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Polar and non-polar components in Fast Pyrolysis Bio-Oil in relation to REACH registration.

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PREFACE

One of the objectives of IEA Task 34 is to facilitate commercial deployment of Direct Thermochemical Liquefaction technologies. Fast pyrolysis is maturing, and significant amounts of pyrolysis oil are introduced on the European market. Consequently, registration in the European REACH system is required, demanding dedicated chemical analyses and expertise. Both VTT and BTG are already active in the fast pyrolysis field for a long time, and in several projects, attention was given to REACH related issues. Therefore, it was decided to have a dedicated effort within IEA-Task 34 to combine and share the experiences of VTT and BTG on this subject which is expected to be beneficial for producers, end-users, project developers and researchers in this field. Additionally, a scientific paper will be prepared focusing specifically on the analysis of aldehydes.

SUMMARY

Fast pyrolysis bio-oil (FPBO) is entering the European market and estimated production capacity will exceed 100 million litres in 2021 with individual production capacities of well above 10 kton/year. So-called REACH registration is mandatory.

REACH stands for **R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emicals. It is the European system aiming to protect human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. In 2013 a FPBO registration dossier was submitted to ECHA (European Chemicals Agency). In the dossier FPBO is classified as a UVCB, i.e. a product with Unknown or Variable composition, Complex reaction products or Biological materials. The registration is valid for FPBO produced by fast pyrolysis from lignocellulosic biomass and is characterized by its chemical and physical properties. In addition, specific restrictions are given on the concentrations of some polar and non-polar compounds. This report focusses on the analyses of these compounds.

The polar compounds considered are formaldehyde, acetaldehyde, methanol, furfural, phenol and cresol. Different analysis methods have been applied by VTT, University of Groningen (RUG) and BTG to measure the concentrations of these compounds in FPBOs of different origin or post-treated in different ways. Taking into account the complexity of measuring individual components in FPBO the agreement between the measuring methods is acceptable. Formaldehyde cannot be measured directly as it is in chemical equilibrium with methylene glycol. The actual concentration is calculated using the equilibrium constant and the sum of concentration of formaldehyde and methylene glycol. Additionally, the formaldehyde concentration in the atmosphere around fast pyrolysis units was measured. Under normal working conditions and proper pre-cautions, the formaldehyde concentration is always well below legal exposure limits.

The specific non-polar compounds in FPBO refer to the poly-aromatic hydrocarbons (PAHs) and more in particular the EPA PAH13. The starting point were the different analysis methods known from literature for measuring PAHs in FPBO. RUG & BTG have evaluated these methods and further improved them. A specific challenge is to avoid the co-extraction of phenolic compounds as it gives overlapping peaks in the subsequent analysis resulting in false PAH values. Some variation in results is observed, but in all cases the total PAH13 content is well below the limit of 35 ppm as given in the Reach registration for FPBO.

Summarizing, the analysis methods have successfully been developed or improved. Based on analysis of FPBOs from different biomass resources it appears that generally FPBOs can comply with the specifications and limits given in the FPBO REACH dossier.

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LIST OF ABBREVIATIONS

BTG	Biomass technology Group BV
DNPH	2,4-Dinitrophenylhydrazine
PFBHA	2,3,4,5,6-Pentafluorobenzyl)-hydroxylamine
DNPH-FA	DNPH formaldehyde complex
EPA	Environmental Protection Agency
FA	Formaldehyde
FAMG	Sum of formaldehyde and Methylene Glycol
FID	Flame Ionization Detector
FPBO	Fast Pyrolysis Bio-Oil
GC-ECD	Gas Chromatography – Electron Capture Detector
HF	Hemiformal
Keq	Equilibrium constant
ME	Methanol
MG	Methylene Glycol
MGn	Methylene Glycol oligomers (n=2-8)
SIP	Substance Identification Profile
W	Water
FID	Flame Ionization Detector
FPBO	Fast Pyrolysis Bio-oil
GC	Gas chromatography
HPLC	High-performance liquid chromatography
JD	Joint Dossier
MS	Mass Spectrometry
PAH	Poly Aromatic Hydrocarbon
REACH	Registration, Evaluation, Authorization and restriction of Chemicals
RRF	Relative Response Factors
RuG	Rijksuniversiteit Groningen
SIM	Single Ion Monitoring
SIP	Substance Identity Profile
UV	Ultra Violet
UVCB	Unknown or Variable composition, Complex reaction products or Biological materials
VF	Volumetric Flask
VTT	Teknologian Tutkimuskeskus VTT Oy – Technical Research Centre of Finland

Introduction

REACH is the European system aiming to protect human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. REACH stands for **R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emicals. To comply with the regulation, companies must identify and manage the risks linked to the substances they manufacture and/or place on the market in the EU. All substances produced or imported in the European Union in quantities above 1 t/y will be obligated for registration in REACH.

Proper registration of products is of crucial importance for the implementation and commercialization of any technology, and therefore also relevant for fast pyrolysis of biomass. IEA Bioenergy Task 34 was very active to provide data needed for REACH registration.[1] In 2013 a 'FPBO REACH consortium' –led by Fortum and Linnunmaa from Finland- was established, with the goal of obtaining the REACH registration for FPBO at the ECHA (European Chemicals Agency). A joint dossier was submitted late 2013.

REACH registration of fast pyrolysis oil

The total capacity of the current European fast pyrolysis plants (see next chapter) is about 15 t/h FPBO exceeding 100 million litres of FPBO annually, and the products are applied commercially. Production capacity of a single production plant exceeds 10,000 t/y.

FPBO is recognized as a 2nd generation advanced biofuel or intermediate energy carrier. However, it is completely different from conventional fossil fuels both in its physical properties and chemical composition.

Due to the nature and properties of FPBO a dedicated REACH registration is required, and first of all the product must be defined in a so-called Substance Identity Profile (SIP) to distinguish this product from any other product in REACH. The FPBO SIP profile is given in Table 1; specific information on the properties and composition are given in Table 2.[2]

[1] Bridgwater, A.; Czernik, S.; Diebold, J.; Meier, D.; Oasmaa, A.; Peacocke, C.; Piskorz, J.; Radlein, D. (eds.) Fast Pyrolysis of Biomass – A Handbook. Published in the UK by CPL Press: Aston University, Bioenergy Research Group, 1999. ISBN: 1 872691 07.

[2] Oasmaa, A., Van De Beld, B., Saari, P., Elliott, D. C. & Solantausta, Y. Norms, standards, and legislation for fast pyrolysis bio-oils from lignocellulosic biomass. Energy and Fuels 29, 2471–2484 (2015).

Table 1: The FPBO - SIP profile

SIP profile Fast Pyrolysis Bio-Oil	
EC name	Fast Pyrolysis Bio-oil
EC number	692-061-0
CAS name	Fast Pyrolysis Bio-oil
CAS number	1207435-39-9
IUPAC name	Fast Pyrolysis Bio-oil
Public name	Fast Pyrolysis Bio-oil
Origin	Fast pyrolysis of lignocellulosic biomass
Definition	Liquid condensate recovered by thermal treatment of lignocellulosic biomass, at short hot vapor residence time (typically less than about 10 seconds) typically at between 450-600°C at near atmospheric pressure or below, in the absence of oxygen.

Table 2: Properties & composition of FPBO.

Properties and composition of Fast Pyrolysis Bio-oil	
pH	>2 – 3.5
Water content	< 40 ww %
Ash content	< 0.5 ww %
Solids content	< 5.0 ww %
Viscosity (40°C)	< 200 mm^2/s
Density	1.1 – 1.3 kg/L
Organic compounds	
Polar components	
Formaldehyde	< 0.5 ww %
Methanol	< 3 ww %
Non-polar components	
PAH13[a]	< 35 ppm (0.0035 ww%)
Bentso[a]Pyrene	< 0.01 ww % (100 ppm)
dibenz[a,h]anthracene	< 0.01 ww % (100 ppm)
Sum of Carc. 1B classified substances[b]	< 0.1 ww % (1,000 ppm)
Sum of Carc. 2 classified substances[b]	< 1.0 ww % (10,000 ppm)

[a] sum PAH13: Anthracene, Benz[a]anthracene, Benzo[a]pyrene, Benzo[a]fluoranthene, Benzo[k]fluoranthene, Benzoperylene, Chrysene, Dibenz[a,h]anthracene, Fluorene, Fluoranthene, Indenopyrene, Phenantrene, Pyrene
[b] Carc. 1B classified substances (Annex VI of CLP regulation 1272/2008): e.g. of sum PAH13: Benz[a]anthracene, Benzo[a]pyrene, Benzo[k]fluoranthene, Chrysene, Dibenz[a,h]anthracene
[c] Carc. 2 classified substances (Annex VI of CLP regulation 1272/2008): e.g. Formaldehyde, acetaldehyde, Furfural

FPBO is classified as a so-called UVCB (Unknown or Variable composition, Complex reaction products or biological materials). General characteristics of FPBO are given like water content, pH, viscosity, and density. The range is rather broad, and normally the pyrolysis oil from a wide range of technologies and lignocellulosic biomass feedstock will be covered. Analytical methods for these properties are well established, and a.o. validated in IEA Round Robin studies.[3]

In addition to these general properties, specifications are included on the content of certain polar and non-polar compounds. The polar compounds include formaldehyde, acetaldehyde, phenol, furfural, methanol and cresol. The non-polar compounds mainly concern poly-aromatic compounds (PAH13/PAH16). Specific limits are included for Bentso[a]pyrene and dibenz[a.h]anthracene, but the allowable content is higher than the total allowable PAH13 content (including the two previous compounds) and the relevance is unclear.

Additionally, the analysis methods for these organic components in fast pyrolysis oil were not well developed and validated whereas it is known that standard existing analysis techniques are often not appropriate for FPBO analysis. In the next chapters the analysis of the polar and non-polar compounds in FPBO will be evaluated in more detail. But first a brief overview of full-scale, European FPBO production plants is given.

[3] Oasmaa, A., Lehto, J., Solantausta, Y. & Kallio, S. Historical Review on VTT Fast Pyrolysis Bio-oil Production and Upgrading. Energy and Fuels (2021) doi:10.1021/acs.energyfuels.1c00177.

Status of commercial implementation of fast pyrolysis in Europe

In this chapter the fast pyrolysis process will be briefly described, and subsequently commercial production facilities in Europe exceeding 1 t/y of FPBO are identified.

Fast pyrolysis

Fast pyrolysis is a process in which organic materials are rapidly heated to 450 - 600 °C in absence of air. Under these conditions, organic vapours, permanent gases and charcoal are produced. The vapours are then quickly condensed to fast pyrolysis bio-oil (FPBO). Typically, 50-75 wt.% of the feedstock can be converted into fast pyrolysis bio-oil (FPBO). Pyrolysis enables the transformation of difficult-to-handle solid biomass of different nature into a clean and uniform liquid. Its energy density is four to five times higher than that of the original solid material, which offers important logistic advantages.

