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GC Analysis of Volatiles and Other Products from Biomass Torrefaction Process

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1. Introduction

Gas chromatography (GC) is a common method used to analyze gases produced during various chemical processes. Torrefaction, for example, is a method for pretreating biomass to make it more suitable for bioenergy applications that uses GC to characterize products formed during the process. During torrefaction, biomass is heated in an inert environment to temperatures ranging between 200–300°C. Torrefaction causes biomass to lose low-energy condensables (liquids) and non-condensable volatiles, initially in gas form, thereby making biomass more energy dense.

The condensable volatiles are divided into three subgroups: reaction water, organics, and lipids. The first subgroup is reaction water, which contains free and bound water released from the biomass by evaporation. The second subgroup consists of organics (in liquid form) that are mainly produced during devolatilization, depolymerization and carbonization reactions in the biomass. The final subgroup, lipids, consists of compounds that are present in the original biomass, such as waxes, fatty acids, and non-condensable gases—mainly CO_2, CO, and small amounts of methane. Knowing the composition of volatiles produced in the torrefaction temperature range can shed light on the raw material adaption process, process control, process behavior and operation, energy process and energy optimization, and green chemical production.

In general, GC with mass spectroscopy is used for both condensable and non-condensable gases. GC configuration plays an important role in accurately identifying the compounds in these gases. A combination of different detectors—like thermal, flame, and photo ionization detectors—combined with mass spectrometers are used for profiling both condensable and non-condensable gases.

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2. Gas Chromatography

Chromatography is an important analytical tool that allows for the separation of components in a gas mixture. GC is a common type of chromatography used to separate and analyze compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance or separating the different components and relative amounts of different components of a mixture. GC can also be used to prepare pure compounds from a mixture (Pavia et al., 2006). In GC, the mobile phase (or "moving phase") is a carrier gas, usually an inert gas such as helium or an unreactive gas such as nitrogen. The stationary phase is a microscopic layer of liquid or polymer on an inert solid substrate inside a glass or metal tube called a column. The gases are analyzed as they interact with the column walls, which have been coated with different stationary phases. This coating results in the compounds eluting at different times, called the retention time for each compound. These compounds are then further analyzed by comparison with calibrated standard gases (Pavia et al., 2006).

The working principle of GC is similar to that of fractional distillation, as both processes use temperature to separate the components. The only difference is that distillation is used in large-scale applications, where GC is only used in smaller-scale applications (Pavia et al., 2006). Because of its mechanisms for analysis, GC is also sometimes known as vapor-phase chromatography (VPC), or gas–liquid partition chromatography (GLPC) (Pavia et al., 2006).

3. GC components

Figure 1 shows the typical components of GC system: the sample injector, column, detector, and carrier gases.

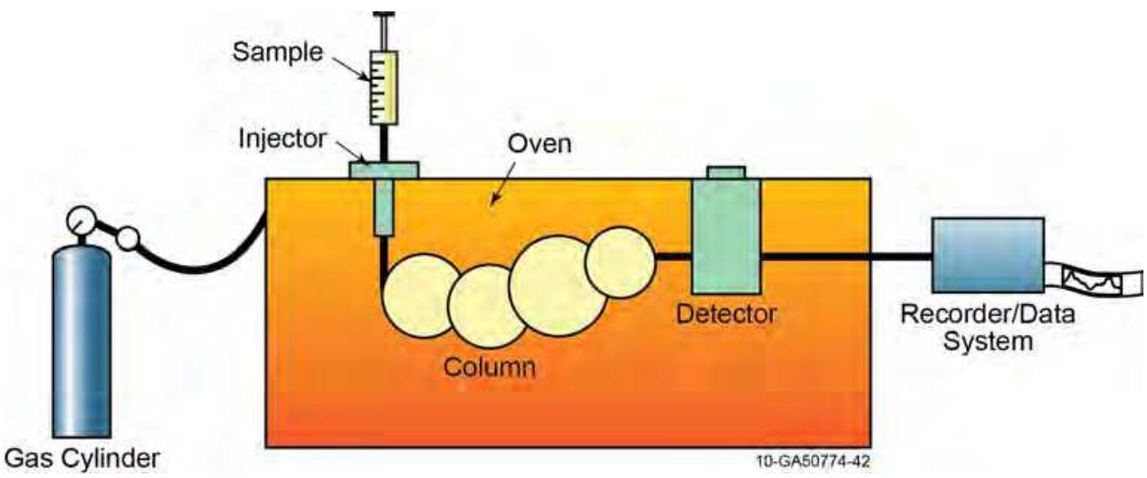

Fig. 1. Schematic view of gas chromatography (Punrattanasin and Spada, 2011)

3.1 Types of samplers

Manual insertion of a sample in a GC system for analysis is possible, but is no longer preferred for reasons of accuracy. In fact, manual injection is avoided where there is a need for high accuracy and precise results. A better option is an auto-sampler that injects samples automatically into the inlets of the GC system. Automatic injection helps achieve consistency and reproducibility and reduces analysis time (Pavia et al., 2006). The several types of automatic samplers are:

- Liquid injection
- Static head-space by syringe technology
- Dynamic head-space by transfer-line technology
- Solid phase microextraction (SPME).

3.2 Types of inlets

An inlet is hardware attached to the column head that introduces the samples into the continuous flow carrier gas. Common types of inlets are split/splitless (S/SL), on-column, programmed temperature vaporization (PTV) injectors, gas switching valve, and purge and trap systems.

An S/SL injector introduces a sample into a heated chamber via a syringe through a septum, and the heat helps volatilization of the sample and sample matrix. In split mode, the sample/carrier gas is exhausted into the chamber through the split vent, and this is preferred when the sample has high analyte concentrations (>0.1%). In the case of the splitless mode, the valve opens after a pre-set time to purge heavier elements in order to prevent the contamination of the system. An on-column inlet is a simple component through which the sample is introduced directly into the column without heat. A PTV injector introduces a sample into the liner at a controlled injection rate. The temperature of the liner is usually slightly below the boiling point of the solvent so that the solvent is continuously evaporated and vented through the split line. PTV injectors are particularly suited to in-liner derivatisation due to the flexibility of control over parameters such as injection volume (Bosboom et al., 1996), carrier gas flow and liner temperature (Poy et al., 1981). A gas-source inlet (or gas-switching valve) injects gaseous samples into the collection bottles through a six-port switching valve. Upon switching, the contents of the sample loop are inserted into the carrier gas stream. Finally, the purge-and-trap system purges insoluble volatile chemicals from the matrix by bubbling inert gas through an aqueous sample. The volatiles are 'trapped' on an adsorbent column (also known as a trap or concentrator) at ambient temperature. The trap is then heated, and the volatiles are directed into the carrier gas stream (Pavia et al., 2006; Kaufmann, 1997).

