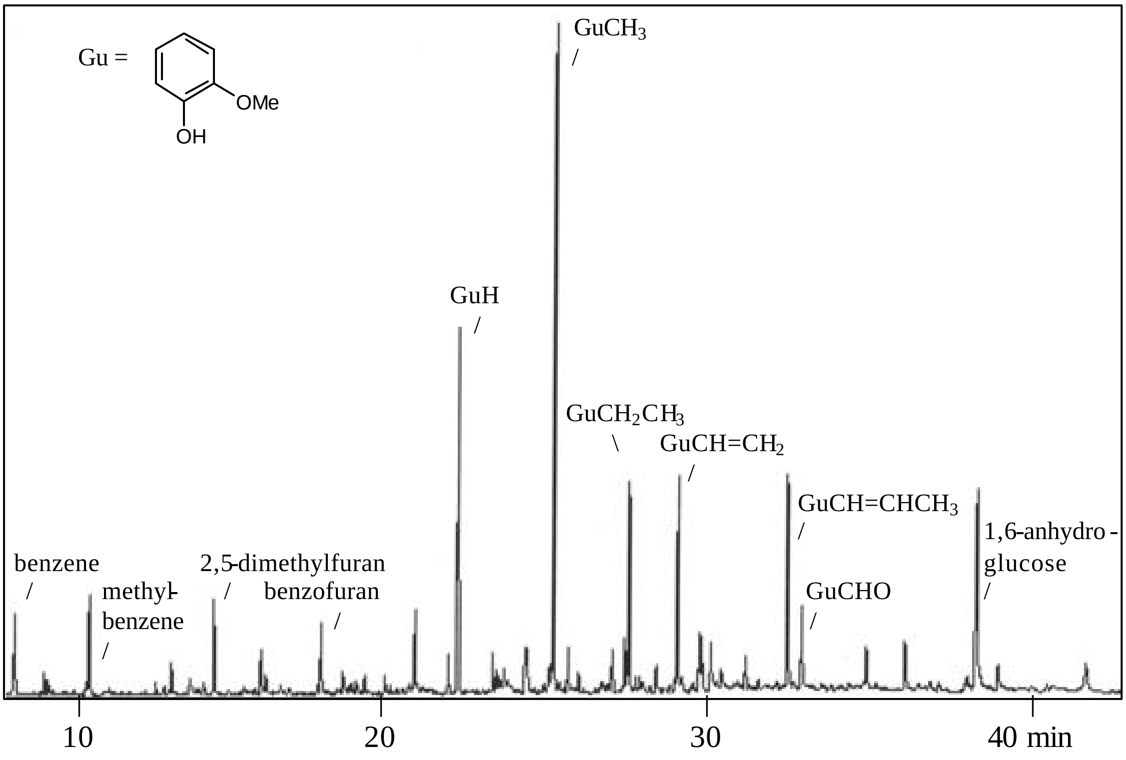

Figure 4.2: Section of total ion current chromatogram illustrating the separation of 2-methoxyphenols emitted on flaming burning of softwood pellets from AB Forssjö Bruk

Benzene and methylbenzene were the major aromatic hydrocarbons emitted from flaming pellets. The concentrations of these compounds were in the range of 0.01 - 0.1 mg m^{-3}. The formation of naphthalene and more health hazardous polycyclic aromatic hydrocarbons was very low.

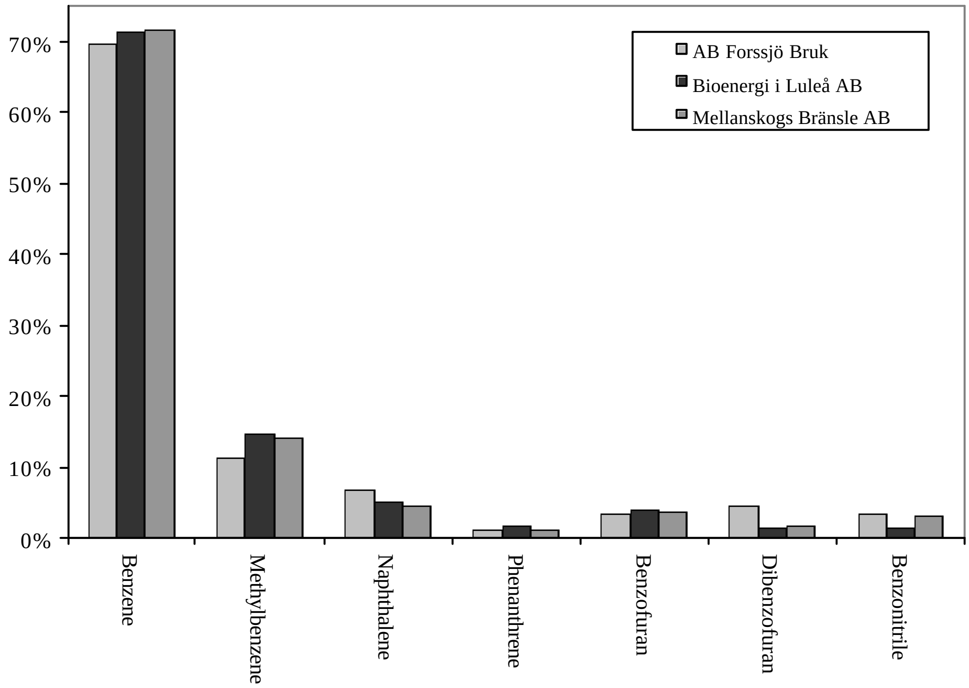

Figure 4.3: Relative proportions of components in smoke from glowing remainders of softwood pellets from three different manufacturers

After the flaming period the pellets glowed with a surface temperature below 400ºC. The predominant component from glowing burning was the carcinogenic hydrocarbon benzene (Figures 4.3, 4.4). The emissions were, however, lower than from flaming burning. The relative proportion between benzene and methylbenzene was much higher than from flaming pellets burning and from flaming wood stove burning of firewood (Kjällstrand and Petersson 2001c, Barrefors and Petersson 1995). The emissions of naphthalene and phenanthrene as well as other polycyclic aromatic hydrocarbons were low, due to the low combustion temperature (Alén *et al.* 1996, Kjällstrand and Petersson 2001c, Hauk *et al.* 1994). The major oxygen containing compounds were benzofuran and dibenzofuran.