Fast pyrolysis processes

Various reactor technologies have been developed for the fast pyrolysis of biomass. The crucial element in the pyrolysis process is to rapidly heat the biomass to maximize the production of organic vapours. These vapours need to be quenched rapidly as well to minimize losses by thermal cracking and polymerisation reactions. As a result, heat transfer is a very important aspect in the process development. Biomass materials typically exhibit relatively poor heat conductivity, which means the biomass must be fed to the reactor in small particles to allow for rapid heating. Well-known reactor technologies are based on fluidized bed reactors, the rotating cone reactor, twin-screw mix reactor and ablative systems, but only the first two are currently applied commercially.

Production plants in Europe

Savon Voima – Joensuu - Finland

The integrated fast pyrolysis plant in Joensuu is based on VTT's patented technology.[4] The plant was built in 2013 by Fortum and in 2019 acquired by Savon Voima -a Finnish energy company. The patented technology concerns the integration of a fluidized bed fast pyrolysis process producing FPBO to an existing fluidized bed boiler combined heat and power (CHP) plant. The purpose of integrating FPBO production into a fluidized bed boiler is to increase overall energy efficiency and profitability and to decrease the production costs of the bio-oil. In the integrated fast pyrolysis concept hot sand from the fluidized bed boiler is used for heating the fast pyrolysis reactor. Simultaneously, fast pyrolysis process by-products

Fig. 1: Integrated fast pyrolysis plant in Joensuu, Finland.

[4] Solantausta, Y.; Oasmaa, A.; Sipilä, K.; Lindfors, C.; Lehto, J.; Autio, J.; Jokela, P.; Alin, J. Heiskanen, J. Bio-oil production from biomass: Steps toward demonstration. Energy & Fuels 2012, 26, 1, 233-240. https://doi.org/10.1021/ef201109t.

such as char and non-condensable gases are cofired in the CHP boiler together with the primary forest residue boiler fuel.
The plant in Joensuu has an hourly biomass intake of around 10 t/h and annual FPBO design capacity is 50,000 ton. The FPBO product is stored on-site and can be used as peak fuel in the heating season.

EMPYRO – Hengelo – The Netherlands

The Empyro fast pyrolysis plant in Hengelo (the Netherlands) is based on BTG-BTL's patented technology. The plant was built in 2014 by a consortium led by BTG-BTL. In 2019 the plant was acquired by Twence, a Dutch biomass and waste recycling company.

The process includes fast heating of biomass followed by rapid condensation of the vapours produced. The original reactor concept is based on the so-called rotating cone. In this reactor biomass particles at room temperature and hot sand particles are intensively mixed in the reactor resulting in rapid heating and a quick release of organic vapours. The produced vapours pass through several cyclones before entering the condenser, in which the vapours are quenched by re-circulated oil. The pyrolysis reactor is integrated in a circulating sand system composed of a riser, a fluidized bed char combustor, the pyrolysis reactor, and a down-comer. In this concept, char is burned with air to provide the heat required for the pyrolysis process. Oil is the main product; non-condensable pyrolysis gases are combusted and can be used e.g. to generate additional steam.
The Empyro plant has a design capacity of 25 MW (biomass input) and produces 3.2 t FPBO per hour (~20 kton/y). Besides pyrolysis oil steam and electricity is generated and the plant is self-sustaining. The pyrolysis oil is used as boiler fuel by FrieslandCampina[5].

Fig. 2: The Empyro fast pyrolysis plant in Hengelo, the Netherlands.

[5] Industrial Process Heat: case study 3: Process steam in a dairy factory via fast pyrolysis bio-oil, Contribution of Task 34 to the intertask project on industrial heat, September 2020, Bert van de Beld and Ardy Toussaint, IEA Bioenergy.

Green Fuel Nordic (GFN) – Lieksa - Finland

The GFN-Lieksa plant in Lieska (Finland) is also based on BTG-BTL technology. The plant was implemented and commissioned in 2020 by Green Fuel Nordic oy (GFN) -a Finnish biorefinery company. The feedstock is sawdust from the nearby sawmill and the design capacity is 3.2 t/h pyrolysis oil. The FPBO is used for a.o. replacing heating oils.

Fig. 3: GFN plant in Lieksa - Finland

Pyrocell – Gävle - Sweden

The Pyrocell plant in Gävle (Sweden) is based on BTG-BTL technology. The plant is implemented by Pyrocell- a joint venture of Setra and Preem. The feedstock will be sawdust from the sawmill and the production capacity is 3.3 t/h of FPBO. The FPBO will be used at the Preem refinery in Lysekil. Commissioning and start-up is expected in Q3/Q4 2021.

Polar compounds in FPBO

The relevant polar compounds identified in the FPBO-SIP are formaldehyde, acetaldehyde, phenol, furfural, methanol, and cresol. Due to the extreme complexity of FPBO, straightforward analysis techniques and methods are not always applicable. The polar compounds considered are shown in Fig. 4.

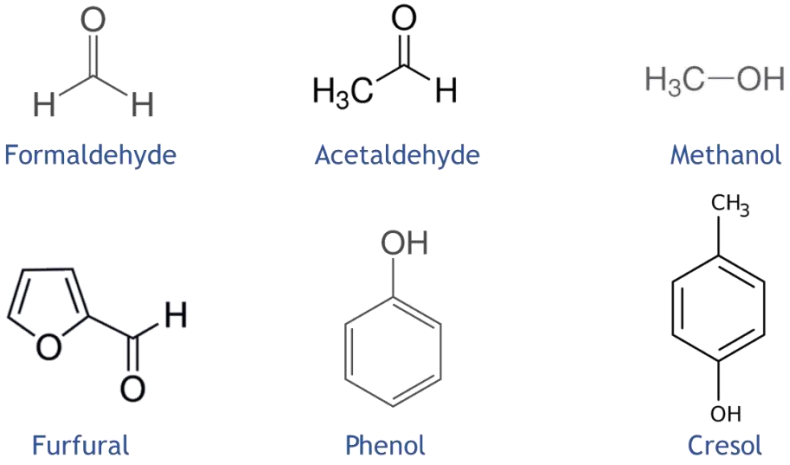

Fig. 4: Polar compounds identified in the FPBO-SIP

In a mini Round Robin, RuG and VTT tested five FPBO samples of different origin. An aged clean wood FPBO was tested because storage time can have a large influence on the concentration of the polar compounds (reacting away in time). Furthermore, a freshly produced clean wood FPBO, a wood FPBO in which a large part of the water was removed, a miscanthus-derived FPBO and a bark-derived FPBO were also tested. The FPBO with reduced water content, was the fresh clean wood oil treated in an evaporator under vacuum. Due to the low boiling points of formaldehyde (BP=-19 °C), acetaldehyde (BP=20 °C) and Methanol (BP=65 °C) it is likely that besides water also these components will be (partly) removed, and lower concentrations are to be expected.

In this section, the analysis of the polar compounds is described applying multiple modified methods developed and tested by the RuG, BTG and VTT.

FURFURAL

Furfural can be found in FPBO as a pyrolysis product, it is produced by the acid catalyzed dehydration of the C5 sugars present in the hemi-cellulose during pyrolysis.

RuG method

The method used by the RuG is based on HPLC (Agilent 1200 series, VWD) applying a Biorad Aminex HPX-87H (300 mm × 7.8 mm, 9 µm particles) column and the NREL/TP-510-42623 method. Preparatory to analysis, the FPBO needs to be water extracted. Extraction is performed by adding 1 part of well homogenized FPBO drop by drop to 8 parts of water using a syringe with needle into a sample flask. During the addition of FPBO to the water, the whole is stirred by a magnetic stirrer. After FPBO addition, the sample flask is closed and stirred for another 2h. Subsequently the extract is filtered by using a PTFE syringe filter (0.2 µm). A 6-point furfural calibration series (in H_2O) is prepared in a concentration range of 25-250 mg/kg and measured. Subsequently the FPBO sample is filtered (0.2

µm PTFE filter) and measured in triplicate. The areas vs. concentration of the calibration points are plotted and the concentration of furfural in the FPBO can then be obtained by extrapolating the furfural area and correcting for the dilution factor.

VTT method 1 (used for Furfural, Acetaldehyde & Formaldehyde)

The furfural, acetaldehyde and formaldehyde content were determined by using static headspace Gas Chromatography with Electron Capture Detector (HS-GC-ECD). Formaldehyde, acetaldehyde, and furfural were analyzed as oximes using an Agilent 7697A Headspace Sampler coupled with an Agilent 7890B gas chromatograph. The compounds were detected using Micro Electron Capture Detector. For the derivatization, well homogenized FPBO was first extracted with water and the water extract was subsequently filtrated to remove solid material. The sample extract was then further diluted with water. Thereafter, a known amount of diluted sample extract and an aqueous solution containing the derivatization agent O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA) (6 mg/L) were pipetted in a headspace vial and run using HS-GC-ECD. After the stabilization at 60 °C for 30 minutes in HS, the aldehyde measurements were performed by GC-ECD using a HP-5 capillary column, 50 m x 0.32 mm x1.05 µm (J&W Scientific, Folsom, CA). For calibration, aqueous solutions of formaldehyde, acetaldehyde and furfural were prepared at three different concentrations. The standards were further prepared and analyzed like the samples.

VTT method 2 (used for Furfural, Acetaldehyde, Methanol, Phenol and Cresols)

The furfural, acetaldehyde, methanol, phenol, and cresol (o-, m-, p-) content was determined from a FPBO water extract by using Agilent 7890A gas chromatography combined with an Agilent 5977B mass selective detector (GC/MSD). The separation of compounds was performed using a J&W HP-INNOWax high polarity fused silica capillary column (length: 60 m, inner diameter: 0.25 mm and film thickness: 0.25 µm). The compound detection was performed by applying a mass scan range of m/z between 27 and 300 (EI 70 eV). For the analysis, 1 g of well homogenised FPBO was weighed and extracted in an ultrasonic bath with 20 ml of water. After extraction, the sample was centrifuged, and 9 ml of water extract was mixed with 1 ml of internal standard (1-butanol, 1 g/L). Before GC/MS analysis, the sample was filtrated using a membrane filter (0.45 µm) to remove solid material. For the quantification, three-point calibration curves for methanol, acetaldehyde, furfural, phenol, o-creseol and m-cresol were prepared. The calibration curve of m-cresol was also used to determine the content of p-cresol.

Results

Firstly, the standards were measured with the methods. The calibration curves for each method were derived by plotting the areas of the standards against the concentrations. All methods gave calibration curves with good correlation coefficients. Subsequently, by extrapolating the area of the furfural peak and correcting for the dilution the furfural concentration could be obtained. The results for the 5 FPBO's measured by each method is given in Table 3. As an example, a typical chromatogram obtained with the RuG method can be found in Fig. 5.

