

STRAW	TWIGS
PAPER	HARDWOOD
COMBUSTION	ANALYSIS
BENZENE	BUTADIENE
ETHENE	PENTENES

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Assessment by GC and GC-MS of volatile hydrocarbons from biomass burning

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Assessment by GC and GC-MS of volatile hydrocarbons from biomass burning

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Abstract

Well over thirty combustion-formed non-methane hydrocarbons were determined from uncontrolled burning of biogenic materials. Results are given for straw, conifer twigs, newsprint and hardwood. Samples were taken on triple-layer adsorption cartridges. After thermal desorption, the hydrocarbons were separated by gas chromatography on an aluminium oxide column. Samples were also taken with a gas syringe and analyzed after gas injection.

The hydrocarbon proportions were found to be remarkably similar for different kinds of biomass. Among 21 recorded alkenes and alkadienes, ethene was predominant, and the next most prominent species were propene and 1,3-butadiene. The large proportions of ethyne and the carcinogenic benzene increased further with increasing combustion efficiency.

1. Introduction

Natural and controlled forest and grassland fires give rise to vast hydrocarbon emissions of great concern with respect to photooxidant formation [1]. Burning of biomass like wood is used by man all over the world for heating and cooking purposes and causes large emissions [2]. It also causes high human exposure to volatile hydrocarbons, including alkenes and the carcinogenic species benzene and 1,3-butadiene which are genotoxic after metabolic biotransformation [3]. The urgent use of renewable raw materials may increase the amount of paper and other technical biomass products which are eventually burnt. These facts emphasize the need for analytical methods which permit the determination of specific organic compounds emitted from incomplete combustion of biomass.

This report on non-methane hydrocarbons from biomass burning makes use of analytical methods previously applied to hydrocarbons in urban air [4]. The approach is thought to be of particular value when it comes to comparisons of air pollutants from biomass burning, traffic and other sources of hydrocarbon emissions.

2. Experimental

2.1 Biomass burning

Small-scale burning with low oxygen supply was performed in a ceramic pot (2 l). A larger clay pot with a bottom hole was placed upside-down over the ceramic pot before sampling through the hole. Open burning of twigs from trees was performed on a gridiron and samples were taken nearby in the smoke plume. Samples from a wood-stove were taken in the exit of the chimney of a remote house. The materials and experiments giving the specific results reported are detailed under the tabulated data.

2.2 Sampling

Triple-layer glass cartridges (150 mm x 4 mm i.d.) were made with separate layers of

Carbosieve S-III (rear layer, 0.1-0.3 g, 60-80 mesh, Supelco), Carbotrap (0.1-0.2 g, 20-40 mesh, Supelco), and Tenax TA (front layer, 0.05-0.1 g, 60-80 mesh, Chrompack). The cartridges were conditioned with helium (20-40 ml min⁻¹), initially (285°C, 60 min) and before each sampling (275°C, 10 min).

On sampling, the cartridge was connected by a swagelok fitting to an air pump providing an accurate constant flow, normally set in the range 10-50 ml min⁻¹. Before and after sampling, the cartridges were kept in tight-stoppered glass tubes placed in brown bottles. Total sampling volumes ranged from less than 10 ml for most of the pot-burning studies to more than 1000 ml for slightly polluted ambient air.

Duplicate samples with widely different air volumes were used to check recovery and break-through. Single-layer Tenax cartridges were used to confirm recovery of compounds potentially sensitive to decomposition on the triple-layer cartridges.

Samples were also taken by a gas-tight syringe (50 ml) without enrichment on adsorption cartridges. This method was applied preferentially for the pot-burning experiments designed to give high hydrocarbon concentrations. It was also used to determine methane.

2.3 Gas chromatography

In the laboratory, the cartridges were placed in a desorption oven and connected to the carrier gas line of a gas chromatograph for desorption (235°C, 20-40 ml He min⁻¹, 14 min) into a cold trap (5 m x 0.32 mm i.d. empty FSOT column in liquid N₂). The helium gas was vented to air during desorption. Before the trap was heated (150°C, polyglycol), the vent was closed, and the carrier gas was passed through the analytical column only (30 cm s⁻¹). An optional drying cartridge placed before the cold trap was filled with magnesium perchlorate (0.2-0.4 g).

Injection of gaseous samples was performed by filling gas from the sampling syringe into an empty column (3.2 ml) which was then connected into the carrier gas line by gas valves. Methane passes the cold trap and is lost with the vented carrier gas. Optional determination of methane was achieved by gas injection without trap cooling and heating and without carrier gas venting.