3.3 Types of detectors

A number of detectors may be selected in gas chromatography, based on the sample to be separated. The most common are the flame ionization detector (FID) and the thermal conductivity detector (TCD). These detectors are sensitive to a wide range of components and work for wide-ranging concentrations. TCDs are essentially universal and can be used to detect any component other than the carrier gas so long as the thermal conductivities are

different from those of the carrier gas at a specific detector temperature. TCD has a detection limit of ~100 ppm (Goorts, 2008).

FIDs are more sensitive than TCDs and have a detection limit of ~1 ppm (Goorts, 2008), but their major limitation is the number of molecules they can successfully detect. FIDs can only detect combustible carbon atoms; therefore, FIDs are primarily used for detecting organic molecules. FIDs cannot detect H_2O or CO_2, so they are undesirable for some applications (Goorts, 2008). As TCD analysis is non-destructive, it can be operated in-series before an FID, which is destructive, thus providing complementary detection of the same analyte (Goorts, 2008).

Other detectors used for specific types of substances or narrower concentration ranges are

- Catalytic combustion detector (CCD), which measures combustible hydrocarbons and hydrogen
- Discharge ionization detector (DID), which uses a high-voltage electric discharge to produce ions
- Dry electrolytic conductivity detector (DELCD), which uses an air phase and high temperature (v. Coulsen) to measure chlorinated compounds
- Electron capture detector (ECD), which uses a radioactive Beta particle (electron) source to measure the degree of electron capture
- Flame photometric detector (FPD)
- Hall electrolytic conductivity detector (ElCD)
- Helium ionization detector (HID)
- Nitrogen phosphorus detector (NPD)
- Infrared detector (IRD)
- Mass selective detector (MSD)
- Photo-ionization detector (PID)
- Pulsed discharge ionization detector (PDD)
- Thermal energy (conductivity) analyzer/detector (TEA/TCD)
- Thermionic ionization detector (TID).

The various detectors, support gases, selectivity, detectability and dynamic range are given in Table 1 (SHU, 2011).

Some gas chromatographs are connected to a mass spectrometer (MS), nuclear magnetic resonance (NMR) spectrometer, or infrared (IR) spectrophotometer that acts as the detector. These combinations are known as GC-MS, GC-MS-NMR, and GC-MS-NMR-IR. However, it is very rare to use the NMR and IR along with GC. The most commonly used is GC-MS (Scott, 2003).

4. Carrier gas

The carrier gas plays an important role in GC analysis and can vary depending on the GC used. Carrier gas must be dry, free of oxygen, and chemically inert. Typical carrier gases include helium, nitrogen, argon, hydrogen, and air. The choice of carrier gas (mobile phase) is important, with hydrogen providing the best separation. Helium is most commonly used as a carrier gas because it has larger flow rates, is non-flammable, and can work with many

detectors. The type of carrier gas used depends on the following factors: (a) detector used; (b) sample's composition; (c) safety and availability (i.e., hydrogen is flammable, high-purity helium can be difficult to obtain in some areas of the world); and (d) purity of the carrier gas (where high pure gases of 99.995% are selected when high sensitivities in the measurement are required) (Guiochon and Guillemin, 1988).

Detector	Type	Support Gases	Selectivity	Detectability	Dynamic Range
Flame ionization (FID)	Mass flow	Hydrogen and air	Most organic compounds	100 pg	10^7
Thermal conductivity (TCD)	Concentration	Reference	Universal	1 ng	10^7
Electron capture (ECD)	Concentration	Make-up	Halides, nitrates, nitriles, peroxides, anhydrides, and organic metals	50 fg	10^5
Nitrogen phosphorous	Mass flow	Hydrogen and air	Nitrogen, phosphorous	10 pg	10^6
Flame photometric (FPD)	Mass flow	Hydrogen and air, possibly oxygen	Sulphur, phosphorous, tin, boron, arsenic, germanium, selenium, and chromium	100 pg	10^3
Photo-ionization (PID)	Concentration	Make-up	Alaphatics, aromatics, ketones, esters, aldehydes, amines, hetrocyclics, organosulphurs, some organometallics	2 pg	10^7
Hall electrolytic conductivity	Mass flow	Hydrogen, oxygen	Halides, nitrogen, nitroamine, sulphur		
Note: pg: picogram; ng: nanogram, and fg: femtogram					

Table 1. Various detectors and their detectability

4.1 GC methods for sample analysis

An analysis method comprises conditions in which a GC operates for a specific analysis. Developing the method involves finding the conditions required for the analysis of a

specific sample. The process conditions that can be used to generate the method file are (a) inlet temperature, (b) detector temperature, (c) column temperature, (d) temperature program, (e) carrier gases and their flow rates, (f) the column's stationary phase, (g) column diameter and length, (h) inlet type and flow rates, and (i) sample size and injection technique. These operating conditions depend on the detector selected and the compounds to be analyzed (Grob et al., 2004).

4.2 Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS uses two techniques that are combined into a single method for analyzing mixtures of chemicals. Gas chromatography separates the components of a mixture, and mass spectroscopy characterizes each of the components individually. Combining the two techniques helps to analyze the samples both qualitatively and quantitatively. As the sample is injected into the chromatograph, the sample mixture gets separated into individual components due to different flow rates. This results in quantitative analysis of the components, along with a mass spectrum of each component. Applications of GC-MS include drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples. Strengths of GC/MS analysis are (a) identification of organic components from complex mixtures, (b) quantitative analysis, and (c) determination of traces of organic contamination. A major limitation of GC/MS is that the sample must be volatile or capable of derivatization (Hübschmann, 2008).

5. Volatile analysis during biomass torrefaction

5.1 Biomass as an energy source

Utilization of biomass for energy can help reduce world dependence on fossil fuels, reduce the impact of greenhouse gasses on the environment, and help meet targets established in the Kyoto Protocol (UN, 1998). Biomass usage as a renewable energy resource is increasing as it is considered carbon neutral (carbon dioxide released is already part of the carbon cycle). Commercial limitations of biomass are its low bulk density, high moisture content, hydrophilic nature, and low calorific value (Arias et al., 2008). Due to its low energy content compared to fossil fuels, it may be necessary to use high volumes of biomass. This results in storage, transportation, and feed-handling problems at bioenergy conversion facilities. These drawbacks have led to the development of new technologies to successfully use biomass for fuel applications. One way to overcome these limitations is pretreating the biomass. There are different pre-treatment methods, including thermal, mechanical, and chemical. Torrefaction is a thermal method that significantly improves the physical and chemical properties of biomass. These compositional changes make torrefaction a promising pre-treatment method for thermochemical conversion and combustion applications (Tumuluru et al., 2011).

5.2 Biomass components

Fig. 2 indicates the low-molecular and macromolecular weight substances in biomass (Mohan et al., 2006). The various components of the biomass are significantly influenced by thermal treatments (Tumuluru et al., 2011).