Primary combustion products from the wood lignin and cellulose such as 2-

methoxyphenlos and 1,6-anhdyroglucose were completely absent in smoke from glowing pellets. These compounds are probably almost totally released during flaming burning. This is a great difference when comparing burning pellets to burning firewood (Kjällstrand and Petersson 2001c), which may be due to a low thermal conductivity in solid wood (Larfeldt *et al.* 2000a, 2000b) and a rapid gas and heat transfer in the more porous wood pellet (Hansson 2000).

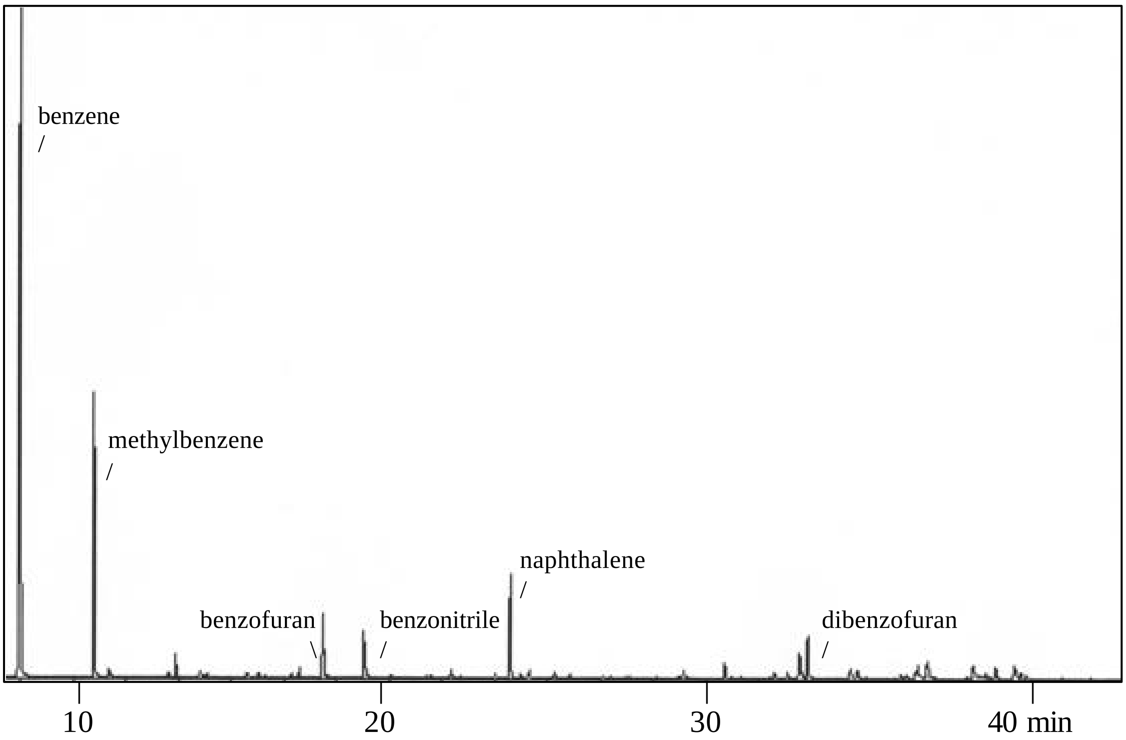

Figure 4.4: Section of total ion current chromatogram illustrating the separation of aromatic compounds emitted from glowing burning of softwood pellets from AB Forssjö Bruk (benzene twice off scale)

The emissions from the glowing burning of softwood pellets largely resemble the emissions from pellet ember and glowing charcoal (**III**). The emissions from continuous burning of softwood pellets in a pellet burning appliance reflect a mixture of the flaming and glowing phases. The large proportion of benzene in the emissions from glowing burning makes it important to consider not only the high emissions of organic compounds from the flaming phase, but also the lower emissions from the glowing phase.

4.2 RESIDENTIAL BURNERS

The emissions of volatile and semi-volatile organic compounds from some different residential pellet burning appliances were sampled and measured in the chimney outlets. The different appliances examined were an EcoTec burner (**II**), a PellX burner (**II**, **V**), a Janfire burner, a Calimax stove (**II**, **V**), and a Baxi boiler (**V**). In all cases the emissions of carbon dioxide, carbon monoxide, benzene (carcinogenic), phenanthrene (representing the health hazardous polycyclic aromatic hydrocarbons, PAH) and guaiacol (phenolic antioxidant) were measured. Additionally, the emissions of methane (greenhouse gas) from some of the appliances were analysed.

Both the amount and the composition of the emissions varied greatly between the different appliances and the different effects (Tables 4.1 and 4.2).

Table 4.1: A comparison of the emissions of carbon dioxide, carbon monoxide, methane, benzene and phenanthrene from different residential pellet burners

	EcoTec	PellX		Janfire
	25 kW	20 kW	10 kW	23 kW
Carbon dioxide (%)	3.1	6.9	2.7	6.5
Carbon monoxide (ppm)	1200	10	400	60
Methane (ppm)	28	0.5	5	-
Benzene (ppm)	3	0.003	0.2	0.006
Phenanthrene (ppm)	0.2	0.0001	0.01	0.001
Benzene (mg/h)	1400	2	120	2

The three different burners were all studied on maximum effect. Additionally, the PellX burner was studied on half effect (Table 4.1). All burners examined were installed in combination boilers and fuelled with softwood pellets. The results from the EcoTec burner were confirmed by measurements on a larger EcoTec burner. The emissions from the PellX burner and the Janfire burner on maximum effect were very low. However, the emissions from the PellX burner on half effect were higher. The highest emissions of all compounds came from the old model of the EcoTec burner. This burner was installed in a rather unsuitable boiler, as the flames probably cooled off too soon on the boiler walls. The large variations in emissions from different examples elucidate the importance of trying to choose the "best technology", both in the design of the burner and the combination of burner and boiler. Simplified analyses of, for example, the total concentration of organic compounds should be sufficient for this.

All samples were taken in the chimney outlet of appliances installed in residences. It is therefore important to emphasise that the results are no general emission figures, but examples of how great the differences may be in individual cases. The emissions are not only related to the brand and design of the burner, but also to the choice of the boiler, the installation, management and maintenance of the burner.