The chromatographic separations were performed on an aluminium oxide column (50 m x 0.32 mm i.d. fused silica, PLOT, Al₂O₃/ 5% KCl, Chrompack). The oven temperature program for the reported detailed separations was 30-110°C (10°C min⁻¹), 110°C (isothermal, 14 min), 110-200°C (4°C min⁻¹), and 200°C (isothermal). The response of the FID detector was set equal for all hydrocarbons. Furans were excluded when the percent composition of non-methane hydrocarbons was calculated.

2.4 Assessments by GC-MS

Mass spectrometric studies were made on a Varian Saturn II ion trap GC-MS instrument. Identifications relied on relative retentions, interpretations of spectra, and comparisons with the NIST library of mass spectra. The reported GC-MS separations were made using a methylsilicone column (50 m x 0.32 mm i.d. FSOT, 1 µm DB-1, J&W). The linear temperature increase was 3°C min⁻¹ from -30°C. The linear helium flow was 20 cm s⁻¹. Injection of combustion gas samples was made by a gas-tight syringe (1 ml). The data acquisition speed was one mass spectrum (*m/z* 35-200) per second.

3. Results

Representative hydrocarbon proportions are given in Table 1 for biomass varieties of particular interest with respect to hydrocarbon emissions from burning. The hydrocarbons are arranged according to structural class, number of carbon atoms, and retention order on the aluminium oxide column. The inefficient flaming and smouldering combustion of straw is similar to that of grassland fires and open burning of agricultural and garden waste. The open burning of twigs from spruce resembles conifer forest fires. Newsprint is likely to be the major type of paper waste used for igniting fires, thereby ending up in uncontrolled burning. Hardwood such as birchwood is commonly used as the major fuel for heating purposes in stoves and fireplaces.

It is evident from Table 1 that the hydrocarbon proportions are remarkably similar for different kinds of biomass even though the combustion conditions are quite different.

Table 1.

Proportions (% weight) of C₂-C₈ hydrocarbons from biomass burning^a

	Straw Barley Pot-burning	Twigs Spruce Gridiron	Paper Newsprint Pot-burning	Wood Birch Stove
Alkenes				
C2 Ethene	31.0	36.2	41.4	40.2
C3 Propene	9.9	8.6	9.3	4.3
C4 <i>trans</i> -2-Butene	0.84	0.33	0.30	0.17
1-Butene	3.0	2.6	1.57	0.82
Methylpropene	1.22	0.80	0.59	0.30
<i>cis</i> -2-Butene	0.61	0.26	0.21	0.12
C5 Cyclopentene	0.3	0.31	0.1	0.1
3-Methyl-1-butene	0.3	0.27	0.1	0.1
<i>trans</i> -2-Pentene	0.46	0.30	0.15	0.10
2-Methyl-2-butene	0.31	0.20	0.07	0.04
1-Pentene	0.82	0.73	0.31	0.21
2-Methyl-1-butene	0.43	0.23	0.14	0.07
<i>cis</i> -2-Pentene	0.31	0.21	0.11	0.06
C6 1-Hexene	1.18	1.41	0.31	0.20
C7 1-Heptene	0.55	0.54	0.16	0.11
C8 1-Octene	0.30	0.27	0.08	0.12
Alkadienes				
C3 Propadiene	0.4	0.5	0.4	0.3
C4 1,3-Butadiene	3.8	4.3	2.6	1.6
C5 Isoprene	0.6	1.5	0.9	0.1
Cyclopentadiene	1.4	1.5	0.37	0.25
<i>trans</i> -1,3-Pentadiene	0.75	0.45	0.24	0.08
Alkynes				
C2 Ethyne	7.3	9.2	16.4	22.7
C3 Propyne	2.1	1.4	2.3	1.4
C4 2-Butyne	0.22	0.08	0.11	0.08
Butenyne	0.59	0.63	0.82	0.73
1-Butyne	0.27	0.16	0.22	0.15
Alkanes				
C2 Ethane	10.4	5.5	5.6	5.8
C3 Propane	2.3	1.0	1.1	0.8
C4 Butane	0.8	0.3	0.24	0.22
C5 Methylbutane	0.09	0.03	0.03	0.05
Pentane	0.18	0.2	0.22	0.10
C6 Hexane	0.10	0.2	0.09	0.05
Arenes				
C6 Benzene	7.9	9.6	8.4	13.6
C7 Methylbenzene	4.0	3.6	2.0	2.2
C8 Ethylbenzene	0.4	0.77	0.35	0.4
Dimethylbenzenes	0.9	1.2	0.27	0.6
Styrene	0.5	1.3	1.2	0.8

^a The total concentrations of C₂-C₈ hydrocarbons were 72, 18, 270, and 42 mg m⁻³ for the tabulated samples. The newsprint sample was taken with a gas syringe and the other samples on triple-layer adsorption cartridges. The materials burnt were last year's barley straw, fresh twigs of Norway spruce, an evening newspaper printed on paper made from spruce-based thermomechanical pulp, and moderately dried birchwood with bark. The pot samples were taken after enclosing the fire, the grill sample in the open air in the smoke plume, and the stove sample in the chimney exit during flaming fire in the stove.