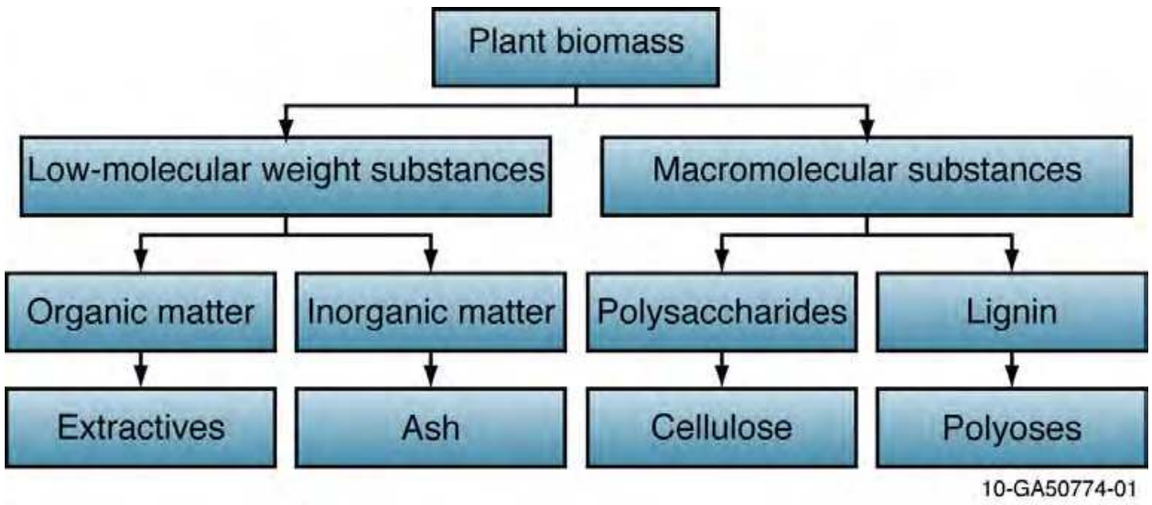

Fig. 2. Plant biomass composition (Mohan et al. 2006)

5.2.1 Cellulose

Cellulose is a high-molecular-weight polymer which provides structural rigidity to the plants. Cellulose degradation begins at 240°C, resulting in anhydrous cellulose and levoglucosan polymer, and makes up the fibers in wood and levoglucosan (Mohan et al., 2006). The crystalline structure resists thermal depolymerization during thermal treatment to a greater degree than is seen in unstructured hemicelluloses.

5.2.2 Hemicellulose

Hemicelluloses are branched polymers which account for about 25–35 wt% in biomass. Thermal degradation of hemicelluloses takes place from 130–260°C, with the majority of weight loss occurring above 180°C (Demibras, 2009; Mohan et al., 2006). Degradation of hemicellulose results in emission of volatiles.

5.2.3 Lignin

Lignin is an amorphous, highly branched, cross-linked macromolecular polyphenolic resin which is covalently linked to hemicellulose and cross-linked with different plant polysaccharides. These linkages give mechanical strength to the cell wall. It is relatively hydrophobic and aromatic in nature. Lignin decomposes when heated above 280°C, producing phenols due to cleavage of ether bonds (Demibras, 2009; Mohan et al., 2006). Lignin converts into char at temperatures >300°C.

5.2.4 Extractables

The other organic extractables present in biomass are fats, waxes, alkaloids, proteins, phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins, and essential oils (Mohan et al., 2006).

6. Torrefaction process

Torrefaction is a process of heating biomass slowly in an inert atmosphere to a maximum temperature of 300°C (Fonseca et al., 1998) and has been defined as the partially controlled and isothermal pyrolysis of biomass occurring in a temperature range of 200–300°C (Bergman and Kiel, 2005). The treatment yields a solid, uniform product with lower moisture and higher energy content compared to raw biomass (Sadaka and Negi, 2009).

The initial heating of biomass during torrefaction removes unbound water. Heating above 160°C removes the bound water due to the thermo-condensation process (Zanzi et al., 2002). Increasing the temperatures to 180–270°C initiates the decomposition of hemicellulose. At temperatures >280°C, the process is completely exothermic and results in significant increase in the production of CO_2, phenols, acetic acid, and other higher hydrocarbons (Zanzi et al., 2002).