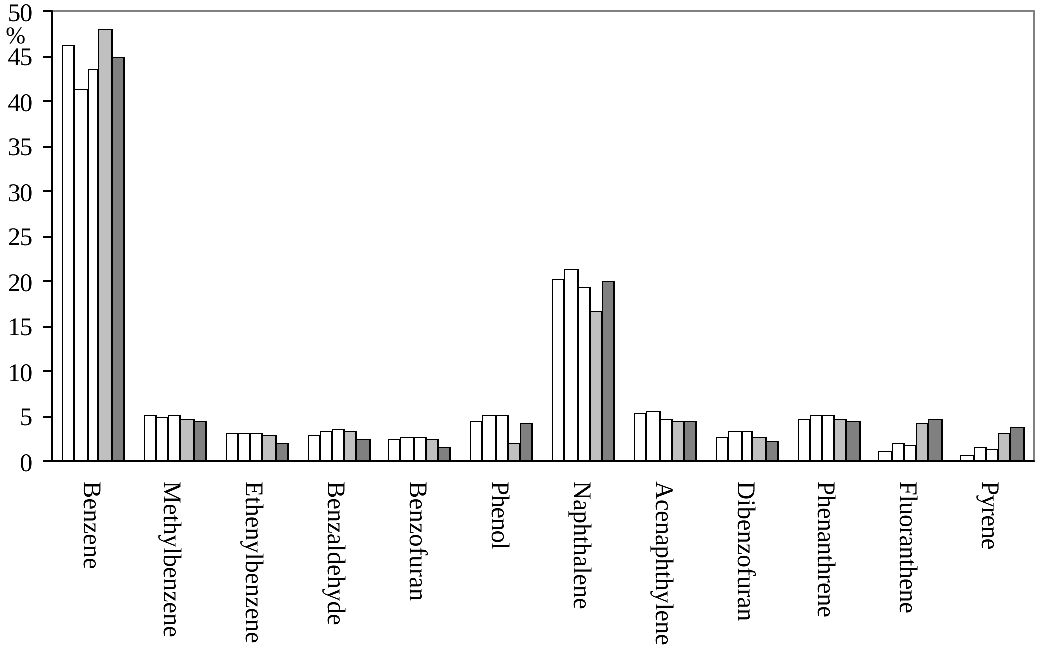

Figure 4.5: Relative proportions (%) of recorded aromatic compounds in chimney smoke from burners. The first three samples were taken on one occasion and the fourth sample weeks later from the EcoTec burner. The fifth sample was taken from a larger EcoTec burner (**II**)

The relative proportions of some of the major aromatic compounds in the chimney smoke from the EcoTec burner are shown in Figure 4.5 (**II**). It is obvious that the relative proportions do not vary much between the different samples, although the total amounts of the compounds may vary greatly.

The major aromatic hydrocarbon was the carcinogenic benzene. The relative proportion of benzene and methylbenzene was even higher than from glowing laboratory burnings of softwood pellets. The second most prominent was naphthalene. Phenanthrene, fluoranthrene and pyrene are other representatives of the polycyclic aromatic hydrocarbons, PAH. The relative amount of PAH formed increases with increasing combustion temperature (Hauk *et al.* 1994, Kjällstrand and Petersson 2001c), which may explain minor variations between the samples. There were many oxygen-containing trace compounds in the smoke, such as phenol, benzaldehyde, benzofuran and dibensofuran. Styrene is a common compound in wood smoke (Kjällstrand and Petersson 2001c).

The primary decomposition compounds 2-methoxyphenols and 1,6-anhydroglucose were not present in the smoke, probably due to a more complete and high temperature combustion. The lowest emissions overall came from the Janfire and PellX burners at maximum effect. The highest methane emissions came from the EcoTec burner. This burner also has the highest emissions of carbon monoxide, benzene and phenanthrene.

The benzene emissions from the EcoTec burner were a lot larger than the benzene emissions from any of the other appliances. It is also important to mention the relatively high emissions from the PellX burner on low effect. It is therefore important to consider the necessity of running the appliances on low effect and the length of time involved.

The emissions of the carcinogenic benzene are important to consider. However, the chimney concentrations are very low, and the emissions are made at roof level, which results in low human exposure.

In addition to studying the emissions of semi-volatile compounds from the PellX burner, the emissions of volatile hydrocarbons were analysed (Figure 4.6). The most prominent alkenes were ethene and propene. The dominant alkyne was ethyne.

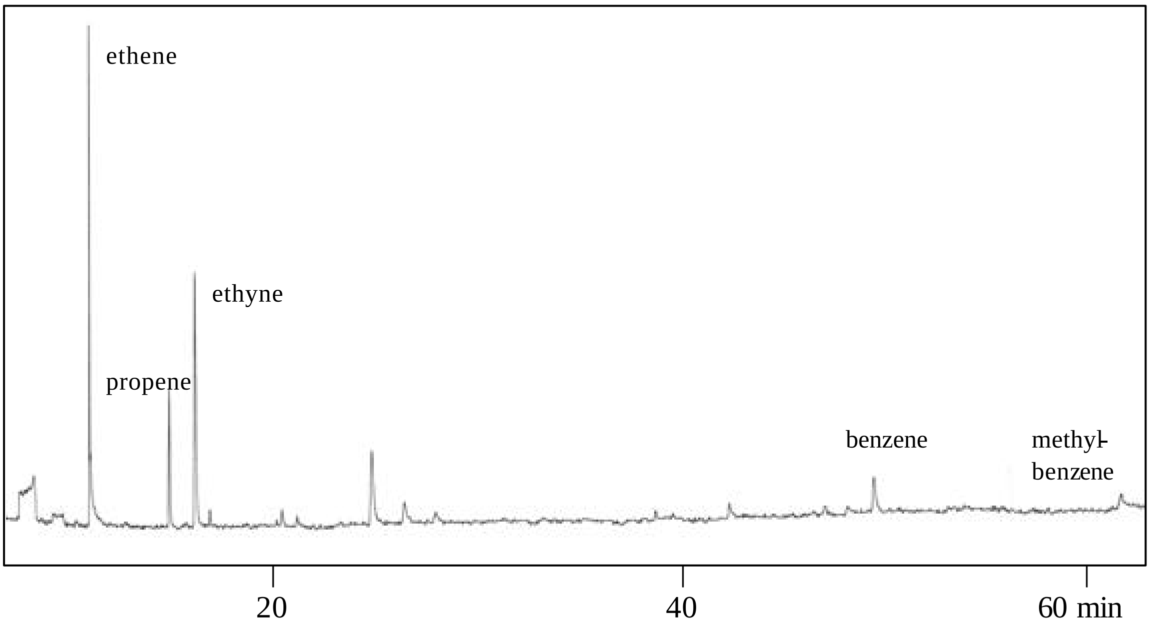

Figure 4.6: Chromatogram showing volatile hydrocarbons emitted from the PellX burner on low effect. Analysis made on an aluminium oxide column using a flame ionisation detector

4.3 RESIDENTIAL STOVES AND BOILERS

The emissions of carbon dioxide, carbon monoxide, methane, benzene, phenanthrene and guaiacol from the Calimax stove and the Baxi boiler on two different effects are shown in Table 4.2 (**II**, **V**). The appliances were installed at a company in the pellet business. 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 primary combustion products such as 2-methxoyphenols and 1,6-anhydroglucose.