Table 3: Results of the furfural analysis

Samples	RuG (wt%)	VTT-1 (wt%)	VTT-2 (wt%)
Aged clean wood oil	0.24 ± 0.01	0.32 ± 0.02	0.21 ± 0.00
Fresh clean wood oil	0.32 ± 0.02	0.32 ± 0.03	0.25 ± 0.00
Clean wood oil after water removal	0.21 ± 0.03	0.21 ± 0.03	0.16 ± 0.02
Miscanthus oil	0.36 ± 0.01	0.48 ± 0.01	0.34 ± 0.00
Bark oil	0.36 ± 0.00	0.45 ± 0.03	0.28 ± 0.00

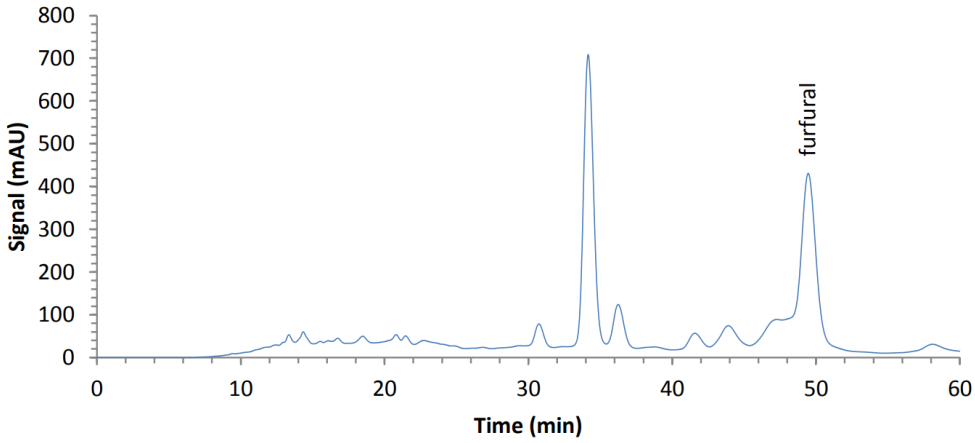

Fig. 5: A typical chromatogram of the furfural (in FPBO) analysis applying the RuG method

Concentrations between 0.16-0.48 wt% were found in the oils. There is some difference in furfural concentration between the different types of FPBO. In general, the highest concentrations were found in the miscanthus- and bark oil. The results obtained with the 3 methods only differ slightly and follow the same trend although the VTT-2 method seems to give some structural lower values.

METHANOL

Methanol can be found in FPBO as a pyrolysis product, sometimes it is also added to the FPBO as a homogenizer mainly to suppress the phase separation of resin material. No methanol was added to the samples measured in the round robin.

RuG method

The method used by the RuG is based on GC-FID applying a Restek Stabilwax-DA column (30 m x 0.32 mm x 1 µm df). Firstly a 5-point methanol calibration series (in IPA) is made in a concentration range of 200-1000 mg/kg and measured. Subsequently a well homogenized FPBO sample is diluted 10x in IPA, filtered (0.2 µm PTFE filter) and measured. The areas vs. concentration of the calibration points are plotted and the concentration of methanol in the FPBO can then be obtained by extrapolating the methanol area and multiplying it times the dilution factor.

VTT method

See VTT method 2, described in the furfural analysis.

Results

With both methods the standards were measured first. The methanol calibration curve for each method was derived by plotting the areas of the standards against their concentrations. Good correlation coefficients were obtained for both curves. By extrapolating the area of the methanol peak and correcting for the dilution, the methanol concentration could be obtained. The results for the 5 FPBO's measured by each method is given in Table 4. A typical chromatogram obtained with the RuG method can be found in Fig. 6.

Table 4: Results of the methanol analysis

Samples	RuG (wt%)	VTT-1 (wt%)
Aged clean wood oil	0.48 ± 0.02	0.46 ± 0.01
Fresh clean wood oil	0.62 ± 0.01	0.58 ± 0.02
Clean wood oil after H2O removal	0.05 ± 0.00	0.07 ± 0.01
Miscanthus oil	0.58 ± 0.04	0.62 ± 0.01
Bark oil	0.79 ± 0.01	0.83 ± 0.02

Depending on the type of FPBO, methanol concentration in the range of 0.05-0.83 wt% were found. The results obtained with the 2 methods only differ minimally and follow the same trend. Aged wood seems to have lost some of the methanol in time ~22%, which could be due to slow in situ reactions such as esterification. Furthermore, the FPBO in which some of the water was removed shows a methanol decrease of ~90%, obviously the methanol is largely removed by evaporation in the water removal step.

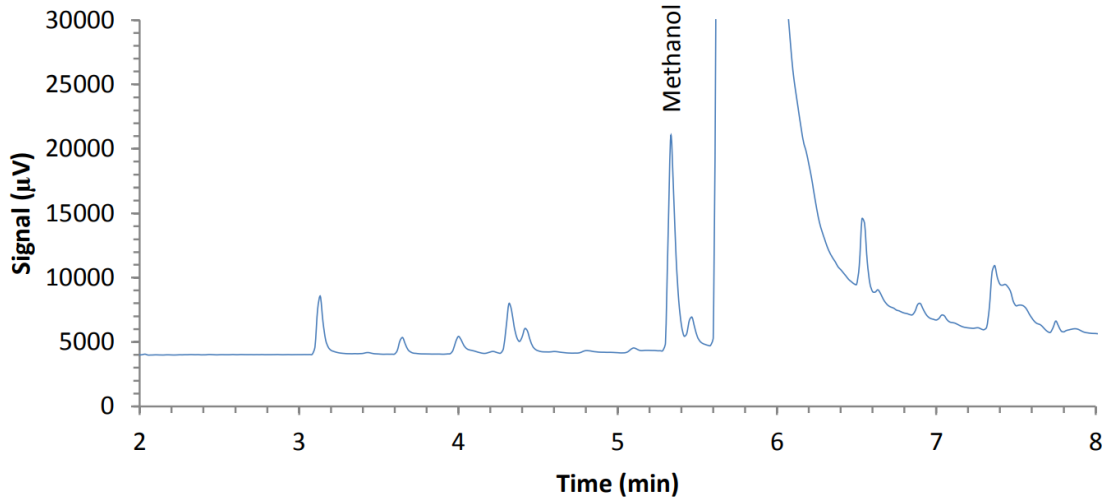

Fig. 6: A typical chromatogram of the MeOH (in FPBO) analysis applying the RuG method

ACETALDEHYDE

Acetaldehyde is component that can be found in pyrolysis oil. As with formaldehyde, acetaldehyde is formed by depolymerization and scissoring reactions during pyrolysis.

RuG method

Formaldehyde and acetaldehyde where analyzed based on the EPA Method 8315A method. 1 g of well homogenized FPBO was mixed with 40 g of water in a centrifuge tube and left overnight at room temperature. After 24 hours the water mixtures were centrifuged for 3 hours at 4500 rpm to obtain clear water layers. 0.5 g of the water extract was taken and added in a 250 ml Florence flask. 100 ml of water, 4 ml of citrate buffer and 6 ml of DNPH reagent was added and the mixture was kept in an orbital shaker at 40 °C for one hour. Agitation was set to a gentle swirl. Immediately after one hour, 10 ml of sat. NaCl was added. The DNPH derivatives were concentrated by use of an SPE setup

with 2 g of C18 cartridges. The derivatives were flushed off the SPE cartridges with 10 ml of acetonitrile and collected in test tubes. The acetonitrile weight was recorded. The DNPH derivatives were analyzed with a HPLC system. A Hewlett Packard 1100 series HPLC was used with a DAD detector set at 360 nm. 5 µl of sample was injected on a 250 × 4.6 mm 5 µm Agilent ZORBAX Eclipse XDB-C18 column at 30 °C. A gradient of acetonitrile/water was used as eluent starting with 65:35 for 15 minutes; 100:0 at 30 minutes; 65:35 at 45 minutes and hold for 15 minutes with a flow of 1 ml/min. The HPLC system was calibrated using a commercial standard of DNPH carbonyl derivatives dilutes to 5 standards in a range of 10 to 50 mg/kg (concentration represented as non-derivatized carbonyl). The samples were extracted, derivatized and analyzed in triplicate.

VTT method

See VTT method 1 & 2, described in the furfural analysis.

Results

Firstly, the standards were measured with the methods. The calibration curves for each method were derived by plotting the areas of the standards against the concentrations. All methods gave calibration curves with good correlation coefficients. Subsequently, by extrapolating the area of the acetaldehyde peak and correcting for the dilution, the acetaldehyde concentration could be obtained. The results for the 5 FPBO's measured by each method is given in Table 5. As an example, a typical chromatogram obtained with the RuG method can be found in Fig. 7.

Table 5: Results of the acetaldehyde analysis

Samples	RuG (wt%)	VTT-1 (wt%)	VTT-2 (wt%)
Aged clean wood oil	0.15 ± 0.04	0.08 ± 0.00	0.11 ± 0.00
Fresh clean wood oil	0.24 ± 0.04	0.31 ± 0.01	0.44 ± 0.03
Clean wood oil after H2O removal	0.06 ± 0.01	0.01 ± 0.00	0.03 ± 0.00
Miscanthus oil	0.38 ± 0.01	0.44 ± 0.04	0.68 ± 0.02
Bark oil	0.53 ± 0.04	0.59 ± 0.04	0.90 ± 0.01

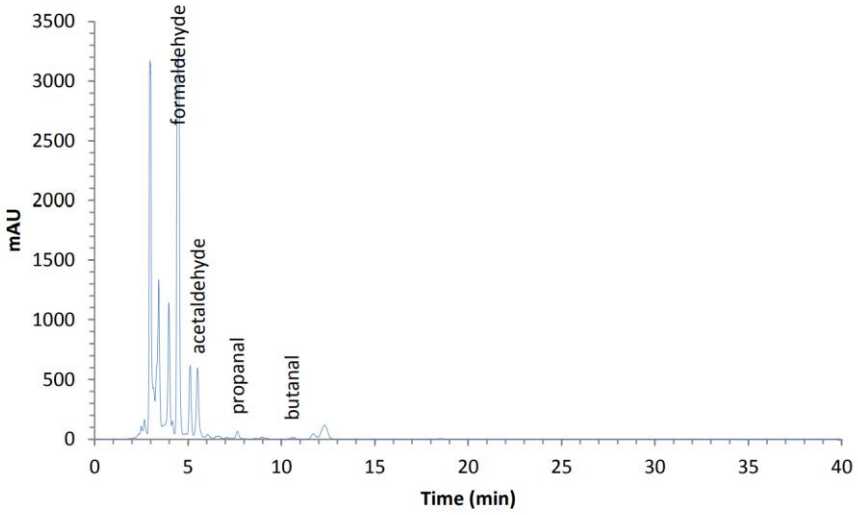

Fig. 7: A typical chromatogram of the acetaldehyde (in FPBO) analysis applying the RuG method

Acetaldehyde concentration in the range of 0.01-0.90 wt% were found in the oils and there is some difference in concentration between the different types of FPBO. In general, also here the highest concentrations were found in the miscanthus- and bark oil. The results obtained with the 3 methods do differ slightly although they seem to follow the same trend. The results obtained with the VTT-2 method are structural higher compared to the VTT-1 method.

PHENOL & CRESOL

Phenol and cresol can be found in pyrolysis oil. The phenolic monomers are produced from the lignin in the biomass. Lignin polymers contain a certain amount of ether bonds with their monomers (phenolics). These ether bonds are relative weak bonds and can readily be broken during the pyrolysis of biomass.

RuG method

The concentration of phenol and cresol was determined using an internal standard method. In this method 2,4,6-tribromophenol was used as the internal standard. The relative response factors (RRF) are determined singular with pure components (standards). The well homogenized FPBO samples were diluted 5x in tetrahydrofuran (THF). Subsequently the internal standard was added to the samples. The samples solutions were then filtered over a PTFE filter (0.2 µm pore size) to remove solid material and directly measured by GC-FID-MS equipped with a Restek Rtx-1701 60 m × 0.25 mm ID. 0,25 µm df column.