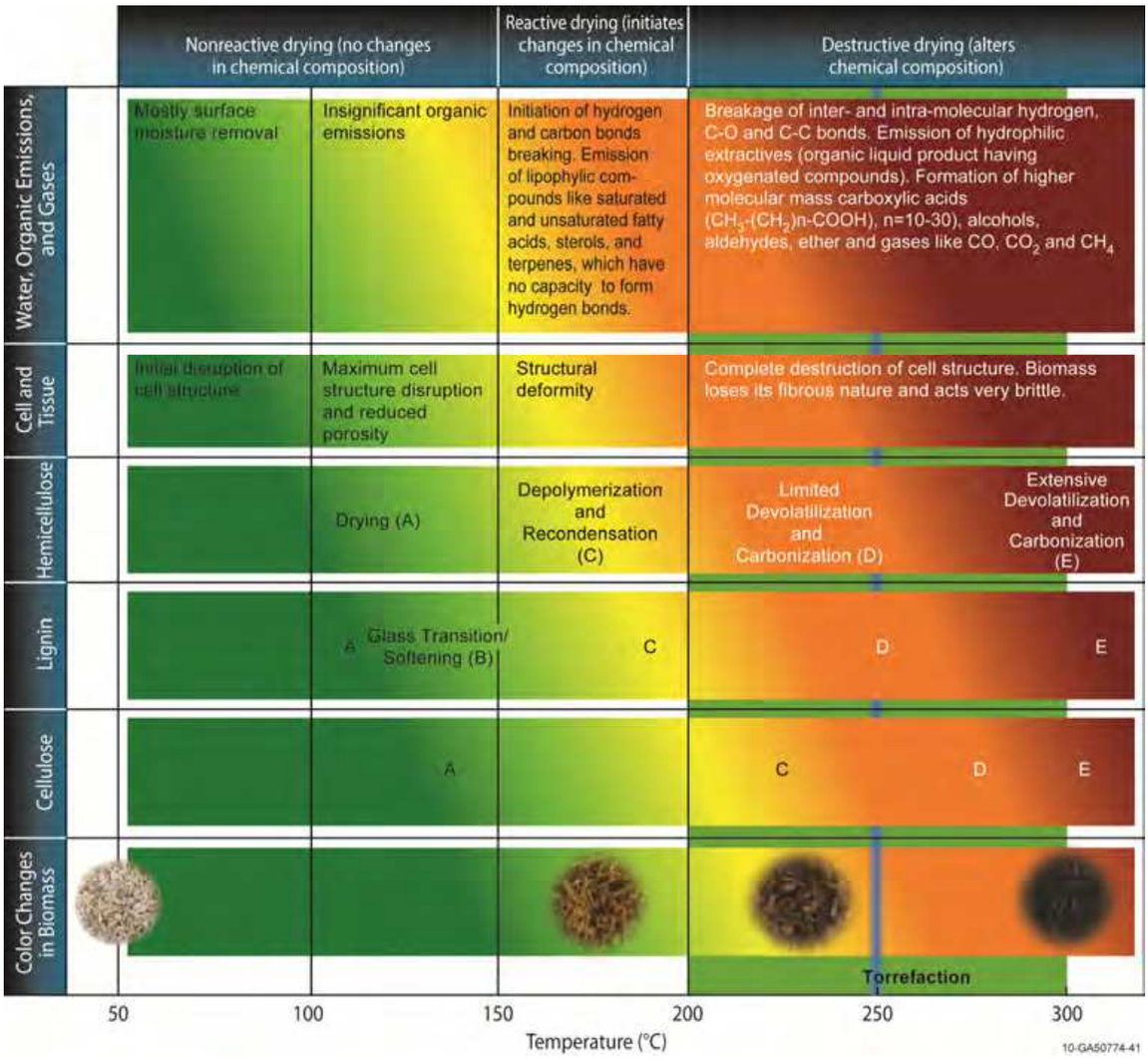

Fig. 3. Structural, chemical, and color changes in biomass at different drying temperatures (Tumuluru et al., 2011)

6.1 Biomass reactions

The physiochemical and structural changes in biomass at different temperature regimes is given in Fig. 3 (Tumuluru et al., 2011). The figure indicates that at higher temperature regimes, the drying is more destructive in terms of breakage of inter- and intra-molecular, hydrogen, C-O, and C-C bonds and leads to emission of some hydrophilic, oxygenated compounds. In addition, these changes lead to formation of higher-molecular-mass carboxylic acids, aldehydes, ethers and some gases like carbon monoxide, carbon dioxide and methane.

6.2 Torrefaction gas composition

The three main products produced during torrefaction are a brown/dark-color solid; a condensable liquid, including mostly moisture, acetic acid, and other oxygenates; and non-condensable gases—mainly CO_2, CO, and small amounts of methane. The last two products can be represented by volatiles. Fig. 4 (Bergman et al., 2005) gives an overview of the torrefaction products, classified based on their state at room temperature, which can be,

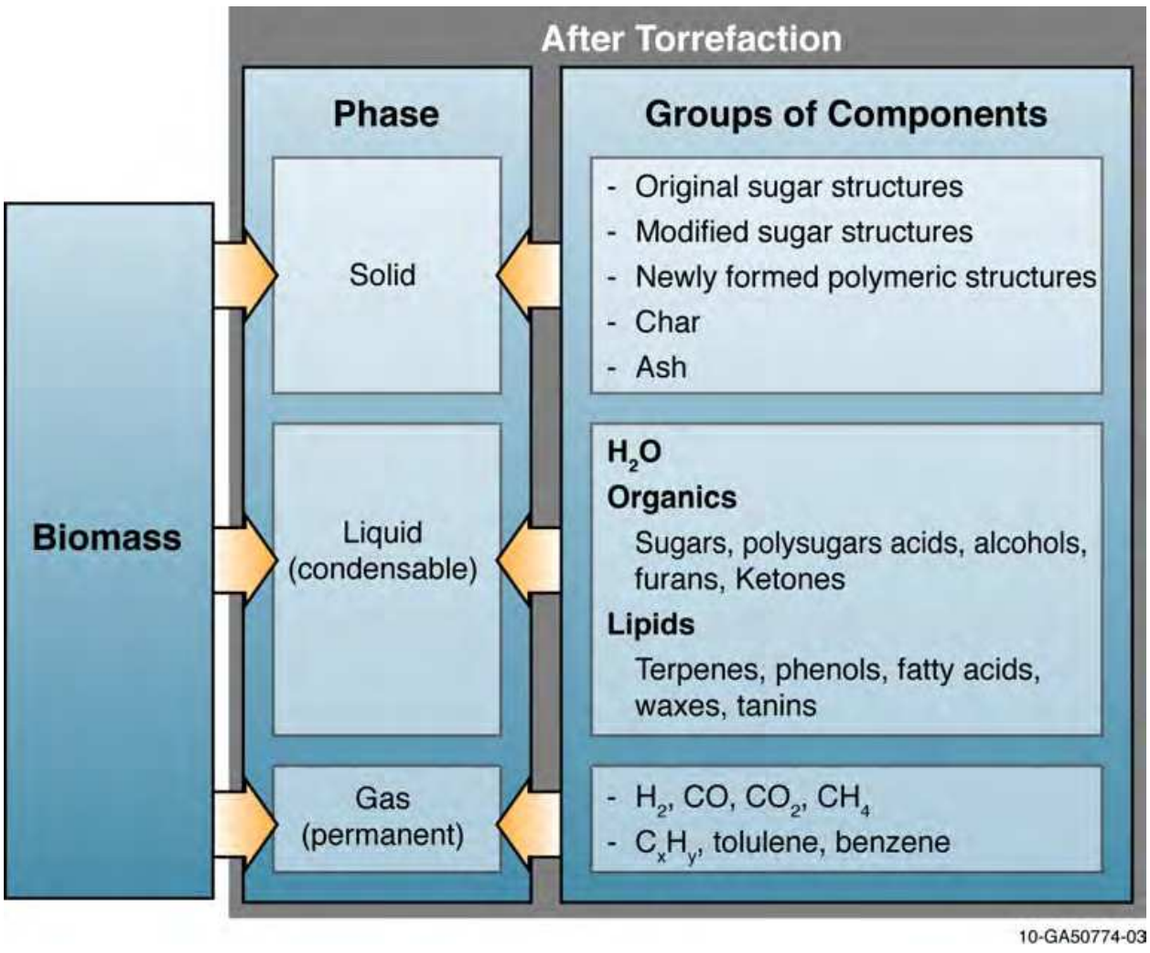

Fig. 4. Products formed during the torrefaction of biomass (Bergman et al. 2005)

solid, liquid, or gas. The solid phase consists of a chaotic structure of the original sugar structures and reaction products. The gas phase includes the gases that are considered permanent gases, but also light aromatic components such as benzene and toluene. The condensables, or liquids, can be divided into three subgroups which include water, organics, and lipids, as shown in Fig. 4. One subgroup is reaction water as a product of thermal decomposition. The liquid also contains the free and bound water that has been released from the biomass by evaporation and dehydration reactions. The organics subgroup (in liquid form) consists of organics that are mainly produced during devolatilization and carbonization. Finally, the lipids are a group of compounds that are present in the original biomass. This subgroup contains compounds such as waxes and fatty acids. The type and amount of the gases that come out depend on the raw material type and torrefaction process conditions, including process temperature and residence time (Tumuluru et al., 2011).