The emissions from the pellet stove showed a striking resemblance to those from the Baxi boiler on low effect, whereas the emissions from the boiler on maximum effect were much lower.

Table 4.2: A comparison of the emissions of carbon dioxide, carbon monoxide, methane, benzene, phenanthrene and guaiacol from a stove and boiler for residential use

	Calimax		Baxi	
	7 kW	4 kW	25 kW	8 kW
Carbon dioxide (%)	3.1	2.1	6.0	1.9
Carbon monoxide (ppm)	500	500	40	400
Methane (ppm)	8	7.8	1.5	-
Benzene (ppm)	0.2	0.2	0.02	0.1
Phenanthrene (ppm)	0.002	0.005	0.01	0.002
Guaiacol (ppm)	0.03	0.08	0.04	0.003
Benzene (mg/h)	30	30	15	90

In Figure 4.7, the relative proportions of aromatic hydrocarbons and methoxyphenols from the Calimax pellet stove are compared to those from the Austroflamm Integra stove. The different samples from the Calimax stove have similar proportions of the prominent compounds, whereas the smoke from the Austroflamm Integra contains the same compounds but in different proportions.

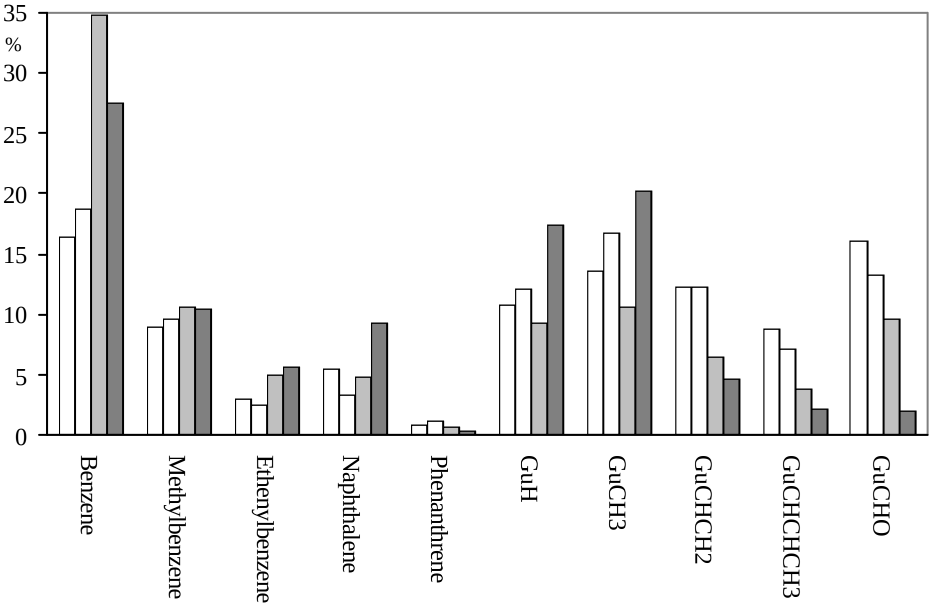

Figure 4.7:Relative proportions (%) of aromatic hydrocarbons and antioxidant methoxyphenols (Gu) in smoke from stoves. The first two chimney samples were taken from a Calimax stove, and the third sample on another occasion from the same stove. The fourth sample was from an Austroflamm Integra stove

The predominant compound group in the smoke from the pellet stoves was the methoxyphenols with guaiacyl (Gu) structure. The 2-methoxyphenols originate from the lignin of the wood (Alén *et al.* 1996). Their presence in the smoke is probably due to a lower and less uniform combustion temperature. Benzene is, as in the emissions from the burners, the most prominent aromatic hydrocarbon. The relative proportions between benzene and methylbenzene are lower than from the burners and more similar to the proportions of wood smoke (Kjällstrand and Petersson 2001c, Barrefors and Petersson 1995, Schauer *et al.* 2001). The relative emissions of naphthalene and PAH were lower than from the EcoTec burners. Low emissions of PAHs from pellet stoves have earlier been found by Barnett *et al.*, 1991. Almost as high benzene emission figures are given for the Calimax stove as for the EcoTec burner if it is taken into account that the effect of the burner is four times the effect of the stove. However, the smoke from the stove and the boiler contained large proportions of phenolic antioxidants. Comparing the results from the burners to those from the stoves and boiler emphasise the importance of measuring not only the total amount of emitted organic carbon (OGC), but also the specific organic substances emitted during wood pellets combustion.

4.4 GLOWING CHARCOAL

The emissions from wood pellet ember were more thoroughly analysed and compared to those from glowing Swedish charcoal and glowing birchwood embers (**III**). When wood pellets or wood chips are fully charred after flaming burning, the combustion characteristics resemble those of glowing charcoal.

In Table 4.3, recorded proportions are given for carbon dioxide, carbon monoxide, methane, ethene, propene, ethyne and benzene. The concentrations of the hydrocarbons are reported as ppmC (ppm × number of carbon atoms in the compound). Therefore the proportions given reflect the relative numbers of carbon atoms released as the specific compounds.