VTT method

See VTT method 2, described in the Furfural analysis (page 14).

Results

For both methods, the standards were measured first. For the RuG method the RRF was determined and for the VTT method calibration curves were prepared by plotting the areas of the standards against the concentrations. Subsequently, by applying the RRF or by extrapolating the area of the phenolic peaks and correcting for the dilution the concentration of individual phenolics could be obtained. The results for the 5 FPBO's measured by the VTT method are given in Table 6. With the RuG method, only a pine oil was analysed. As an example, a typical chromatogram obtained with the RuG method can be found in Fig. 8.

Table 6: Results of the acetaldehyde analysis; Concentrations in ppm.

Samples	Phenol	o-Cresol	m-Cresol	p-Cresol
Aged clean wood oil (VTT)	673	255	114	214
Fresh clean wood oil (VTT)	543	367	230	272
Clean wood oil after water removal (VTT)	656	407	262	312
Miscanthus oil (VTT)	1393	407	255	467
Bark oil (VTT)	783	453	325	364
Fresh clean wood oil (RuG)[1]	559	419	226	453

[1]: Fresh clean wood oil from other batch than used by VTT

Depending on the type of FPBO, the concentration of phenolics found in the oils ranges from 114-1395 ppm. With the RuG method only 1 sample was analysed and although this was a different sample as analysed by VTT, the results do not differ a lot and follow the same trend. In general, the highest concentrations of phenolics were found in the miscanthus- and bark oil. The lowest concentration of phenol was obtained in the fresh clean wood oils and the lowest concentration of cresol isomers in

the aged clean wood oil. The decrease in the cresol concentration in the FPBO during storage could be due to reactions of cresols with for instance reactive aldehydes. [6]

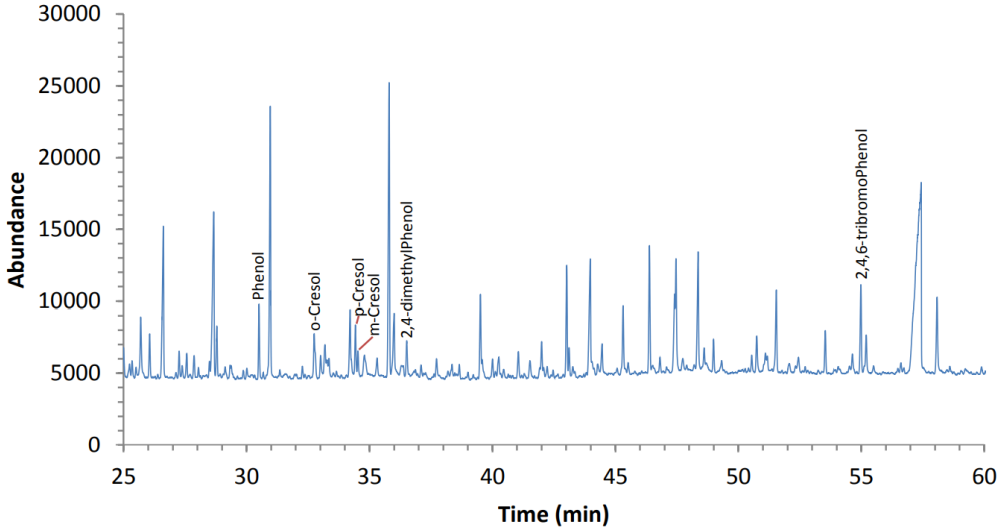

Fig. 8: A typical chromatogram of the phenolics (in FPBO) analysis applying the RuG method

FORMALDEHYDE

General

Formaldehyde is a flammable and strongly pungent smelling gas at ambient temperature, the boiling point of formaldehyde is -19 °C. At low temperature formaldehyde dissolves in non-polar solvents such as toluene, ether, etc. With increasing temperature, the solubility quickly reduces. Formaldehyde in polar solvents such as water, alcohols, acids, etc. can polymerize and/or react with the solvent. In aqueous solutions formaldehyde will primarily convert into methylene glycol, and the presence of free formaldehyde will be very low. It forms a clear solution with a strong pungent smell.

Formaldehyde is a toxic and reactive chemical and the main risk is exposure by inhalation. It can also be very sensitive to the skin, and it is genotoxic (DNA and RNA reactions) and carcinogenic. When inhaled, the formaldehyde directly reacts (absorbs very fast in moisture) with molecules on site of impact, meaning that it will mainly react/be absorbed in the respiratory organ(s), rather than being absorbed in the blood. As for inhalation, contact to the skin will result in reactions with the skin, and due to fast metabolisation it is not further penetrated into the body. In the EU, the maximum allowed concentration of formaldehyde in finished products is 0.2% (2000 ppm), and any product that exceeds 0.05% (500 ppm) must include a warning that the product contains formaldehyde[7]. In oral products the maximum concentration is 0.1 %. Formaldehyde and mixtures containing ≥ 0.1% (1000 ppm) are classified as a Carc. 1B substance(s). Furthermore, some formaldehyde releasers -which are substances or product emitting formaldehyde during use- can also be classified as Carc. 1B substances

[6] Diebold, J. P. A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-oils. In: Fast Pyrolysis of Biomass: A Handbook; Bridgwater, A. V. (ed.), CPL Press: Newbury, U.K, 2002, pp. 243-292

[7] ECHA investigation report Formaldehyde and formaldehyde releasers 15 March 2017. Available online https://echa.europa.eu/documents/10162/13641/annex_xv_report_formaldehyde_en.pdf/58be2f0a-7ca7-264d-a594-da5051a1c74b

depending on the concentrations emitted. Examples of these releasers are for instance different kind of formaldehyde-based resins used in wood based products, paint, coatings, etc.

As mentioned, in aqueous solutions formaldehyde will convert into methylene glycol. With respect to safety & toxicity is methylene glycol and formaldehyde should not be considered as equivalents. However, standard analytical methods cannot distinguish between both components. In 2014 Golden & Valentini[8] wrote a critical assessment on the properties and analysis of formaldehyde and methylene glycol. They emphasized that formaldehyde and methylene glycol are chemically and toxicologically certainly not equivalent.

Chemical Equilibrium

From a chemical point of view only small quantities of formaldehyde are present in water. The majority of formaldehyde is hydrated to methylene glycol and methylene glycol oligomers (n = 2–8 in $HO(CH_2O)_nH$), see Golden & valentini[8]. The equilibrium in water between monomeric formaldehyde and methylene glycol and derivatives is strongly directed to the hydration side. The presence of acids, a low temperature and/or high formaldehyde concentration will enhance the polymerisation. Methanol is often added to formaldehyde solutions to suppress/slow down the polymerisation into paraformaldehyde which would result in an insoluble polymer-precipitate. Similar to methylene glycol polymerization, formaldehyde can react with methanol forming water-soluble hemiformal and poly(oxymethylene) hemiformal molecules[9,10] as illustrated in Fig. 9.

Formaldehyde in aqueous solutions is in chemical equilibrium with methylene glycol (see also Eq. 1). Winkelman *et al*[11], calculated the chemical equilibrium constant of formaldehyde/methylene glycol in water (Eq. 2) by first determining the reaction rate constant of formaldehyde hydration via enhanced absorption of formaldehyde into water in a stirred tank reactor.[8]

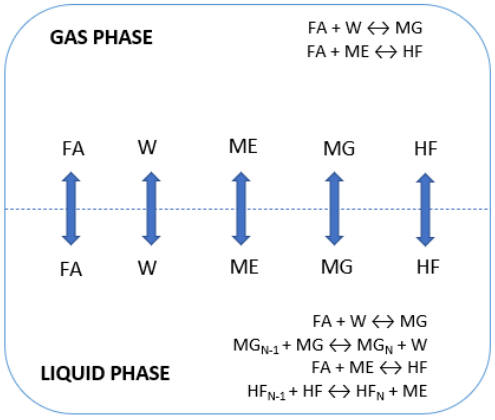

Fig. 9: Formaldehyde equilibria in water and gas phase
(FA=Formaldehyde, W=Water, ME=Methanol, MG=Methylene Glycol, HF=Hemiformal)

[8] R. Golden, M. Valentini, Formaldehyde and methylene glycol equivalence: Critical assessment of chemical and toxicological aspects, Regulatory Toxicology and Pharmacology 69 (2014) 178–186

[9] A review of the effects of formaldehyde release from endodontic materials, International Endodontic Journal, 48, 829–838, 2015

[10] Journal of Molecular Liquids 134 (2007) 58-63

[11] Winkelman et al, Chemical Engineering Science, 57 (2002), 4067-4076

$$CH_2O + H_2O \underset{k_d}{\overset{k_h}{\rightleftarrows}} CH_2(OH)_2 \qquad \text{(Eq. 1)}$$

$$K_h = \frac{k_h}{k_d} = \exp\left(\frac{3769}{T} - 5.494\right) \qquad \text{(Eq. 2)}$$

The results obtained by Winkelman *et al.* are shown in Fig. 2 (blue solid line) and fall well within the data of other researchers. In the same figure the experimental data from different resources are presented, and a trendline is shown (red solid line). The temperature range covered is roughly from 20 to 65 °C.

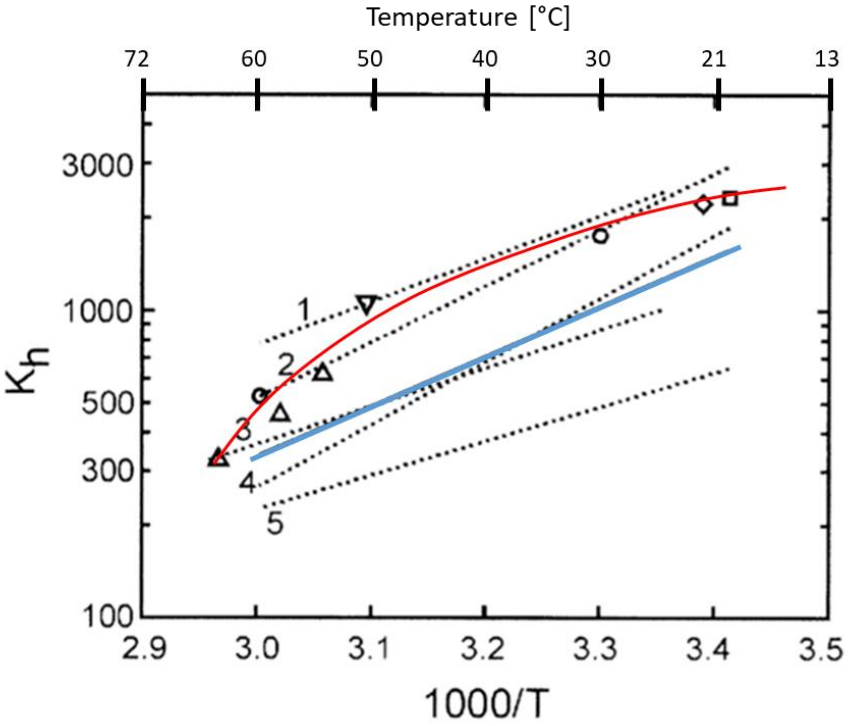

Fig. 10: Equilibrium data for FA-MG equilibrium (blue solid line) compared to literature data, and experimental data (red solid line).