Alkenes make up about half of the amount of non-methane hydrocarbons with ethene as the predominant species followed by propene and 1-butene. The major alkadiene is 1,3-butadiene. As with the alkenes, the lowest analogues are the most prominent for alkynes (ethyne and propyne), alkanes (ethane and propane) and arenes (benzene and methylbenzene). Butenyne and styrene are significant products which may also be classified as alkenes.

4. Discussion

4.1 Chromatographic separations

The chromatogram in Fig. 1 illustrates the separation of C_2 - C_8 hydrocarbons emitted from biomass burning. Contrary to non-polar columns, the aluminium oxide column clearly separates hydrocarbons with the same number of carbon atoms in the order alkanes < alkenes < alkadienes < alkynes. Isomeric alkenes are favourably separated in a retention order which markedly differs from that on the conventional methylsilicone columns [5]. Complete determinations of all volatile hydrocarbons are facilitated by the fact that compounds other than hydrocarbons are not eluted from the Al_2O_3 column. An exception is the furans with their stable aromatic structure.

The strong retention on the Al_2O_3 column permits the separation of the volatile C_2 hydrocarbons without using sub-ambient column temperatures. On the other hand, the alkylbenzenes elute late even at the maximum recommended temperature (200°C) of the column. The temperature program was chosen to ascertain a clear-cut separation of the carcinogenic 1,3-butadiene from pentane. For routine determinations of the major combustion-formed hydrocarbons, the time required can be much decreased by using a rapid linear temperature program and by leaving out the minor late-eluting alkylbenzenes. The resulting higher elution temperature then makes easily polarized hydrocarbons like alkynes and alkadienes appear earlier relative to alkanes.