Table 4.3: Concentrations of prominent carbon-containing compounds in smoke from decreasingly charred pellet embers, glowing charcoal and firewood embers, reflecting the quantitative proportions of carbon incorporated into the species

	Pellet embers	Pellet embers	Pellet embers	Charcoal glowing	Firewood embers
Carbon dioxide (%)	3.7	2.7	4.9	6.2	5.3
Carbon monoxide (%)	0.3	0.4	1.0	0.9	1.2
Methane (%)	0.0004	0.001	0.05	0.006	0.07
Ethane (ppmC)	0	0	110	1	143
Ethene (ppmC)	0.06	0.5	71	1	66
Propene (ppmC)	0	0.05	29	0.07	35
Ethyne (ppmC)	3	3	7	14	9
Benzene (ppmC)	1	2	25	5	23
Ethene / ethyne	0.02	0.2	10	0.07	7

Benzene was the predominant aromatic compound emitted from all fuels, whereas methane, ethene and ethyne were prominent among the more volatile hydrocarbons (**III**). The emissions from glowing charcoal and birchwood embers were in general one order of magnitude higher than from glowing pellet embers, which is an advantage in favour of wood pellets. It should be noted that benzene and ethyne are thermally unusually stable unsaturated hydrocarbons. Their relative proportions of total unsaturated volatile hydrocarbons from wood fuels therefore also increase with combustion temperature (Barrefors and Petersson 1995).

Different results were obtained for pellet embers depending on how charred the ember was. The incompletely charred pellet ember emitted greater amounts of all the tabulated compounds than the more completely charred embers. The relation between ethene and ethyne varies remarkably and was two orders of magnitude higher for the incompletely charred pellet embers. This is consistent with a hydrogen-deficient combustion for charcoal. The firewood ember bore a close resemblance to the least charred pellet ember, whereas the emissions of hydrocarbons from the most charred pellet ember were similar to those from glowing charcoal.

In general, the formation of benzene relative to carbon dioxide for pellet ember and the Swedish charcoal in Table 4.3 was an order of magnitude lower than for Polish charcoal (**III**). This may be explained by a higher proportion of carbon in the fuels and a more complete combustion of the more porous materials. The results for glowing pellets are consistent with previous studies of pyrolysis of wood pellets (**I**).

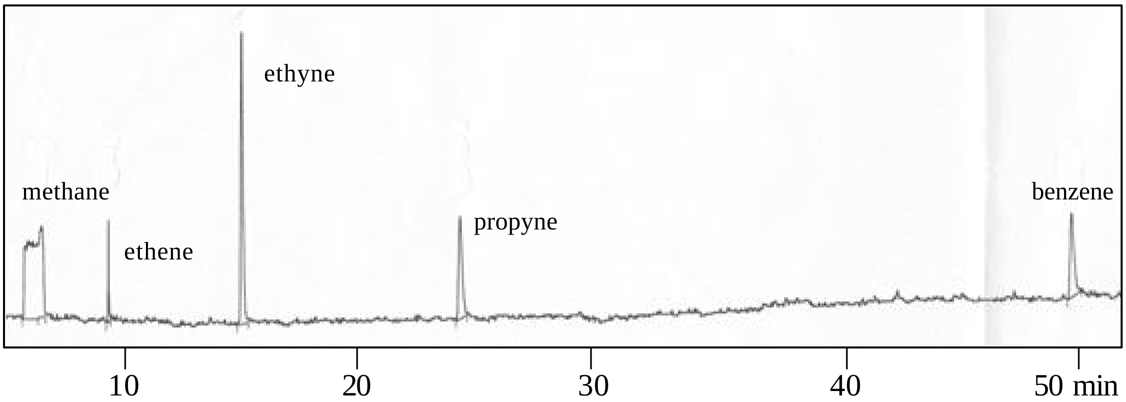

Figure 4.8: Chromatogram showing volatile hydrocarbons emitted from glowing softwood pellet embers. Analysis made on an aluminium oxide column using a flame ionisation detector

Figure 4.8 shows a chromatogram of volatile hydrocarbons emitted from almost completely charred softwood pellets. The results for glowing remainders of solid firewood were quite different, although the final phase of flaming burning was assisted by a butane torch to avoid unburnt wood. The relative proportions of ethene and propene to benzene were much higher. The proportion of methylbenzene relative to benzene was also much higher than for charcoal. The observed proportions of these compounds are in accordance with previous studies of birchwood burning (Barrefors and Petersson 1995).

Elevated proportions of benzene and ethyne with a high C/H ratio characterise the hydrocarbon emissions from charcoal relative to firewood. This is probably explained by the carbon content, which increases from about 50 percent in dry wood to more than 80 percent in the charcoal studied. The results also demonstrate a low methane formation from charcoal with a high carbon content.

5. SPECIFIC POLLUTANTS

The emissions from residential burning of wood pellets in burners, stoves and boilers on maximum effect are generally low. However, the emissions during ignition, low effect, temporary disturbances and poor maintenance are higher. The pollutants emitted have totally different effects on health and the environment. It is important to minimise the emissions of pollutants with negative effects, as for example the greenhouse gas methane, photo-oxidant forming alkenes and carcinogenic aromatic hydrocarbons. On the other hand, some compounds, as the antioxidant methoxyphenols, may have a positive effect.

5.1 INORGANIC GASES

The inorganic gases mainly focused on during chimney analyses of pellet appliances were carbon monoxide and carbon dioxide. This was done in order to investigate the combustion conditions and to be able to relate the different emissions to each other and to emissions from other appliances.

High carbon monoxide emissions indicate an oxygen deficiency during combustion and hence incomplete combustion with poor energy efficiency. The emissions of carbon monoxide from new pellet burners varied between 10-60 ppm, the corresponding figure for the pellet stove was 500 ppm and from the pellet boiler 40 ppm (**II**, **V**). The carbon monoxide emissions were about ten times higher from appliances on half effect and about 100 times higher from the old burner model.

In view of global warming, biofuels such as wood pellets are excellent, since the plants take up as much carbon dioxide during their growth as is later released during the combustion. The carbon dioxide concentration was normally about 6 percent in the chimney outlets of pellet burning appliances at maximum effect and 2-3 percent at low effect (**II**, **V**).

Nitrogen oxides are formed at all high-temperature combustion. They contribute to acidification and the creation of ground-level ozone. Traffic is the by far the main source for emissions of nitrogen oxides (**IV**). The emissions of nitrogen oxides from the examined pellet burning appliances were around 50 ppm or below. The emission of nitrogen oxides from a pellet burner had earlier been assessed as about 100 ppm (Johansson 2002).