More recently, Rivlin *et al.*[12] applied ^{1}H- and ^{13}C-NMR to determine a.o. the equilibrium constant of formaldehyde hydration and dimerization in aqueous solutions at various pH (2.1-7.4) and temperatures (273-333 K). An overview of the experimentally determined hydration and dimerization equilibrium constant as a function of temperature and pH is given in Fig. 11.

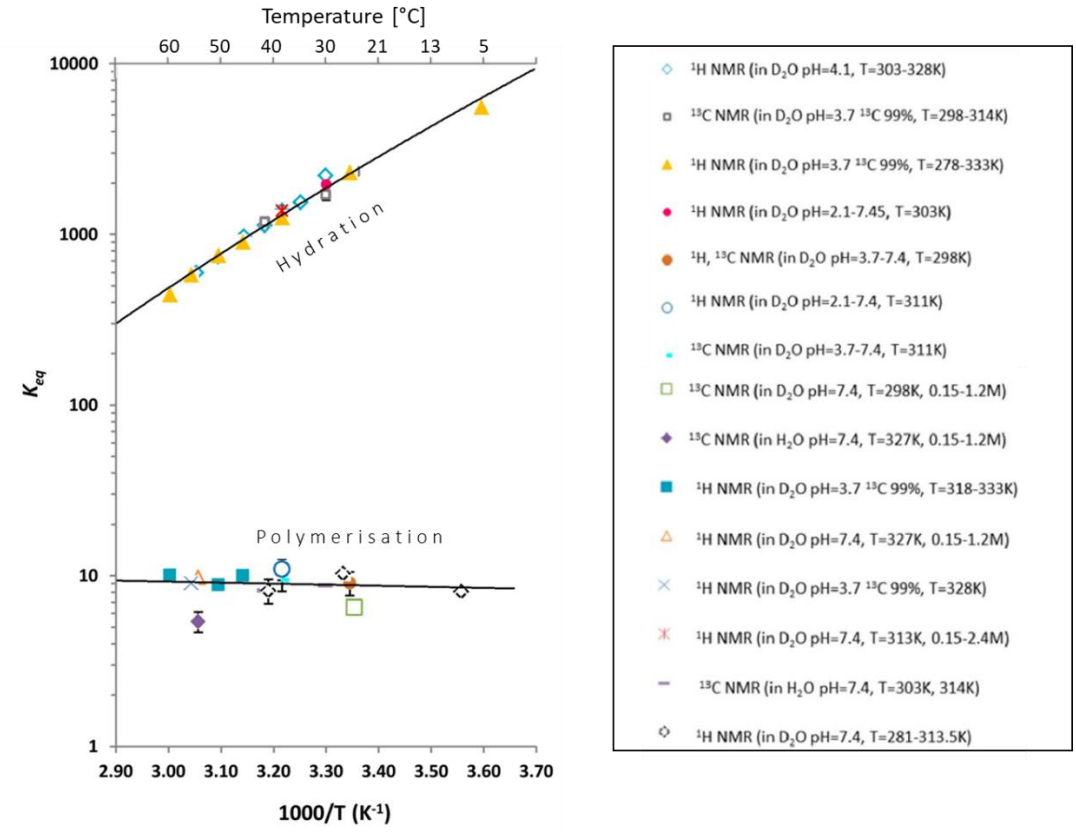

Fig. 11: Formaldehyde hydration and dimerization equilibrium constant as a function of the temperature and for varying pH (range 2.1 – 7.4)[12]

From these results it can be concluded that in particular the hydration equilibrium is temperature dependent, and the equilibrium constant decreases (less hydration) with increasing temperature. However, in all cases the hydrated form (i.e. methylene glycol) is strongly preferred. The polymerization equilibrium is less sensitive to temperature, and both equilibria are hardly influence by pH. The hydration equilibrium constants obtained by Rivlin *et al*[11]. are comparable to the data collected and calculated by Winkelman *et al*[13].

Summarizing -on basis of the data above- it is concluded that in an aqueous media, and for temperatures between of 5 to 65 °C the equilibrium between FA and MG is completely on the side of methylene glycol. The equilibrium constant ranges from 200-300 for high temperature (~ 65 °C) to more than 2,000 at room temperature. It means that the FA concentration is always at least a factor 200-300 lower than the MG concentration.

Formaldehyde analysis

Golden & Valentini[8] evaluated the analysis method for determining the FA content in aqueous media. Typically, a derivation method is applied using DNPH as derivatization agent; DNPH reacts quickly with FA to form DNPH-FA complex, and the latter one is actually analysed. To restore the equilibrium between MG and FA some MG will be converted to FA, and subsequently the FA will react with the

[12] Rivlin *et al.*, J. Phys. Chem. B, 2015, 119, 12, 4479-4487 – reproduced with permission from publisher.
[13] Winkelman et al, Chemical Engineering Science, 57 (2002), 4067-4076

excess DNPH. Ultimately, all MG is converted to FA and then reacts with DNPH to DNPH-FA. As a consequence, this analysis method determines FAMG, i.e. the sum of formaldehyde and methylene glycol.

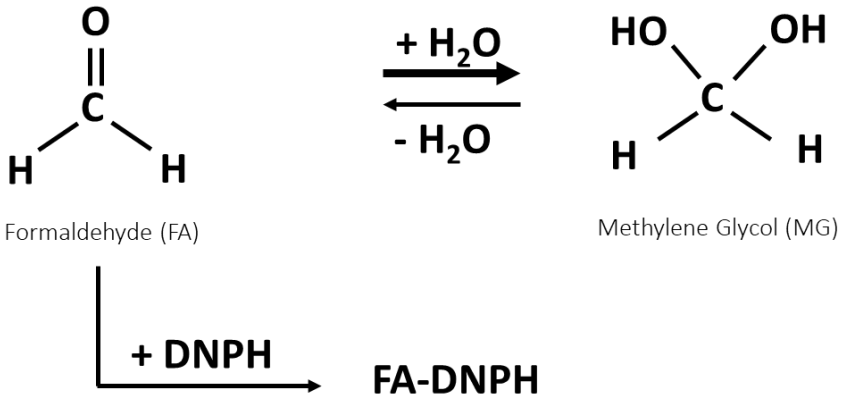

Fig. 12: DNPH derivatization of formaldehyde and methylene glycol

RuG method

The method is the same as used for acetaldehyde, see page 16.

VTT method

The method used is the same as used by VTT for Acetaldehyde, see page 14.

BTG method

The UV-VIS method was used to determine the formaldehyde- and formaldehyde derivatives (methylene glycol + oligomers) content in FPBO and fractions thereof. The method uses acetylacetone and ammonium acetate to form a complex (Diacetyldihydrolutidine) with formaldehyde and its derivatives[14],[15]. Prior to sample preparation, a reagent solution with and without acetylacetone was prepared (With: In a 100 ml VF (volumetric flask) with 25 ml of demi-water, dissolve 15 g of anhydrous ammonium acetate, 0.3 ml glacial acetic acid and 0.2 ml acetyl acetone and fill to the mark with demi-water. Without: In a 100 ml VF with 25 ml of demi-water, dissolve 15 g of anhydrous ammonium acetate, 0.3 ml glacial acetic acid and fill to the mark with demi-water). Subsequently, four formaldehyde standard solutions ranging in concentrations from 0.000-0.370 mg/l were prepared in 50 ml VFs to which also 5.0 ml of reagent solution incl. acetylacetone was added (and filled to the mark with demi-water). A sample solution was prepared by weighing 0.16 g of well homogenized FPBO in a 100 ml VF and adding 50 ml of demi-water. After placing the cap, the flask was gently swerved for 5 min and then placed in an ultrasonic bath for 5 min (at ambient T). Again, the flask was gently swerved for 5 min and filled to the mark with demi-water. The solution was then filtered by applying a plastic syringe and a suitable 0.45 µm filter. Subsequently, 0.5 ml of the filtered solution was pipetted into a VF of 50 ml and 5.0 ml of reagent solution with acetylacetone and 44.5 ml of demi-water was added. The sample reference solution was prepared by pipetting 0.5 ml of the filtered solution into a VF of 50 ml and adding 5.0 ml of reagent solution without acetylacetone and 44.5 ml of demi-water. All solutions (standards & samples) were then shaken for at least 15 s and immersed (whole flask with cap) in a thermostatic water bath set at 60 °C for 10 min, followed by

[14] Determination of Formaldehyde Content in Toys and Fabrics Using UV/Vis Spectrometry, https://www.perkinelmer.com/lab-solutions/resources/docs/APP__FormaldehydeInToysUVVis.pdf
[15] HAYUN et al., Orient. J. Chem., Vol. 33(3), 1400-1405 (2017)

cooling for 2 min in a cooling bath (0 °C). After cooling, the flasks were shaken again for at least 15 s. Absorbance measurements at 412 nm (λ of max. absorbance) were performed between 35-60 min from the time when the flasks were placed in the heated water bath. Absorbance measurements of the standard solutions were performed against water and the sample solutions were measured against their sample reference solutions. The solutions were measured by applying a double-beam Perkin Elmer, Lambda 25, UV/VIS spectrophotometer, and applying the UV WinLab V6.0 software package.

Results

Mini Round robin

RuG and VTT tested five similar FPBO samples of different origin in 2020. Back-up samples were stored at BTG in a freezer, and under these conditions aging will be very limited. In 2021, the same samples were used by BTG for the UV-VIS analysis. In Table 7, the results obtained by the RuG, VTT and BTG for the 5 FPBO's are given. Values are indicated as FAMG, i.e. the sum of methylene glycol and formaldehyde content. The FPBO with reduced water content, was the fresh clean wood oil treated in an evaporator under vacuum. Likely, due to the low boiling point of FA (BP=-19 °C) besides water also FA will be removed, and lower values are to be expected. Methylene glycol has a much higher boiling point (BP=194 °C) and its removal is unlikely.

Table 7: Experimental results of the mini Round Robin by RUG and VTT

Samples	FAMG meas. by RuG (wt%)[1]	FAMG meas. by VTT (wt%)[1]	FAMG meas. by BTG (wt%)[1]
Aged clean wood oil	1.27 ± 0.04	1.10 ± 0.01	1.25 ± 0.00
Fresh clean wood oil	1.85 ± 0.30	1.76 ± 0.12	1.84 ± 0.01
Clean wood oil after H2O removal	1.90 ± 0.25	1.52 ± 0.02	1.84 ± 0.02
Miscanthus oil	1.05 ± 0.03	0.83 ± 0.06	0.84 ± 0.02
Bark oil	1.49 ± 0.06	1.44 ± 0.05	1.35 ± 0.04

[1]: Total measured FAMG concentration (formaldehyde + methylene glycol).

Keeping in mind the complexity of the matrix, it is concluded that all 3 methods are giving similar results, and the methods are equally applicable to determine FAMG in FPBO. Reduction of FAMG concentration by evaporation is not effective, which is another indication that FAMG-content is mainly determined by MG concentration.