Currently, there is much emphasis on understanding the torrefaction gas composition, as its energy content plays a major role in improving the overall efficiency. Some researchers like Bergman et al. (2005, 2005a), Prins et al. (2006), and Deng et al. (2009) have investigated the torrefaction gas composition.

6.3 Non-condensable gases

Carbon monoxide (CO) is the main source of calorific value among the non-condensable torrefaction products. The formation of CO_2 may be explained by decarboxylation of acid groups in the wood, but the formation of CO cannot be explained by dehydration or decarboxylation reactions. The increased CO formation reported in literature (White and Dietenberger, 2001) is due to reaction of carbon dioxide and steam with porous char. Traces of hydrogen and methane are also detected in the non-condensable product. The ratio of CO to CO_2 increases with temperature because cellulose and lignin decompose at higher temperatures (Prins et al., 2006).

6.4 Condensable gases

In torrefaction, the major condensable product is water, which is released when moisture evaporates as well as during dehydration reactions between organic molecules. Acetic acid is also a condensable torrefaction product, mainly originating from acetoxy- and methoxy-groups present as side chains in xylose units present in the hemicelluloses fraction. Prins et al. (2006) showed that smaller quantities of formic acid, lactic acid, furfural, hydroxy acetone, and traces of phenol are also present in the volatile component liberated during the decomposition of biomass. As a result, more energy is transferred to the volatiles fraction in the form of combustibles such as methanol and acetic acid. Bridgeman et al. (2008) have provided the energy and mass yields, as well as the volatiles lost during the torrefaction of reed canary grass, wheat straw, and willow at different temperatures, as shown in Table 2. Table 3 indicates the physiochemical composition of pine and torrefied pine at temperatures from 240–290°C. With the increase in torrefaction temperature, fixed carbon in the pine increased while volatiles and moisture content decreased. Tables 3 and 4 indicate that, in the torrefaction range (200–300°C), there is significant change in the volatile concentration within the biomass.

	Temperature (K)			
	503	**523**	**543**	**563**
Reed Canary Grass				
Mass yield (daf)	92.6	84.0	72.0	61.5
Energy yield (daf)	93.5	86.6	77.1	69.0
Volatiles (daf)	7.4	16.0	28.0	38.5
Wheat Straw				
Mass yield (daf)	91.0	82.6	71.5	55.1
Energy yield (daf)	93.5	86.2	78.2	65.8
Volatiles (daf)	9.0	17.4	28.5	44.9
Willow				
Mass yield (daf)	95.1	89.6	79.8	72.0
Energy yield (daf)	96.5	92.7	85.8	79.2
Volatiles (daf)	4.9	10.4	20.2	28
Note: daf: dry ash free basis				

Table 2. Energy and mass yields and volatiles lost during torrefaction of reed canary grass, wheat straw, and willow at different temperatures (Bridgeman et al., 2008)

T[a],°C[b]	**p[c]**	**240**	**250**	**260**	**270**	**290**
Fixed carbon, %	20.64	23.55	25.59	25.69	29.38	35.39
Elementary analysis **C, %** **O, %**	 50.98 42.80	 51.14 42.70	 51.93 42.18	 53.78 40.66	 53.57 40.67	 58.08 36.40
Pentosans, %	9.61	5.93	5.90	3.10	2.54	1.40
Lignin, %	22.84	24.90	28.72	33.44	39.23	53.47
Extractable, %[d]	14.67	8.19	14.09	19.35	16.49	17.98
Moisture, %[e]	10.80	5.66	4.08	3.96	3.76	3.88
Yield, %	–	86.2	81.8	75.7	66.4	48.8

a. in each case, the mean result given was obtained from a minimum of four different experiments
b. roasting time: 30 minutes
c. native pine
d. neutral-solvent extractable (ethanol, benzene, boiling water)
e. powder samples left at the laboratory atmosphere still had a constant humidity

Table 3. Physiochemical analysis of pine and torrefied pine

6.5 Significance of torrefaction gas

The knowledge of the composition of volatiles produced in the temperature range of torrefaction is a topic of interest for understanding of

- Raw material adaption to the process
- Process control
- Process behavior and operation
- Energy process and energy optimization
- Production of green chemicals.

6.5.1 Improving torrefaction process efficiency

Volatiles produced during torrefaction have relatively low calorific values, but the gas is still flammable. If the gases produced during torrefaction are flammable, they may be combusted and used to heat the torrefaction reactor in a recycle loop as suggested by Bergman et al. (2005), as shown in Fig. 5. The torrefaction gas composition must be studied further to find out if the gas is combustible, if autothermal operation of the reactor is possible, or if an external fuel is required, as well as what torrefaction temperature and residence times give flammable gases and the best efficiencies for the process. Using gas chromatography to identify and quantify compounds in these gases can reveal what portion of the gas is flammable, what flame temperature is required to ignite all the flammable components, and theoretically what heating value the gas would have. With this information, the potential use of these gases as a heat source for the reactor can be further evaluated.

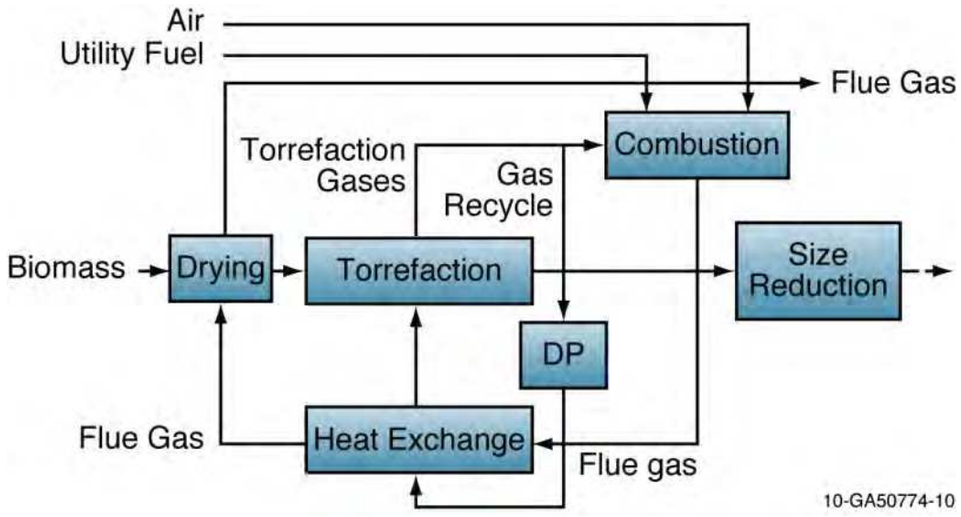

Fig. 5. Combined drying and torrefaction process developed by the Energy Research Centre of the Netherlands (ECN).