5.2 VOLATILE ORGANIC COMPOUNDS

Methane is one of the main hydrocarbons emitted when burning materials containing carbon. Methane has a global warming potential about 20-30 times higher than carbon dioxide. The emissions of methane from the pellet burners and stoves in the survey varied between 0.5-30 ppm (**II**, **IV**, **V**). As methane is a greenhouse gas it is important to minimise emissions. The emissions of methane from the pellet appliances correspond to less than 5 percent of the global warming potential of the fossil oil that is replaced by the pellets. Comparing the methane emissions from pellets to those from firewood is difficult as the emissions from wood boilers vary greatly. A twenty-year-old residential fire place-like boiler emitted 180 ppm methane whereas a new eco-labelled wood boiler only emitted 5 ppm methane (Kjällstrand 2002). Methane has been assessed in many different uses of biomass fuels (Bhattacharya *et al.* 2000, Ndiema *et al.* 1998, Chanton *et al.* 2000, Delmas 1994)

Alkanes, alkenes and alkynes are formed from incomplete combustion. Ethene, ethyne, propene, propyne and benzene were, apart from methane, the major volatile hydrocarbons emitted from a pellet burner and glowing pellet embers (**III**). Alkenes have photo-oxidant formation potential due to their double-bonds. Ethene and propene are also genotoxic (Thörnqvist and Ehrenberg 1994). Volatile hydrocarbons have previously been studied in smoke from oak, pine and eucalyptus in residential fireplace combustion (Schauer *et al.* 2001). Alkanes, alkenes and alkynes have also been studied in smoke from firewood, cigarette smoke and car exhaust fumes (Barrefors and Petersson 1995, 1993).

5.3 AROMATIC HYDROCARBONS

The carcinogenic benzene (Figure 5.1) is a major aromatic hydrocarbon from the incomplete combustion of wood and from car exhaust fumes (Barrefors and Petersson 1995, 1993). It was found to be present in high proportions in the smoke from pellet burners and in the smoke from glowing burning of wood pellets (**I**, **II**). It was also present in the smoke from the pellet stoves and in the smoke from flaming burning of wood pellets, but in lower proportions (**I**, **II**). Benzene was the predominant aromatic compound from glowing charcoal and pellet embers (**III**). Benzene has previously been found in high concentrations in chimney smoke from a residential wood boiler (Kjällstrand and Petersson 2001c).

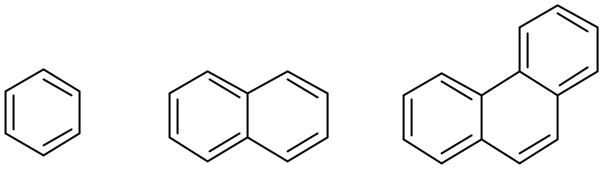

Figure 5.1: Benzene, naphthalene and phenanthrene

The carcinogenic naphthalene and the more hazardous polycyclic aromatic hydrocarbons (PAH) (Figure 5.1) were found in smoke from wood pellets and glowing charcoal (**I**, **II**, **III**). The most prominent PAHs were naphthalene, phenanthrene, fluoranthene and pyrene (**I**, **II**, **III**, Kjällstrand and Petersson 2001c). High amounts of polycyclic aromatic hydrocarbons have previously been found in chimney smoke from a residential wood boiler (Kjällstrand and Petersson 2001c). The total PAH concentration has been measured in smoke from pellets of biogenic material (Vierle *et al.* 1999). Many different polycyclic aromatic hydrocarbons have been found in emissions from wood burning (Oros and Simoneit 2001a, 2001b), smoke from hardwood charcoal (Dyremark *et al.* 1995) and the smoke from a Vietnamese cooking stove for sawdust briquettes (Oanh *et al.* 2002). Polycyclic aromatic hydrocarbons were found in grilled meat and many other foods (Kazerouni *et al.* 2001, Chen *et al.* 1997, Larsson *et al.* 1983, Rivera *et al.* 1996).

The relative proportion of benzene, naphthalene and more hazardous polycyclic aromatic hydrocarbons increases with increasing combustion temperature (Alén *et al.* 1996, Kjällstrand and Petersson 2001c, Hauk *et al.* 1994, McGrath *et al.* 2001)

The emissions of the carcinogenic benzene and PAHs may seem alarming. It is, however, important to realise that the chimney concentrations of these compounds were very low and that they are emitted at high chimney levels, resulting in low human exposure. The benzene concentrations in rooms with tobacco smokers and inside cars in urban traffic are even higher (Barrefors and Petersson 1993).

The main nitrogen-containing aromatic 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 checked by sampling pure benzonitrile vapour.

5.4 METHOXYPHENOLS

Wood consists of about 30 percent lignin, from which the methoxyphenols in the smoke originate (Kjällstrand 2000, Oros and Simoneit 2001a). Due to differences in the lignin structure of the wood, the methoxyphenols with guaiacyl structure (Gu, 4-hydroxy-3-methoxyphenyl, Figure 5.2) are primary compounds in smoke from both softwood and hardwood, whereas those with syringyl structure (Sy, 4-hydroxy-3,5-dimethoxyphenyl, Figure 5.2) are present only in hardwood smoke (Kjällstrand *et al.* 2000).

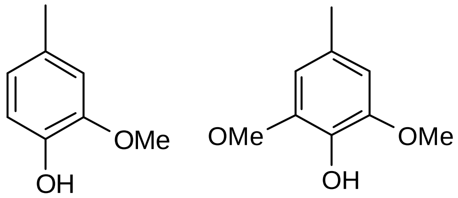

Figure 5.2: Guaiacyl structure (Gu) and syringyl structure (Sy)

Methoxyphenols are one of the most prominent groups of semi-volatile compounds in wood smoke. During pyrolysis of lignin at temperatures of about 400°C, primary combustion products such as methoxyphenols predominate (Alén *et al.* 1996). At 600°C they start decomposing to for example phenol. Phenol is also formed from wood components other than lignin (Faix *et al.* 1990). Phenol has been found in the smoke from flaming burning of wood pellets (**I**), a pellet burner (**II**), a tiled firewood stove and a residential wood boiler (Kjällstrand and Petersson 2001c). At even higher temperatures, 800-1 000°C, polycyclic aromatic hydrocarbons are formed.

The most prominent methoxyphenols in smoke from incomplete burning of flaming softwood pellets (Figure 5.3) are guaiacol, methylguaiacol, ethylguaiacol, ethenylguaiacol, *trans*-propenylguaiacol and vanillin (**I**, Kjällstrand 2000).