Formaldehyde concentration in FPBO

The data given in Table 7, concerns the total concentration of formaldehyde and methylene glycol (FAMG) in FPBO. Assuming chemical equilibrium between FA and MG is achieved the actual concentration of FA can be calculated. From the data presented in Fig. 10 and Fig. 11, the values presented in Table 8, can be derived showing the upper and lower values for the formaldehyde hydration equilibrium constant at 3 temperatures. K_{min} is the lowest value found (= highest FA concentration), K_{max} is the highest value, K_W is the value determined by Winkelman, and K_{exp} is the equilibrium constant according to experimental work.

Table 8: Formaldehyde hydration chemical equilibrium constants for different equilibrium temperatures based on Fig. 10 & Fig. 11.

Equilibrium	T = 20 °C	T = 40 °C	T = 60 °C
K_{min}	600	380	220
K_{max}	2,800	1,250	800
K_W	1,560	686	333
K_{exp}	2,100	1,200	450

The lower and upper values were taken to calculate the minimum and maximum (worse case) formaldehyde concentration in the FPBO samples of the mini-round robin. In Table 9 (RuG), Table 10 (VTT) and Table 11 (BTG), these calculated min and max formaldehyde concentration range are given. The lowest values are found at 20 °C and are often below 10 ppm. At 60 °C the formaldehyde concentration in FPBO can increase to almost 100 ppm.

Table 9: Minimum and maximum formaldehyde concentrations in FPBO calculated from RuG analysis data

Samples	FA calc. min-max at 20 °C (ppm)	FA calc. min-max at T 40 °C (ppm)	FA calc. min-max at 60 °C (ppm)
Aged clean wood oil	5-20	10-33	16-58
Fresh clean wood oil	7-31	15-49	23-84
Clean wood oil after H2O removal	7-32	15-50	24-86
Miscanthus oil	4-18	8-28	13-48
Bark oil	5-25	12-39	19-68

Table 10: Minimum and maximum formaldehyde concentrations in FPBO calculated from VTT analysis data

Samples	FA calc. min-max at 20 °C (ppm)	FA calc. min-max at 40 °C (ppm)	FA calc. min-max at 60 °C (ppm)
Aged clean wood oil	4-20	9-31	15-54
Fresh clean wood oil	7-34	16-54	26-93
Clean wood oil after H2O removal	6-30	14-47	22-80
Miscanthus oil	4-19	9-30	14-52
Bark oil	6-30	14-48	23-82

Table 11: Minimum and maximum formaldehyde concentrations in FPBO calculated from BTG analysis data

Samples	FA calc. min-max at 20 °C (ppm)	FA calc. min-max at T 40 °C (ppm)	FA calc. min-max at 60 °C (ppm)
Aged clean wood oil	4-21	10-33	16-33
Fresh clean wood oil	7-31	15-31	23-84
Clean wood oil after H2O removal	7-31	15-31	23-84
Miscanthus oil	3-14	7-22	11-38
Bark oil	5-23	11-36	17-61

FORMALDEHYDE IN THE VAPOUR PHASE

Concerning the potential exposure of humans to formaldehyde, the most likely route is through inhalation of formaldehyde from the gas phase. Formaldehyde is not only in equilibrium with different chemical components in the liquid phase, but also forms an equilibrium with the vapour phase above the liquid assuming a closed system and sufficient residence time.

Measurement of formaldehyde in the gas phase

To investigate the presence of formaldehyde in the gas phase, measurements were performed at BTG and at the Empyro FPBO production facility. To determine the presence of formaldehyde in the gas phase, a specialized company '*Strooming BV*' was hired to perform dedicated measurements. These measurements are conducted using small adsorption columns (orbo-24 tube) containing XAD-2 beads coated with 2-hydroxymethylpiperidine (Fig. 13). A measured amount of air is pumped for a certain period through the column. Formaldehyde is chemically adsorbed and reacts to form formaldehyde-oxazolidine. The total amount of formaldehyde-oxazolidine is measured and used to calculate the original formaldehyde concentration in the air. The objective of the measurements was to determine the formaldehyde exposure of employees during a normal working day. For these measurements, sample tubes were placed on the clothing of the employees close to mouth and nose to ensure the sample was representative for the air which is normally inhaled.

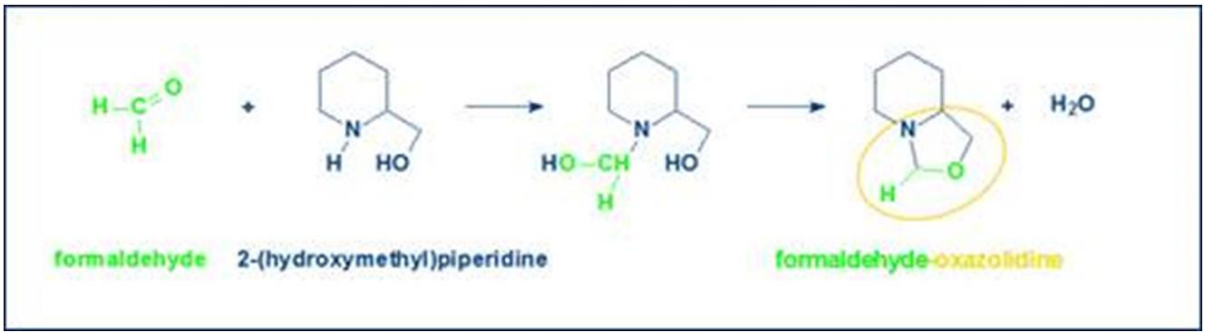

Fig. 13: Formaldehyde measurement from the gas phase

In addition, five 'worst-case' scenarios were tested where formaldehyde was measured in a specific environment, being:

1. A non-ventilated environment directly above stirred, heated (40°C) FPBO (Fig. 14).
2. A non-ventilated environment directly above stirred FPBO at room temperature.
3. A non-ventilated environment directly above a 1m^3 FPBO container which was closed for at least 1 month prior to the measurement (Fig. 15).
4. An environment open to the atmosphere in the Empyro pyrolysis plant where filters in the FPBO circulation loop are regularly changed.
5. An environment open to the atmosphere in the Empyro pyrolysis plant next to the large FPBO storage tank.

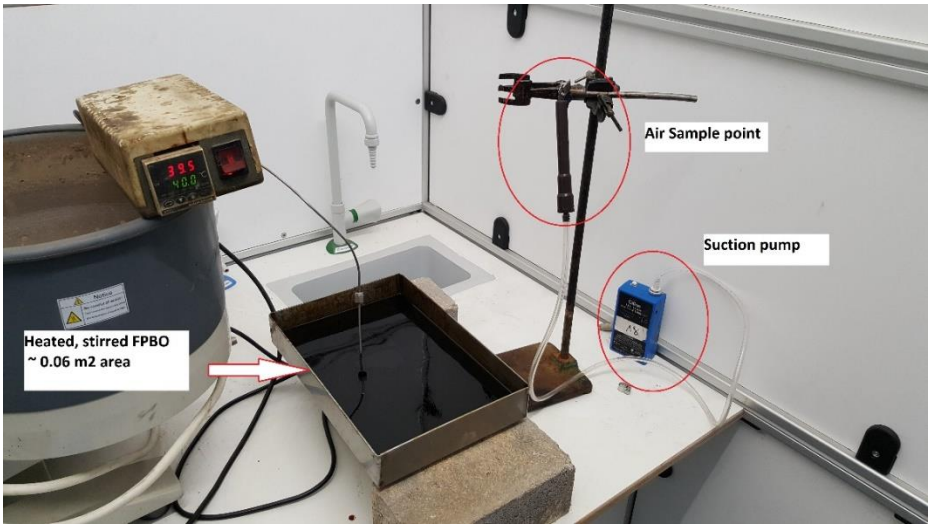

Fig. 14: photograph of formaldehyde measurement in the gas phase 'worst-case scenario 1'

Fig. 15: photograph of formaldehyde measurement in the gas phase 'worst-case scenario 3'

Results of the gas phase formaldehyde measurements

The results of the various measurements of formaldehyde in the gas phase on three employees during a normal working day are presented in Table 12. The exposure to formaldehyde in the gas phase is much lower than the maximum allowable, daily concentration of 0.15 mg/m^3 for each of the workers.

Table 12: Results of the dedicated formaldehyde measurements for three employees during a normal working day

Measurement	Time	Concentration mg/m^3	MAC value[A] mg/m^3	Pass?
Empyro plant operator	Daily limit (measured 11.7 hours)	< 0.034	0.15	**Yes**
BTG pilot plant operator	Daily limit (measured 5.5 hour)	< 0.0063	0.15	**Yes**
BTG laboratory personnel	Daily limit (measured 5.5 hour)	< 0.0062	0.15	**Yes**

[A] = Maximum Allowable Concentration – The Netherlands 2019.

The results of the five 'worst-case' scenarios are presented in Table 13. Here, the 'peak limit concentration' of 0.5 mg/m^3 is used as reference for the potential exposure to liquid FPBO assuming incidental activities, while the 'daily limit' is used for the locations in the Empyro plant where operators are regularly present.

Table 13: Results of the 'worst-case' scenarios to determine the presence of formaldehyde in the gas phase.

	Liquid FPBO Present?	Temp. Liquid.	Ventilation	Analysis Time	Measured Concentration	MAC value[A]	Pass?
		[°C]			[mg/m^3]	[mg/m^3]	
1	Yes	40	No	Peak limit (1 hour)	1.8	0.50 (15 min.)	**No**
2	Yes	25	No	Peak limit (7 hours)	< 0.59	0.50 (15 min.)	**No**
3	Yes	Ambient	No[B]	Peak limit (15 min.)	< 0.17	0.50 (15 min.)	**Yes**
4	Incidental[C]	~50	Yes ("outdoor")	Daily limit (13.3 hours)	< 0.031	0.15	**Yes**
5	No[D]	ambient	Yes ("outdoor")	Daily limit (13.3 hours)	< 0.027	0.15	**Yes**

[A] = Maximum Allowable Concentration – The Netherlands 2019.

[B] = no active ventilation, sample point located in large room (> 200 m^3)

[C] = during filter change some fresh-FPBO is present near the sample point, some minor FPBO spillage in leak-trays is continuously present.

[D] = some minor FPBO spillage in leak-trays is continuously present, in this area the tank-truck filling hoses are connected and disconnected to the storage tank.

Potential exposure to gas phase formaldehyde

The results of the gas phase formaldehyde measurements show that during a normal workday, the exposure of the employees is far below the maximum allowable concentration. Only, when worst-case scenarios are created to investigate the potential exposure to formaldehyde in the gas phase, results show that the peak limits to which workers may be exposed can be exceeded. To prevent exposure to formaldehyde in the gas phase, FPBO should be kept in closed systems and containers as much as possible. In case some handling is needed, for example when changing FPBO-filters or cleaning containers, proper ventilation (e.g. fume box) is crucial to prevent exposure to gas phase formaldehyde. Only in case personnel performing the activity cannot be physically separated from the area where FPBO is handled, suitable personal protection devices should be used. For formaldehyde in FPBO, filter type A2B2E2K2HgP3 for example is suitable.