6.5.2 Chemical production

Other uses of the condensable fraction of torrefaction gases are for the production of chemicals like concentrated acetic acid, formic acid, methanol, and furfural. The yield of these chemicals depends greatly on torrefaction parameters, including temperature, biomass type, and residence time. In a study of the torrefaction of willow, acetic acid was found to be as much as 5% of the total yield. Formic acid and furfural were as much as 4%, and methanol was at just over 1% (Prins, 2006).

Acetic acid is used mainly to derive more specialized compounds. The largest use of acetic acid is in making vinyl acetate monomer (VAM), which is used in the production of paints, adhesives, paper coatings, and textile finishes. VAM is also used in the production of ethylene vinyl alcohol (EVOH) polymers, which are used in food packing films, plastic bottles, and automobile gasoline tanks. Acetic acid is also used in creating purified terephthalic acid, which is used in making bottle resins and polyester fiber. Another

derivative is ethyl acetate, used as a solvent in oil-based lacquers and enamels, including polyurethane finishes and in inks and adhesives. Another large use of acetic acid is in deriving acetate esters, which are used in a wide variety of paints, inks, and other coatings, as well as in many other chemical processes (ICIS News).

Formic acid is a chemical intermediate in the production of various other chemicals and pharmaceuticals, such as caffeine, enzymes, antibiotics, artificial sweeteners, plant protection agents, PVC-plasticizers, and rubber antioxidants. Formic acid is used directly in dyeing, pickling, and tanning processes for leather, the coagulation of rubber, and in various cleaning products (BASF).

Furfural and its derivatives can be used as a replacement for crude-oil-based organics used in industry, such as flavoring compounds, furane resin, surface coatings, pharmaceuticals, mortar, polymers, adhesives, and moulds. Tetrahydrofurfuryl alcohol and tetrahydrofuran (THF) are also used to create specialty chemicals in a wide range of chemical synthesis (Win, 2011).

7. Gas chromatography methods for torrefaction gases

Various GC configurations are used for the analysis of pyrolysis gases that can also be used to analyze gases from the torrefaction processes. GC systems used for pyrolysis should be reviewed because those volatiles and permanent gases produced during pyrolysis are likewise produced in the torrefaction process. The authors feel that with less or no modification, these GC systems can be adequately adapted for torrefaction-gas analysis.

In the study of Prins et al. (2006b), the volatile products are split into a liquid and gas phase in a cold trap at –5°C. Liquid products collected in the cold trap were diluted with 2-butanol because not all the products dissolved in water. The diluted liquid was analyzed with high-performance liquid chromatography (HPLC) using a Chrompack Organic Acids column with detection based on refraction index. The composition of the non-condensable gas was analyzed with a Varian Micro GC with a Poraplot Q and a Molsieve column.

In the study of Deng et al. (2009), torrefaction products were removed from the hot zone to minimize the secondary reactions between the liquid and char and to maximize the solid yield. A two-necked flask immersed in liquid nitrogen was used as a trapping system for the condensable gases. Non-condensable gases went through a filter to remove the carbon soot before entering an infrared gas analysis. The gas composition and concentration were recorded continuously throughout the heating process. Finally, the weight of the biochar and the amount of liquids obtained were measured.

In Bridgeman's (2008) study, a Nicolet Magma-IR Auxiliary Equipment Module (AEM), connected to a Stanton Redcroft Simultaneous Analyser STA-780 Series, was used to perform torrefaction experiments at laboratory scale while simultaneously analyzing the volatile pyrolysis products for corresponding thermogravemetric analyzer (TGA) data.

Bergman et al. (2005) used two impinger bottles immersed in a cold bath (<5°C) for collection of the condensables during the torrefaction process. Torrefaction gas is sucked through the bottles at a pre-specified rate so that yields can be determined. A polar solvent (water or ethanol) is used in the bottles. Tests showed that two bottles removed all the

condensables from the gas phase. Some aerosols are formed by quenching (going from ~200°C to ~0°C). Quantification of water was found to be unreliable due to aerosol formation and because reaction water mixes with physically bound water. It is unclear whether lipids are collected efficiently because the components of the lipid subgroup were not quantified afterwards. Analysis of the product was done with a combination of GC-FID, GC-MS, and ion chromatography. These quantified products are shown in Table 4.

2-furaldehyde (furfural)	1-Hydroxy-2-butanone
5-methyl-2-furaldehyde	Eugenol
Acetaldehyde	Isoeuganol
2(5H)-Furanone	Propionic acid
Ethylene-glycol diacetate	3,4,5 trimethoxytoluene
Ethanol	Furan-2-methanol
Pyrrole	Furan-3-methanol
Methanol	Methylacetate
Methylformiate	Hydroacetone
Cyclohexanone	Butanone
Propanal	2-butenal
Pyrrole-2-carboxaldehyde	Phenol
2-methoxyphenol	3-methoxyphenol
4-methoxyphenol	2,6 dimethoxyphenol
Acetone	3-methoxypyridine
4-methoxypyridine	2-methoxypyridine
Acetic acid	Formic acid

Table 4. Quantified condensable products produced during torrefaction of wood

Permanent gases, as shown in Table 5, are also measured using an online measurement procedure. This comprises micro-GC, by which the composition of the dry gas is determined. Before the gas is charged to the micro-GC, water is removed in a cold trap because the presence of the water disturbs the measurement.

O_2	C_2H_2
Ar	C_2H_4
CO_2	C_2H_6
CO	Benzene
N_2	Toluene
H_2	Xylenes
CH_4	

Table 5. Non-condensable gases quantified during torrefaction of wood

In Pommer et al.'s 2011 studies on torrefaction of different biomass sources using GC-MS, the most abundant compounds were identified due to the decomposition of hemicellulose, cellulose, and lignin, as shown in Table 6.

4-Allyl-syringol	Formaldehyde
Acetaldehyde	Formic acid
Acetic acid	Furaldehyde
Carbon monoxide	(3H)-Furan-2-one
Carbon dioxide	2-Furfuralalcohol
Conifer alcohol	Hydroxyacetaldehyde
Eugenol	Methanol
Propanal-2-one	Sinapaldehyde
Pyranone	Synapyl alcohol
Syringaldehyde	Vanillin
4-Vinyl-syringol	Water

Table 6. GC-MS analysis of abundant compounds produced due to the torrefaction of biomass

In addition, the analysis of biomass tar can also be used for reference. Two methods for the sampling and analysis of tar produced from wood pyrolysis were compared in the study of Dufour et al. (2007). A Clarus 500 GC system (Perkin-Elmer) coupled to a Clarus 500 MS quadrupole MS system (Perkin-Elmer) was used for the analysis. The gas chromatograph was equipped with an electronically controlled split/splitless injection port. GC was carried out on a 5% diphenyl-/95% dimethylpolysiloxane fused-silica capillary column (Elite-5 ms, 60 m × 0.25 mm, 0.25 µm film thickness; Perkin-Elmer). Helium (Alphagaz 2, Air Liquide) was used as the carrier gas, with a constant flow of 1.2 mL/min. The first method used a conventional cold-trapping technique in solvent-filled impingers followed by liquid injection. The second employed a new application of multi-bed solid-phase adsorbent (SPA) tubes, followed by thermal desorption (TD). Both methods are based on GC coupled with MS. Quantification was performed with a well reproducible GC–MS method with three internal deuterated standards. The main compounds sampled by impingers with methanol or 2-propanol and SPA tubes are listed in Table 7.