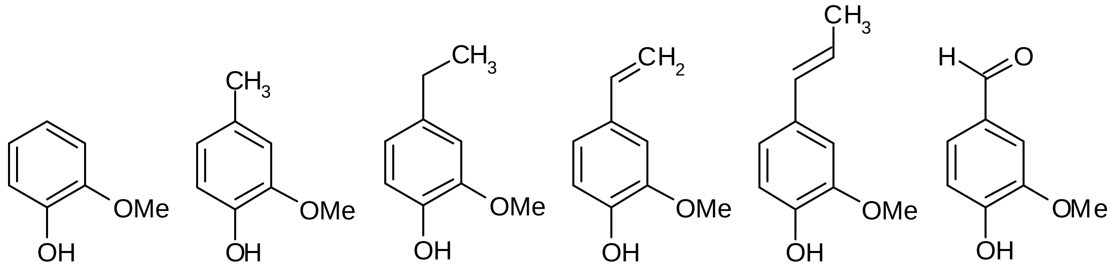

Figure 5.3: Guaiacol, methylguaiacol, ethylguaiacol, ethenylguaiacol, propenylguaiacol and vanillin

Guaiacyl compounds were found in high concentrations in the smoke from incomplete flaming burning of pellets (**I**), from the smoke from two pellet stoves (**II**) and in the smoke from a pellet boiler (**V**). They have previously been studied in wood smoke from spruce, pine and other forest plant materials (Kjällstrand *et al.* 2000). Syringyl compounds are prominent in laboratory, as well as chimney emissions, from incomplete burning of hardwood (Kjällstrand and Petersson 2001b, Kjällstrand *et al.* 1998, Kjällstrand and Petersson 2001c). Furthermore, methoxyphenols have been studied in emissions from fireplace combustion of a number of different tree species (Fine *et al.* 2001, 2002, Nolte *et al.* 2001, Schauer *et al.* 2001, Rodrigues *et al.* 1999, Hawthorne *et al.* 1989, Oros and Simoneit 2001a, 2001b) and pyrolysed rye grass (González-Vila *et al.* 2001). 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 (Reeves and Francis 1997) and wheat straw (Rodríguez *et al.* 1997).

The methoxyphenols have antioxidative qualities (Kjällstrand and Petersson 2001b, Ogata *et al.* 1997, Barclay *et al.* 1997), which means that they are able to protect the cells in the body against attacks from free radicals. The explanation is that the phenoxy radical is stabilised through resonance.

High amounts of methoxyphenols have been found in alder smoke from meat curing where it both preserve and add flavour to the food (Kjällstrand and Petersson 2001a). The 2,6-dimethoxyphenols from hardwood smoke are stronger antioxidants than 2-methoxyphenols from softwood smoke (Kjällstrand and Petersson 2001b). The presence of methoxyphenols with antioxidant properties may render smoke from firewood and wood pellets less hazardous (Kjällstrand and Petersson 2001b). Methoxyphenols have been found in urine after exposure to wood smoke (Dills *et al.* 2001).

5.5 1,6-ANHYDROGLUCOSE

1,6-Anhydroglucose (Figure 5.4) originates from the cellulose and hemi-cellulose of the wood (Simoneit *et al.* 1999, Kleen and Gellerstedt 1991, Kjällstrand 2002, Faix *et al.* 1991). This compound was found in large proportions in the smoke from flaming burning of wood pellets, a pellet stove and a pellet boiler (**I**, **II**).

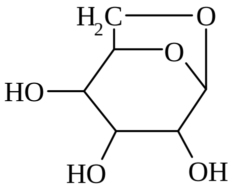

Figure 5.4: 1,6-Anhydroglucose

1,6-Anhydroglucose has previously been studied in smoke from choked flaming birchwood (Kjällstrand and Petersson 2001b), a tiled firewood stove and a residential wood boiler (Kjällstrand and Petersson 2001c). It has been suggested as a molecular tracer for wood combustion (Fine *et al.* 2001, 2002, Nolte *et al.* 2001, Schauer *et al.* 2001, Simoneit *et al.* 1999, Simoneit and Elias 2001, Simoneit 2002).

6. ECOLOGICAL ASPECTS

The ecological and ecotoxicological aspects are immensely important when discussing the potential role of pellets in a sustainable biofuel system. The general conclusion of this discussion is that wood pellets should be reserved for residential heating whereas other, more contaminated, biomass wastes must be burnt in large-scale combustion plants with flue-gas purification (**II**, **V**). These conclusions are illustrated in Figure 6.1.

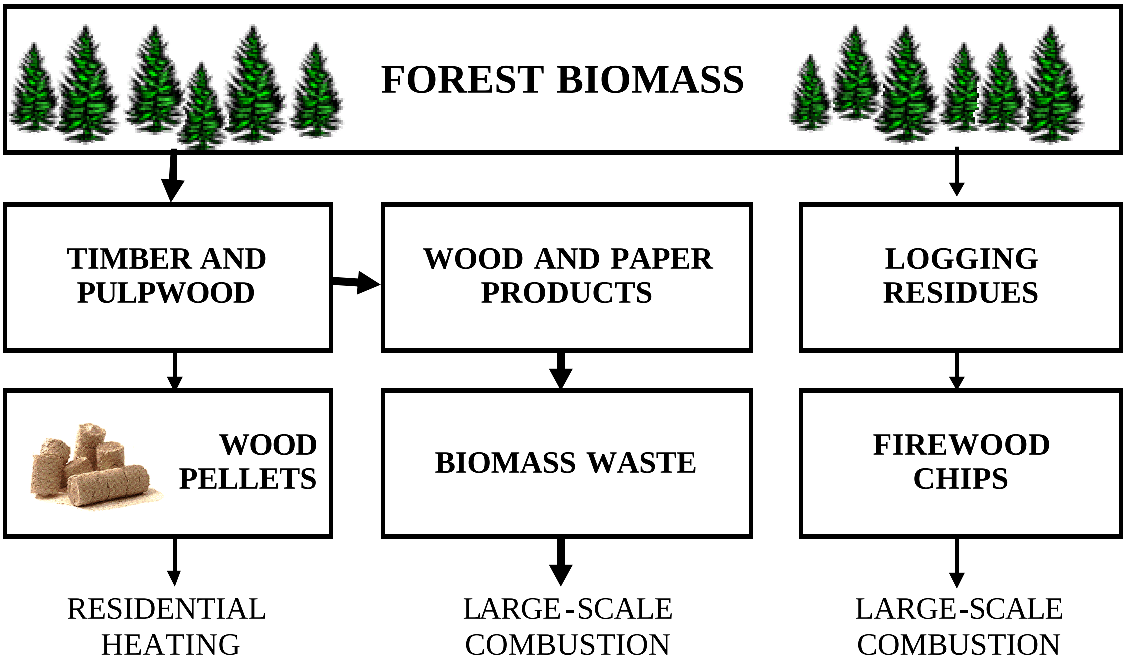

Figure 6.1: Sustainable use of biofuels from different biomass sources with respect to biomass resources and environmental pollution

In order to discuss pellets in an ecologically and environmentally correct way they should be compared with logging residues and biomass waste.