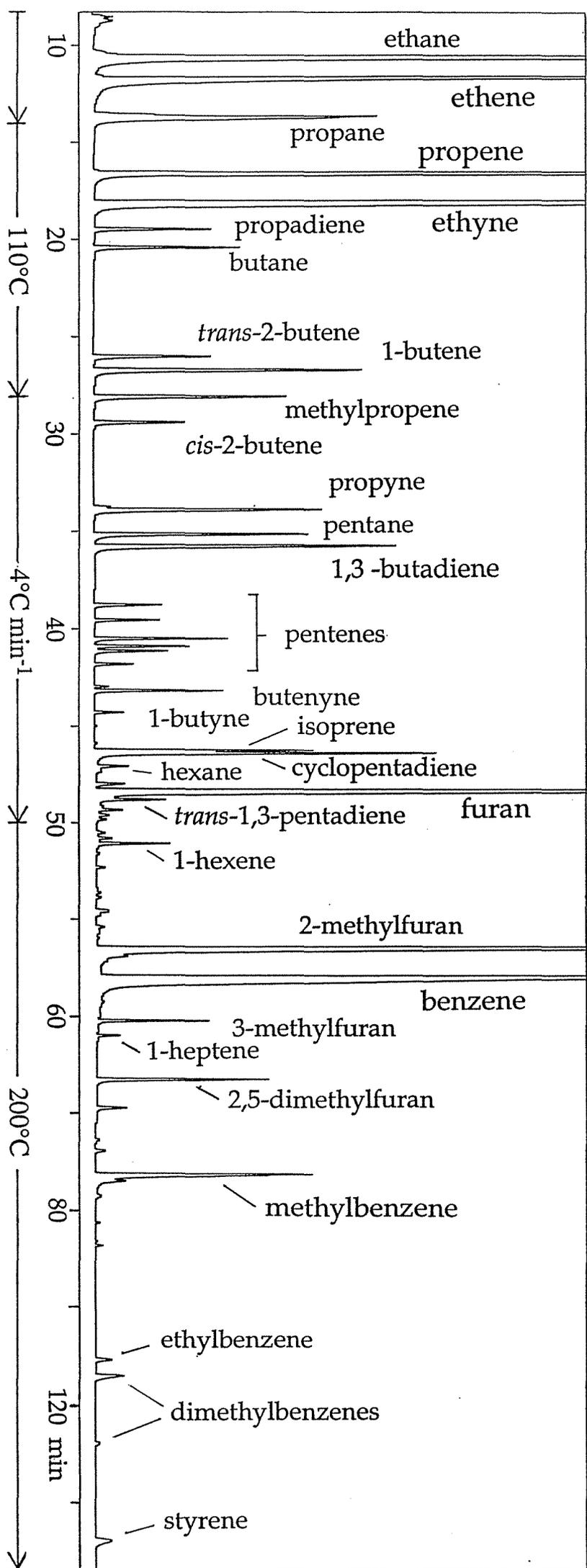


Fig. 1 Gas chromatographic separation of non-methane hydrocarbons from the burning of birchwood (aluminium oxide column, 3.2 ml gas sample, paper speed decreased after 60 and 80 min).

4.2 Sampling and recovery

An analytical difficulty is the presence of acidic and other reactive combustion products which may cause chemical decomposition of sensitive hydrocarbons on the adsorption cartridges. As illustrated by Fig. 1, samples taken by a gas syringe can be favourably analyzed by gas sample injection if the concentrations of the combustion-formed hydrocarbons are high. Comparisons with the results for pot-burning samples, taken on the triple-layer adsorption cartridges, did not indicate significant losses for any of the hydrocarbons emitted from inefficient biomass burning.

Aggressive combustion products may give rise to extensive losses of reactive alkenes on the triple-layer adsorption cartridges, as demonstrated for diesel exhaust [6]. Potential losses for samples from biomass burning should therefore be checked, especially for high-volume samples from stoves and other efficient combustion devices. A proper peak for the particularly reactive 2-methyl-2-butene was found to indicate complete recovery of the other tabulated alkenes. Isoprene was found to be more easily lost than 1,3-butadiene among the alkadienes. Complementary low-volume samples on single-layer Tenax cartridges were useful for checking complete recovery, although exceptionally reactive hydrocarbons like monoterpenes may still be lost [7].

Ethyne is the non-methane hydrocarbon most easily lost by break-through on the triple-layer cartridges. When necessary, low-volume samples were used to ensure correct proportions of ethyne and the other C₂ hydrocarbons.

4.3 Assessments by GC-MS

Identifications and complementary separations on a methylsilicone column were made using the capabilities of an ion trap GC-MS instrument. Relative retentions on methylsilicone and aluminium oxide columns are available for a wide range of C₄-C₇ alkenes [5]. Comparisons were also made with the hydrocarbons identified in vehicle-polluted air and tobacco smoke [4].

The mass fragmentograms in Fig. 2 for the complex mixture of unsaturated C₅ hydrocarbons were chosen to illustrate the use of GC-MS for combustion-formed compounds from biomass. The upper chromatogram in Fig. 2 illustrates the presence in the