Barrefors and Petersson (1995) used GC and GC−MS for volatiles produced during the pyrolysis of wheat straw. Mahinpey et al. (2009) have carried out GC and GC−MS analysis of bio-oil, biogas, and biochar from pressurized pyrolysis of wheat straw using a tubular reactor. The GC system used was a gas chromatograph (Agilent Technologies 6890 N) equipped with two columns (Porapak; molecular sieve), flame ionization detection (FID), and thermal conductivity detection (TCD). Standard gas mixtures were used for quantitative calibration, and argon was used as the carrier gas.

Benzene	1,2,4-Trimethylbenzene; 1-methylethylbenzene
Acetic acid	3,3-Dimethylphenol
Pyridine	Phenol
Pyrrole	2- or 3-Methylstyrene
Toluene	Benzofuran
Ethylbenzene	Indene
1,3-Dimethylbenzene	2- or 3- or 4-Methylphenol
Ethynylbenzene	5-Methylpyrimidine
o-Xylene	2- or 3- or 4-Methylphenol
1- or 2-Propenylbenzene	7- or 2-Methyl-benzofuran; 3-phenyl-2-propenal
7- or 2-Methyl-benzofuran	3-Phenylfuran; 1- or 2-naphthol
4,7-Dimethylbenzofuran; 1-hydroxy-5,8-dihydronaphthalene	1- or 2-Naphthol
2-Methylnaphthalene	7- or 2-Methyl-benzofuran or 3-phenyl-2-propenal
1-Methylnaphthalene	Diethenylbenzene
Fluorene	3-Phenyl-1,2-butadiene; 1-, 2-methylindene
4-Methyldibenzofuran; 9H-xanthene	3-Phenyl-1,2-butadiene; 1-, 2-methylindene
1H-phenalene	Biphenyl
2-, 3-, or 4-Methylbiphenyl	Acenaphthene
1-Phenylmethylene-1H-indene; 1,9-dihydropyrene	2-Ethenylnaphthalene
Phenanthrene	Acenaphthylene
Anthracene	2-Methylanthracene
1-Phenylmethylene-1H-indene; 1,9-dihydropyrene	6H-Cyclobuta[J,K]phenanthrene; 8,9-dihydrocyclopenta [D,E,F]phenanthrene
Dibenzofuran	1- or 2-Phenylnaphthalene
Acenaphthenone	Fluoranthene
1H phenalene	11H-benzo[A] or [B]fluorene
1-Methylpyrene	11H-benzo[A] or [B]fluorene
Pyrene	

Table 7. Main identified compounds sampled with SPA tube

The GC−MS system consisted of an Agilent HP6890GC coupled to a quadrupole mass spectrometer (Agilent 5973 Network MSD). Electron ionization (EI) was used with an ion source temperature of 230°C and an interface temperature of 280°C, with EI spectra obtained at 70 eV. In EI, the instrument was used in SCAN mode initially to confirm the identity of the 18 compounds and then in selected ion monitoring (SIM) mode for quantitative analysis. The GC system was equipped with a split/splitless inlet with a splitless sleeve containing carbofrit (4 mm i.d., 6.5 × 78.5 mm, Restek). The injector temperature was 225°C. A LEAP Technologies autosampler with a 10 µL syringe was used for injections of 1 µL at a rate of 10 µL s^{-1}. The analytical column was DB-5 ms, 5% polydiphenyl-95% dimethylpolysiloxane, 30

× 0.25 mm i.d., and 0.25 µm film thickness (J&W Scientific). The carrier gas was helium (UHP) at a constant flow of 1.0 mL min^{-1}. The oven temperature program had an initial temperature of 65°C, which was held for 4 min, rising by 10°C/min to 120°C, 15°C/min to 170°C, 3°C/min to 200°C, and finally 30°C/min to 300°C, where it was held for 5 min for a total run time of 31.17 minutes. This temperature program was selected to provide adequate separation of most of the 18 compounds of interest, as shown in the total ion chromatogram (TIC) for a standard and sample. Only two compounds coeluted (pyrocatechol and phenol 2-methoxy 4-methyl), and the remaining compounds are provided in Table 8.

Phenol	4-methylcatechol	3,5-dimethoxy-4′-hydroxy acetophenone
Methylhydroquinone	2,6-dimethoxyphenol	Syringaldehyde
Guajacol	Eugenol	2-methoxy -4-propylphenol
4-ethyl phenol	Vanillin	phenol 2 -methoxy 4-methyl
pyrocatechol	Isoeugenol	3-methoxycatechol
4′-hydroxy-3′-methoxyacetophenone	4-ethyl guaiacol	2-propanone, 1-(4-hydroxy-3-methoxyphenol

Table 8. GC and GC−MS analysis of gases produced during pyrolysis of wheat straw

In the studies conducted by Bacidan et al. (2007), product distribution and gas release in pyrolysis of thermally thick biomass residues samples have used micro GC and FTIR analyzer for gases like CO_2, CO, CH_4, H_2, C_2H_2, C_2H_6, and C_2H_4. The FTIR analysis of the gases was performed with a Bomem 9100 analyser (sampling line and cell heated at 176 °C with a volume of 5l and an optical path length of 6.4 m). The instrument is equipped with a DTGS detector at the maximum resolution of 1 cm^{-1}. The gas samples were also quantified online using a Varian CP-4900 micro-GC equipped with two TCD detectors and a double injector connected to two columns: (1) a CP-PoraPLOT Q column (10 m length, 0.25 mm inner diameter and 10 µm film thickness produced by Varian, Inc.) to separate and quantify CO_2, CH_4, C_2H_2 + C_2H_4 (not separated), and C_2H_6 ; and (2) a CP-MolSieve 5 Å PLOT column (20 m length, 0.25 mm inner diameter and 30 µm film thickness produced by Varian, Inc.) to analyse H_2, O_2, CH_4, CO, and N_2. Helium and argon were used, respectively, as carrier gases in the two columns.

Lappas et al. (2002) focused on identifying the composition of the gases produced during biomass pyrolysis, where an online connected GC (HP 5890) with two detectors (TCD and FID) was used, along with a split/splitless injector and four columns (OV 101, Molecular sieve 5A, Porapaq N, and a capillary Poraplot Al2O3/KCl). The composition of the regenerator gas exit stream (i.e., flue gases) was determined with a GC (HP 5890) detector (TCD, Molecular sieve 5A and Porapaq N columns), and the hydrocarbons, CO and CO_2 were analyzed.