Non-Polar compounds in FPBO

In the FPBO REACH registration restrictions are included on the concentration of non-polar organic compounds or more specifically on poly aromatic hydrocarbons (PAHs). In this chapter the determination of these compounds in FPBO is discussed & evaluated. This evaluation is based on a compilation of analysis results obtained in multiple projects, no round robin was executed.

POLY AROMATIC HYDROCARBONS (PAH)

PAHs are poly aromatic hydrocarbons, which can be formed by the incomplete combustion or high temperature pyrolysis of materials such as biomass, plastics and fuels. PAHs are also naturally occurring, e.g. in coals or formed during forest fires and volcano eruptions. PAHs are complex fused aromatic ring structures with the simplest being naphthalene and they are notorious of having carcinogenic and/or mutagenic effects on the human body. The PAHs belonging to PAH1 and PAH13 are shown in Fig. 16. Typically, PAH's are highly non-polar and therefore have a relative low solubility in water.

From literature it is known that in general fast pyrolysis oils have a low total PAH's concentration of below 35 ppm (PAH-13), slow pyrolysis oils tend to have much higher concentrations (100 ppm). Not only the residence time, but also the temperature applied in pyrolysis is an important factor on PAH's formation. Especially at temperatures above 700 °C, significant quantities of PAH's are being formed due to secondary thermochemical reactions[16,17]. Apparently, the cellulose structures in biomass tend to produce more PAH's via the decomposition of char than lignin's do[18].

PAH'S TOXICITY AND REGULATIONS

Frequently encountered PAH's are the PAH's in the so called PAH-16 group (see Fig. 16), which are known to be of serious health safety concern. The PAH-16 were first identified by the US-Environmental Protection Agency in the seventies and these 16 PAHs are therefore often referred to as the 16-EPA-PAHs[19]. The most important PAHs of this group in terms of toxicity are; benzo[*a*]pyrene (group 1B), naphthalene, crysene, ben[*a*]anthracene, benzo[*k*]fluoranthene and benzo[*b*]fluoranthene (group 2B), these are carcinogenic or highly suspected of being carcinogenic.

[16] http://www.euro.who.int/data/assets/pdf_file/0015/123063/AQG2ndEd_5_9PAH.pdf
[17] M. Garcia-Perez, The formation of Polyaromatic Hydrocarbons and Dioxins During Pyrolysis, Washington State University, June 2008: https://research.libraries.wsu.edu/xmlui/bitstream/handle/2376/5966/TheFormationOfPolyaromaticHydrocarbonsAndDioxinsDuringPyrolysis.pdf?sequence=1&isAllowed=y
[18] Daniele Fabri *et al.*, GC-MS determination of polycyclic aromatic hydrocarbons evolved from pyrolysis of biomass, Anal. Bioanal. Chem., 2010, p309-317
[19] Chen Jing, Determination of PAHs in Edible Oils by DACC-HPLC with Fluorescence Detection, Application note, 2016, available at: https://tools.thermofisher.com/content/sfs/brochures/AN-196-LC-PAHs-Edible-Oils-AN71492-EN.pdf

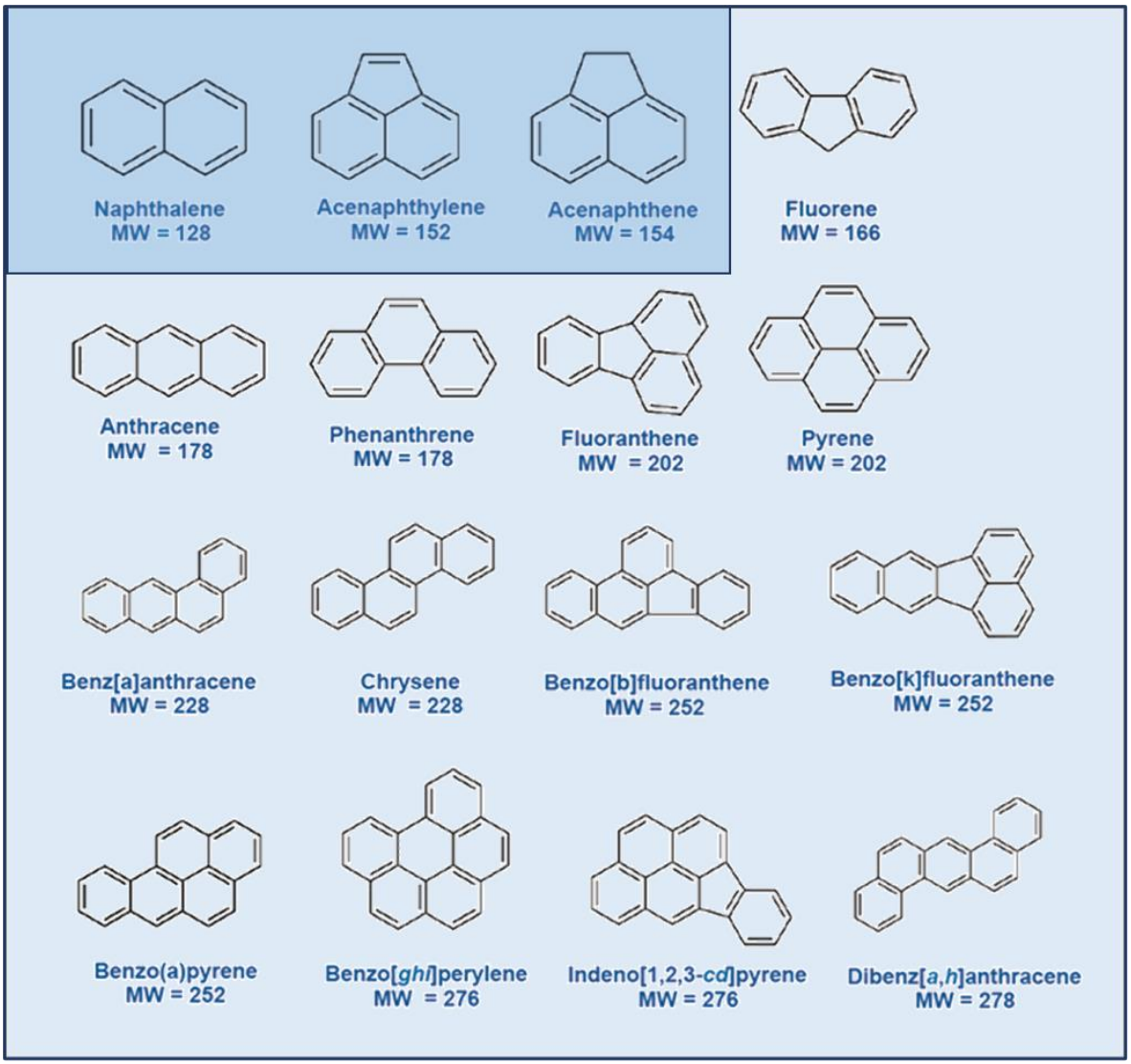

Fig. 16: Chemical structure of the PAH16 compounds. In PAH13 napthalene, acenapthalene and acenapthene are excluded.

PAH'S ANALYSIS

Standard PAH-analysis applied e.g. for bitumen, water samples, liquid smoke or foodstuffs, are mainly based on HPLC- or GC-methods. In HPLC often fluorescence is used for detection, since most PAH's emit light of a certain wavelength when excited. Also UV detection is used in the analysis of PAH's by HPLC, because PAH's show very characteristic UV-spectra. Often the two detection methods are also combined in the analysis of PAH's by HPLC. The GC methods applied to do PAH's analysis are typically based on GC-MS combined with GC-FID or by GC-MS-SIM. In the combination of MS and FID, the MS-detector is used to qualify the components, and subsequently the FID applied for further quantification. In the GC-MS-SIM analysis, a MS is used for both qualification and quantification by applying the single ion monitoring mode. This means that when a component is ionized, characteristic fragments are produced in specific amounts. Qualification is done by comparing these ion fragments (qualifier ions) to the library, and quantification is performed by using the peak area of the most

abundant ion fragment (quantifier) to calculate the concentration (by applying standards)[20,21,22,23,24]. FPBO is extremely complex and due to this GC-MS-SIM is preferred as the method to be applied.

EXPERIMENTAL ANALYSIS WORK

Goals and purpose

It is well-known that standard analysis methods are not always applicable to FPBO due to its chemical complexity, and validation of methods is highly preferred or desired. In this contribution, experimental work on PAH's analysis by different laboratories and with different FPBO samples is given.

HPLC method: HPLC1&2 Eurofins/ACMAA

PAH's HPLC analysis was performed by a commercial Laboratorium (Eurofins/ACMAA). The HLPC method used was based on a standard HPLC method (PAH-16), typically used for PAH's analysis of wastewater. In this standard method (**HPLC1**), a FPBO sample is dissolved in acetone and this mixture is then further diluted with a substantial amount of water and extracted with petroleum ether. The petroleum ether is subsequently removed and the remaining components (PAH's) are dissolved in acetonitrile and analyzed. During analysis applying HPLC1, it was observed that due to severe overlapping of countless peaks in the obtained chromatogram reliable values for the PAH's concentration could not be obtained. There was a strong indication that a.o. phenolic components were co-extracted and possibly overlapping PAH's peaks in the HPLC-chromatogram. After consultation with the Laboratorium, it was decided to adapt the method by replacing the acetone and water by a 1 mol/l NaOH-solution followed by the petroleum ether extraction (**HPLC2**). Phenolics are weak acids and therefore largely retain in the NaOH-solution rather than being dissolved/extracted in the petroleum ether.

GC-MS-SIM method: GCMS1 (Nablabs)

The GCMS1 method is a GC-MS-SIM (single ion monitoring) method used by the laboratory (Nablabs) who performed all the FPBO analysis (polar and non-polar compounds) for the establishment of the SIP profile (Table 1) of FPBO, The PAH's method used by this laboratory is an adapted method based on the method developed in the BIOTOX-project[25] (**Biotox method**). The main difference between the two methods lays in the sample preparation. In the BIOTOX method the samples were extracted with cyclohexane after dissolving the FPBO in a NaOH-solution. In the new method the FPBO was extracted with n-hexane. Also a different sample clean-up and different internal standards were used. The reason for this adaptation is not entirely clear. The SIM (single ion monitoring) mode implies that when a component is ionized, characteristic fragments are produced in specific amounts. In the SIM mode, these most abundant fragments are used to qualify and quantify the component. Qualification is done by comparing these ion fragments (qualifier ions) to the library, and quantification is done by using the peak area of the most abundant ion fragment (quantifier) to calculate the concentration (by applying standards).

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[25] BioTOX - an assessment of bio-oil toxicity for safe handling and transportation, contract NNE5-2001-00744, Sept 2005. https://task34.ieabioenergy.com/wp-content/uploads/sites/3/2017/04/BIOTOX-Final-Publishable-report.pdf

GC-MS-SIM method: GCMS2 (RuG)

This method was developed most recently and is adapted based on the GCMS1 method. The FPBO samples are first dissolved in ethanol, then four deuterated internal standards are added and subsequently this liquid is extracted with n-hexane and washed with DMSO. The PAH-compounds are analysed from the cleaned n-hexane extract using Gas-Chromatography-Mass Spectrometry (GC-MS) running in SIM (single ion monitoring) mode. For all PAH's the relative response factors (RRF) were determined by making a 5-point calibration line in which the amount of internal standard is kept constant. For each PAH, the peak area is determined and divided by the peak area of the internal standard. Similar to the areas also the concentrations are divided by the concentration of the internal standard. Then the values are plotted (concentration against area) in a graph with the obtained slope being the RRF.