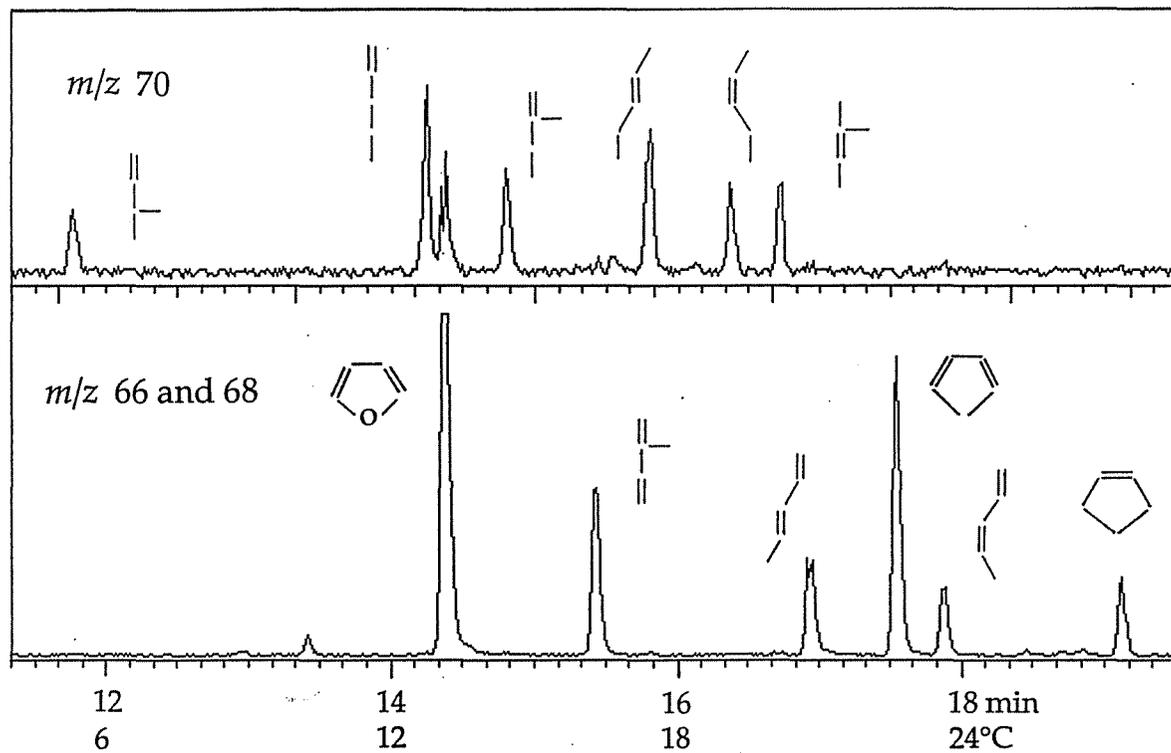


Fig. 2 Single-ion monitoring by GC-MS of C_5 alkenes and alkadienes from the burning of biomass (barley straw, methylsilicone column).

combustion gases of the six isomeric acyclic pentenes, by single-ion monitoring of the m/z 70 molecular ion. The lower chromatogram records furan, isoprene, the two 1,3-pentadienes, and cyclopentene, which all give rise to a prominent m/z 68 molecular ion. Cyclopentadiene is recorded from its abundant m/z 66 molecular ion. The separation on the methylsilicone column complements that of the Al_2O_3 column from which 3-methyl-1-butene and cyclopentene as well as furan and *cis*-1,3-pentadiene were eluted as unresolved compound pairs. Furthermore, isoprene and cyclopentadiene were incompletely resolved for rapid temperature programs.

The six isomeric pentenes are also significant components in petrol [5] and vehicle-polluted urban air [4], although in different mutual proportions. The pentadienes are more characteristic products of biomass combustion and are more seldom reported in air pollution studies. They are of potential interest with respect to health hazards due to their structural relationship to the carcinogenic 1,3-butadiene. Cyclopentadiene was reproducibly determined in spite of its acidic properties. The proportion of *trans*-1,3-pentadiene was normally almost twice that of *cis*-1,3-pentadiene which is not included in Table 1.

4.4 Combustion-formed compounds

The stove sample in Table 1 deviates from the other three samples by more efficient and complete combustion. This results in lowered proportions of alkenes other than ethene and increased proportions of ethyne and benzene. Flame-less oxygen-deficient burning of glowing biomass such as wood and straw tended to give increased proportions not only of C_3 - C_5 alkenes and alkadienes but also of C_2 - C_5 alkanes. The chromatogram in Fig. 1 illustrates that inefficient burning of birchwood gives rise to large proportions of furan and alkylfurans, of which 2-methylfuran is the most prominent. The furans were recorded in varying proportions from all samples studied and are likely to be formed from the biomass content of cellulose, hemicelluloses and other carbohydrates.

The hydrocarbons from biomass burning differ markedly from urban hydrocarbons originating mainly from petrol-fuelled vehicles [4]. A prominent portion of the pollutants in urban air consists of exhaust-emitted unburnt C_4 - C_8 petrol hydrocarbons with large proportions of alkanes and alkylbenzenes. On the other hand, the major combustion-

formed hydrocarbons ethene, propene and ethyne are the same from biomass and petrol. For less prominent combustion-formed products, certain differences pertaining to fuel structures are observed.

The unbranched 1-alkenes are the most prominent alkene isomers from biomass burning. This is probably explained by their formation from unbranched biomass components such as lipids. Analogous formation from unbranched petroleum alkanes [8, 9] explains their presence in diesel exhaust [6]. In vehicle-polluted urban air, branched isomers of C₄-C₆ alkenes are the most prominent [4]. They are emitted from petrol-fuelled vehicles as combustion products from branched petrol alkanes [8, 9] and as unburnt cat-cracked components of the fuel [5].

The carcinogenic 1,3-butadiene was a prominent component from all biomass samples, although its formation from cyclohexanes has been shown to be favoured [10]. The proportion of isoprene is very high in tobacco smoke [4] and probably linked to a high content of terpenoid components in tobacco. High proportions of biomass lignin with its aromatic nuclei are likely to contribute to an increased formation of benzene, in a similar way as high levels of alkylbenzenes in petroleum fuels [10]. The formation of styrene from biomass appears to be linked to the characteristic phenylpropane units of lignin.

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