Qing et al. (2011) analyzed the gases and volatiles produced during the pyrolysis of wheat straw. They used a Shimazu QP2010 Plus GC-MS, and the GC column type was a DB-Wax fused silica capillary column (30 m × 0.25 mm; i.e., film thickness = 0.25 µm).

And finally, Wang et al. (2011) concentrated on the pyrolysis of pine sawdust by using a GC-MS (Finnigan Trace MS). The column used in these studies was a GC-MS with a capillary column DB-1301 (30 m x 0.25mm; i.e., film thickness = 0.25 µm). Helium was the carrier gas, with a constant flow of 0.5 ml/min. The MS was operated in electron ionization mode with a 70 eV ionization potential, and an m/z range from 30 to 500 was scanned. The peaks were identified based on the computer matching of the mass spectra with the National Institute of Standards and Technology (NIST) library. The summary of the systems used for analysis of torrefaction and pyrolysis gas analysis is given in Table 9.

S. No	**GC configuration**	**Process**	**Volatiles and permanent gases**		**Reference**
			Volatiles	Gases	
1	HPLC using Chrompack organic acids column for volatiles. Varian micro gas chromatography with Porapolt Q and Molsieve column for non condensable gases	Torrefaction	Water, acetic, lactic acid, formic acid, furfural, hydroxyl acetone, phenol, methonal	CO, CO_2	Prins et al. (2006b)
2	Infrared gas analysis (Gasboard-5110, Wuhan, China).	Torrefaction	Moisture, acetic acid and other oxygenates	CO_2, CO and small amounts of methane	Deng et al. (2009)
3	TGA-FTIR (A Nicolet Magma-IR AEM connected to a Stanton Redcroft Simultaneous Analyser STA-780 Series)	Torrrefaction	Volatiles	CO_2, CO	Bridgeman et al. (2008)
5	GC–MS (A Clarus 500 GC system (Perkin-Elmer, Shelton, CT, USA) coupled to a Clarus 500 MS quadrupole MS system (Perkin-Elmer)	Torrefaction	Benzene, acetic acid, pyridine, pyrole, toluene, ethylbenzene, 1,3-dimethylbenzene,etc		Dufour et al. (2007)
6	GC-FID and GC-MS	Torrefaction	2-furaldehyde (furfural), 1-Hydroxy-2-butanone, acetic acid, formic acid etc.	O_2, Ar, CO_2, H_2, CO	Bergman et al. (2005)
7	GC-MS	Torrefaction	Acetic acid, formic acid, formaldehyde, vanillin, methanol, acetaldehyde etc.	CO, CO_2	Pommer et al. (2011)

S. No	GC configuration	Process	Volatiles and permanent gases		Reference
8	GC-MS	Pyrolysis	Acetic acid, formic acid, formaldehyde etc.		Barrefors and Petersson (1995)
9	GC-MS (Agilent HP6890GC coupled to a quadrupole mass spectrometer) (Agilent 5973 Network MSD) GC (Agilent Technologies 6890 N) equipped with two columns (Porapak; Molecular sieve), flame ionization detection (FID), and thermal conductivity detection (TCD)	Pyrolysis	Phenol, vanillin, acetophenone, syringaldehyde etc.	CO, CO_2 etc	Mahinpey et al. (2009)
10	FTIR (Bomem 9100 analyser) and Micro GC	Pyrolysis	Hydrocarbons	CO, CO_2	Bacidan et al. (2007)
11	Gas chromatograph-GC (HP 5890) with two detectors (TCD and FID)	Pyrolysis		CO, CO_2	Lappas et al. (2002)
12	Shimazu QP2010 Plus GC-MS. GC Column Type: A DB-Wax fused silica capillary column (30 m × 0.25 mm, i.e., film thickness = 0.25 µm)	Pyrolysis			Qing and Wu (2011)
13	GC-MS: The column used in GC-MS was a capillary column DB-1301 (30mx0.25mm i.d., 0.25µm film thickness) and MS was operated in electron ionization mode with a 70 eV ionization potential.	Pyrolysis	Higher hydrocarbons	CO, CO_2	Wang et al. (2011)

Table 9. GC systems for torrefaction and pyrolysis gas analysis

8. Conclusions

Torrefaction of biomass produces a product that has a higher energy content compared to that of raw biomass. During torrefaction, biomass loses moisture as well as some condensable and non-condensable gases. The condensable gases include water, organics, and lipids. The liquid contains the free and bound water that has been released from the biomass by evaporation. The organics subgroup (in liquid form) consists of organics that are mainly produced during devolatilization, depolymerization, and carbonization reactions in the biomass. The knowledge of the composition of volatiles produced in the temperature range of torrefaction is a topic of interest as it helps in the raw material adaption process, process control, process behavior and operation, energy process and energy optimization, and in the production of green chemicals. Lipids are a group of compounds that are present in the original biomass and contain compounds such as waxes and fatty acids. The non-condensable gases are CO_2, CO, and small amounts of methane. GC configuration plays an important role in the accurate identification of the compounds. A combination of different detectors, such as thermal, flame, and photo ionization detectors, in combination with a mass spectrometer, are used for the profiling of both condensable and non-condensable gases. It can be concluded that a GC-MS can help to analyze most of the volatiles emitted from biomass during torrefaction as well as a micro GC for the analysis of permanent gases like CO, CO_2, and CH_4.

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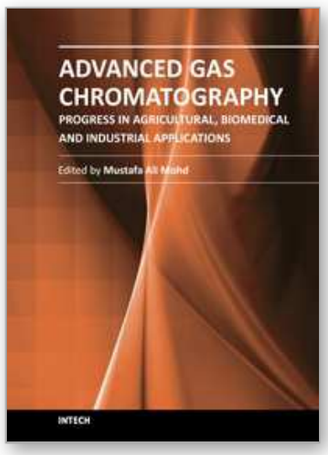

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Progress in agricultural, biomedical and industrial applications' is a compilation of recent advances and developments in gas chromatography and its applications. The chapters cover various aspects of applications ranging from basic biological, biomedical applications to industrial applications. Book chapters analyze new developments in chromatographic columns, microextraction techniques, derivatisation techniques and pyrolysis techniques. The book also includes several aspects of basic chromatography techniques and is suitable for both young and advanced chromatographers. It includes some new developments in chromatography such as multidimensional chromatography, inverse chromatography and some discussions on two-dimensional chromatography. The topics covered include analysis of volatiles, toxicants, indoor air, petroleum hydrocarbons, organometallic compounds and natural products. The chapters were written by experts from various fields and clearly assisted by simple diagrams and tables. This book is highly recommended for chemists as well as non-chemists working in gas chromatography.

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