6.1 LOGGING RESIDUES

Logging residues comprise twigs and foliage that can be collected as biofuels when timber for wood and pulp is taken out from the forest. This gives rise to ecological problems in the forest and may lead to increased emissions during the later biomass combustion. In the forest, the outtake of logging residues leads to a loss of nutrients and an increased acidification. Logging residues contain most of the mineral nutrients of the trees, such as calcium, potassium, nitrogen and phosphor (Olsson *et al.* 1996b). The nutrients are removed from the forest with the logging residues and the forest becomes less fertile and, in long-term, less productive (Kimmins 1977). The logging residues may also have a long-lasting positive effect on nitrogen mineralisation in the soil (Olsson *et al.* 1996a). On the other hand, removal of felling residues has been found to reduce the leaching of nitrogen in the cleared area and to counteract nitrogen accumulation in the forest ecosystem (Lundborg 1997).

The soil becomes more acid as the trees are taking up nutrient ions from the surrounding soil during the growth (Olsson *et al.* 1996b). Most of these ions are cations. Thus, the trees must return H^+ ions to the soil to keep the neutral ion balance. This process leads to an increased acidification of the soil. When a tree dies and is mineralised, the nutrition cations are returned to the soil, which once again becomes less acid. According to Lundborg, 1997, the most critical environmental aspect of whole-tree harvesting is that it leads to an unsustainable base cation balance.

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 dsturbances in the forest can possibly be solved by returning the ashes to the forest ecosystem. The ash must not be contaminated and must be returned in a suitable way. Spread, slowly-dissolving, stabilised ashes can compensate for the removal of forest fuels with no observed undesirable environmental effects (Lundborg 1998). The returning of the ash to its forests of origin is not an option with small-scale combustion.

6.2 BIOMASS WASTE

Waste consisting of wood, paper and other biomass is a potentially useful biofuel. Even if the material is recycled a few times, it finally ends up as waste. A total amount of almost 10 million tonnes of waste is produced in Sweden yearly (**IV**) and European trade with biomass waste is increasing (Hillring and Vinterbäck 1999). Some of the waste has previously been deposited on dumps, but new waste regulations and higher deposition taxes will decrease this amount. If the amount of biomass waste burnt will increase, the amount of forest biofuel used can be decreased and thus also the impact on the natural 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.

6.3 WOOD PELLETS

Fuel pellets are made from wood shavings and sawdust. These raw materials are by-products of sawmills and the timber industry and are therefore regarded as waste. An important difference when comparing this sort of waste to other biomass waste is the high purity. Wood pellets are clean and homogeneous, with a low mineral nutrient and moisture content, and are thus a suitable fuel for combustion in small heating devices (Vierle *et al.* 1999, Lehtikangas 2001).

6.4 FUTURE RAW MATERIALS FOR PELLETS

The increased demand for wood pellets, both for residential and large-scale use, may lead to a future shortage of sawdust and shavings. If the price and demand continues to rise, other sources of biomass waste might be considered for pellets. Examples of such future raw materials are; logging residues, energy crops, farming residues, sewage sludge and the organic fraction of the household waste. For example, studies have been carried out on pellets produced from bark, logging residues (Lehtikangas 2001), reed canary grass

(Hadders and Olsson 1997, Paulrud *et al.* 2001), lignite (Heschel *et al.* 1999), wheat straw, hay (Vierle *et al.* 1999), palm fibre and palm nut shell (Husain *et al.* 2002).

These new 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 larger tendency towards sintering and a lower energy content, but they are also more contaminated by pollutants and mineral nutrients. This will give rise to uncontrolled emissions of environmental and health hazardous compounds and may give pellets a bad reputation. It is therefore of great importance to study the emissions of different organic compounds from new pellet fuels before they are burnt in residences.

For example, the nitrogen content of the fuel directly influences the formation of nitrogen oxides (Leckner and Karlsson 1993, Obernberger 1998). Chlorine in the fuel is partly emitted to air and forms HCl and dioxins. Dioxins are formed in reactions on the surface of fly ash particles at temperatures of between 250 and 500°C in the presence of C, Cl and O (Orenberger 1998). Dioxins have also been found to be formed from coal pyrolysed in the presence of hydrogen chloride (Crummet 1982), and higher amounts of dioxins have been found in smoke from household waste and wood from demolished buildings than from natural wood (Schatowitz *et al.* 1994).

7. CONCLUSIONS

- Wood pellets are produced from sawdust and shavings of pine and spruce at more than 20 production sites all over Sweden (**IV**). The Swedish production capacity is about one and a half million tonnes annually.
- Wood pellets are increasingly replacing petroleum oil and firewood for residential heating in Sweden (**IV**). Today more than 145 000 tonnes are used annually in small-scale pellet burners, stoves and boilers.
- Flaming incomplete laboratory burning of wood pellets emitted large amounts of phenolic antioxidants, whereas glowing burning emitted the carcinogenic benzene and polycyclic aromatic hydrocarbons in low concentrations (**I**).
- The burning of softwood pellets in residential pellet stoves gave rise to emissions of 2-methoxyphenol antioxidants together with aromatic hydrocarbons (**II**).
- The burning of wood pellets in residential pellet burners was more complete than the combustion in a pellet stove, but emitted benzene and other aromatic hydrocarbons in small amounts (**II**).
- The observed large differences between emissions from different residential burning appliances for wood pellets make it important to choose one of the best available equipments and to install it correctly.
- Glowing pellet ember and charcoal emit benzene as the predominant aromatic compound, whereas methane, ethene and ethyne were prominent non-aromatic volatile hydrocarbons (**III**). Birchwood ember emissions were typically one order of magnitude higher than those from glowing charcoal and from glowing pellet embers.
- Pellets made of pure wood shavings and sawdust should be reserved for the residential market in order to avoid unnecessary emissions, ash formation and ecological impact on the forest ecosystems (**II**).
- The emissions of organic compounds and other combustion characteristics of new raw materials for pellets must be thoroughly studied before they are introduced to the residential fuel market.

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