The recoveries of the PAH components by applying GCMS2 were determined, this was done by spiking samples with known amounts of individual components. The recoveries of the PAH's are given in Table 14: Recovery of PAH's, GCMS2 method (RUG). In general, the recovery values obtained are deviating (from 100%) to some extent, but these deviations are comparable to data found in literature for comparable PAH's analysis with similar techniques[26].

Table 14: Recovery of PAH's, GCMS2 method (RUG)

No:	Component	Recovery %
1	Fluorene	120
2	Phenantrene	80
3	Anthracene	88
4	Fluoranthene	88
5	Pyrene	86
6	Benzo[a]anthracene	106
7	Chrycene	97
8	Benzo[b]fluoranthene	105
9	Benzo[k]fluoranthene	110
10	Benzo[a]pyrene	109
11	Indeno[1,2,3-cd]pyrene	196, 136[1]
12	Dibenzo[a,h]anthracene	113
13	Benzo[g,h,i]perylene	104
14	Naphtalene	74
15	Acetnaphtylene	84
16	Acetnaphtene	148

[1]: After adaption of internal standard concentration (adding more spike component)

[26] Rupert Simon *et al.*, Composition and analysis of liquid smoke flavouring primary products, J. Sep. Sci., 2005, 28, p871-882

RESULTS

A complete overview of the results of the PAH's analysis performed with four methods on different pyrolysis oil samples are given in Table 15. For comparison, also the results of PAH's analysis obtained in the BIOTOX project of 2 typical pyrolysis oils are given (column 1&2). A pyrolysis oil produced by Empyro was analysed by applying the HPLC1 method (column 3). The analysis showed unexpected high values for Phenanthrene (38 ppm), Chrysene (9.17 ppm) and Naphtalene (10.00 ppm). Compared to the typical data obtained in the BIOTOX project (column 1&2), the values obtained with the HPLC1 method seem very high. Further evaluation of the obtained data and chromatograms strongly indicated overlap of the PAH peaks (similar retention time) by presumably phenolic components. The phenolic components are probably co-extracted due to the use of acetone to make the FPBO soluble in water. The acetone might facilitate the transfer of phenolics to the petroleum ether in the subsequent extraction.

The HPLC2 method is a modified method in which the use of acetone and water is replaced by a NaOH-solution. The hypothesis here was that when FPBO is dissolved in a NaOH-sol and followed by the extraction with petroleum ether, the lignin derived phenols (being weak acids) will largely remain in the watery phase. When comparing the data obtained with HPLC1 and HPLC2 for the PAH's-13 and PAH's-16, it can clearly be observed that the amount of PAH's is roughly reduced by > 60% when applying the modified method. The large reduction is mainly caused by the large drop of the phenantrene concentration (from 38.3 ppm → 6.5 ppm). Nevertheless, compared to the BIOTOX data, the values for PAH-13 and PAH-16 obtained with HPLC2 are still relatively high, but well within the specifications given in the REACH registration.

Two samples were analysed by an external lab using the GCMS1 method, namely an oil produced by BTG and an oil produced by Empyro (column 5&6). Remarkable in these measurements are the relative high values obtained for fluorene and naphthalene (24.6 ppm and 39.5 ppm) in the BTG sample compared to the values found using the other methods and the BIOTOX data. The high fluorene value contributes to almost 60% of the total PAH-13 and the naphthalene to 40% of the total PAH-16. In the BIOTOX project, 21 different FPBO's were analysed for PAH-13, none of the FPBO samples showed comparable high concentrations for fluorene (highest observed: 5 ppm). Only for a slow pyrolysis oil sample a fluorine value of 39.0 ppm was obtained. In view of the SIP profile (Table 1

), the high value for fluorene is much more of a concern here than that of naphthalene. Here it is also likely that a component (phenols) other than the PAH contributes to this relative large value. The Empyro sample analysed applying the GCMS1 method did not show any deviating results. The values obtained comply with the specifications for the maximum PAH-13 content in FPBO (< 35 ppm).

Based on the uncertainties in the results described above, it was decided to initiate a dedicated activity to further develop the PAH analysis method and include a validation of the method by spiking the FPBOs with known quantities of the PAH components. This ultimately resulted in the GCMS2 method described on the previous page.

In Table 15, the samples given in column 7-14 were analysed using the GCMS2 method. From the table it can be seen that especially the value for dibenz[a,h]anthracene in the Empyro sample is higher compared to all other analysis performed. When analysing measured data, it is important to check the ratio(s) of qualifier and quantifiers (calculated from the standards), if this value is deviant to the theoretic value for that certain component, overlapping of ion fragments by other present components might be interfering the results. This means that the PAH peak in the chromatogram probably contains another component which has the same retention time and gives the same ion-fragments, which is most likely the case with dibenz[a,h]anthracene.

In addition, FPBOs produced from different types of biomass have been analysed. Some variations can be observed in the PAH13 content in these oils, but generally, the values are rather low and all

of them within the specifications give in the REACH registration.

For Benzo[a]pyrene and Dibenzo[a,h]anthracene individual limits have been specified, and in the SIP table concentrations of less than 0.01 wt.% (100 ppm) are given. When the measured value for PAH-13 does not exceed the max concentration of 35 ppm, automatically the specifications for Benzo[a]pyrene and Dibenzo[a,h]anthracene are fulfilled as well.

Table 15: Analysis performed of different samples and methods

Samples and applied methods[1]															
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
PAH No:	Component (mg/kg)	Pine S BIOTOX	Beech BIOTOX	Empyro HPLC1	Empyro HPLC2	BTG GCMS1	Empyro GCMS1	Empyro GCMS2	Grass GCMS2	Bark GCMS2	Miscanthus GCMS2	Forest R GCMS2	Wheat S GCMS2	Sawdust GCMS2	Sunflower GCMS2
1	Fluorene	0.89	2.81	1.92	1.40	24.6	1.6	4,1	6.0	8.5	2.6	6.0	3.0	3.5	5.9
2	Phenanthrene	0.46	0.97	38.33	6.49	7.75	1.0	1,9	3.8	5.4	1.9	2.8	0.9	2.0	3.5
3	Anthracene	0.15	0.29	1.58	3.84	2.13	0.2	0,9	<0.0	<0.0	<0.0	<0.0	0.3	<0.0	1.1
4	Fluoranthene	0.11	0.35	3.83	1.85	1.75	0.4	0,5	1.3	1.7	0.5	1.2	0.2	0.5	1.3
5	Pyrene	0.18	0.35	3.42	1.95	2.76	0.4	0,7	2.0	2.3	1.0	1.7	0.3	0.6	1.3
6	Benzo[a]anthracene	0.02	0.06	3.58	1.35	1.68	0.1	1,4	4.5	7.5	3.2	4.7	0.4	2.0	5.6
7	Chrysene	0.03	0.10	9.17	4.94	0.871	0.1	0,1	0.8	1.4	0.5	0.7	0.2	0.8	0.6
8	Benzo[b]fluoranthene	0.03	0.03	1.17	0.02	Nd	0.1	0,6	<0.0	1.2	0.3	0.6	0.1	0.4	0.2
9	Benzo[k]fluoranthene	0.03	0.01	0.08	0.02	Nd	0.1	0,9	<0.0	0.4	<0.0	0.2	<0.0	<0.0	0.1
10	Benzo[a]pyrene	0.04	0.47	0.23	0.11	Nd	0.1	1,0	0.7	0.9	0.3	0.5	0.2	0.3	0.2
11	Indeno[1,2,3-cd]pyrene	0.01	0.03	0.08	0.02	Nd	0.1	0,4	<0.0	1.6	0.4	0.6	0.3	1.0	<0.1
12	Dibenzo[a,h]anthracene	Nd	Nd	0.21	0.02	Nd	0.1	8,0	0.5	0.7	<0.0	0.2	0.1	0.5	5.7
13	Benzo[g,h,i]perylene	0.02	0.03	0.08	0.02	0.221	0.1	0,7	0.7	2.1	<0.0	0.5	0.3	1.3	<0.1
	Tot. PAH13	**2.0**	**5.5**	**63.7**	**22.0**	**41.8**	**4.4**	**21.2**	**20.3**	**33.7**	**10.7**	**19.7**	**6.3**	**12.9**	**25.7**
14	Naphthalene	-	-	10.00	8.48	39.5	2.3	4,0	2.4	5.5	2.8	4.0	1.9	4.1	9.8
15	Acenaphthylene	-	-	0.42	0.09	7.14	0.3	0,8	1.1	1.6	0.5	0.9	0.7	0.5	0.7
16	Acenaphthene	-	-	1.17	0.60	10.1	0.3	1,4	2.1	3.1	1.0	2.4	1.1	1.1	1.8
	Tot. PAH16	**-**	**-**	**75.3**	**31.2**	**98.5**	**7.3**	**27.4**	**25.9**	**43.9**	**15.0**	**27.0**	**10.0**	**18.6**	**38.0**

[1]:

Conclusions

The polar compounds considered are formaldehyde, acetaldehyde, methanol, furfural, phenol and cresol. Different analysis methods have been applied by VTT, University of Groningen (RUG) and BTG to measure the concentrations of these compounds in FPBOs of different origin or -treated after production in different ways (e.g. dewatering, ageing). Considering the complexity of measuring individual components in FPBO the agreement between the measuring methods is acceptable. Formaldehyde in aqueous media is in equilibrium with methylene glycol, and chemical and toxicological properties are completely different. However, analytical methods are using DNPH, PFBOA or acetyl acetone (+ ammonium acetate) as derivatizing agent and both formaldehyde and methylene glycol will be measured simultaneously without any selectivity. Therefore, the actual concentration is calculated using the equilibrium constant and the concentration of formaldehyde and methylene glycol together. For all the FPBOs tested the calculated value for formaldehyde concentration is always below 100 ppm for temperatures between 20 and 60 °C.
Additionally, the formaldehyde concentration in the atmosphere around fast pyrolysis units was measured. Under normal working conditions and proper pre-cautions, the formaldehyde concentration is always well below legal exposure limits. Only in open vessels, directly above the surface of (heated) pyrolysis oil the formaldehyde concentration could exceed allowable limits. Obviously, such situation can be easily prevented.

The specific non-polar compounds in FPBO refer to the poly-aromatic hydrocarbons (PAHs) and more in particular the EPA PAH13. The starting point were the different analytical methods known from literature for measuring PAHs in FPBO. RUG & BTG have evaluated these methods and further improved them. A specific challenge is to avoid the co-extraction of phenolic compounds as these compounds result in severe interference/overlap with PAH compounds in the HPLC/GC chromatograms, and consequently in overestimating the PAH concentrations. Eight different oil samples produced from different feedstocks were analyzed using the GCMS2 method. Although there are still some indications of potential peak overlap, the actual concentrations of PAH13 in all the oils did not exceed the maximum allowable level given in the SIP.

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