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Rapeseed oil methyl ester pyrolysis: On-line product analysis using comprehensive two-dimensional gas chromatography

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ABSTRACT

Thermochemical conversion processes play a crucial role in all routes from fossil and renewable resources to base chemicals, fuels and energy. Hence, a fundamental understanding of these chemical processes can help to resolve the upcoming challenges of our society. A bench scale pyrolysis set-up has been used to study the thermochemical conversion of rapeseed oil methyl ester (RME), i.e. a mixture of fatty acid methyl esters. A GC × GC, equipped with both a flame ionization detector (FID) and a time-of-flight mass spectrometer (TOF-MS), allows quantitative and qualitative characterization of the reactor feed and product. Analysis of the latter is accomplished using a dedicated high temperature on-line sampling system. Temperature programmed analysis, starting at −40 °C, permits effluent characterization from methane up to lignoceric acid methyl ester ($C_{25}H_{50}O_2$), in a single run of the GC × GC. The latter combines a 100% dimethylpolysiloxane primary column with a 50% phenyl polysilphenylene-siloxane secondary column. Modulation is started when the oven temperature reaches 40 °C, thus dividing the chromatogram in a conventional 1D and a comprehensive 2D part. The proposed quantification approach allows to combine the quantitative GC × GC analysis with 2 other on-line 1D GC analyses, resulting in a complete and detailed product composition including the measurement of CO, CO_2, formaldehyde and water. The GC × GC reveals that the product stream contains a huge variety of valuable products, such as linear alpha olefins, unsaturated esters and aromatics, that could not have been identified and quantified accurately with conventional 1D GC because of peak overlap.

1. Introduction

At an ever increasing pace, environmental, economic, geopolitical and ethical concerns related to the use of fossil resources drive the chemical industry to speed up the transition from fossil to renewable resources. Investments in innovation, in particular through an accelerated introduction of clean technologies, are rapidly taking off and promise to become an engine for economic growth. Recently, the term 'Cleantech' has been introduced to refer to clean technologies, i.e. products, processes and services enabling to optimize the use of natural resources while minimizing its environmental impact. Recent advances in genetics, biotechnology, process chemistry, and chemical engineering are leading to new routes to produce valuable fuels and products from biomass.

The term biomass refers to all organic material that comes from plants, trees, crops, and algae, including wood, short-rotation woody crops, agricultural wastes, short-rotation herbaceous species, wood wastes, bagasse, industrial residues, waste paper, municipal solid waste, sawdust, bio-solids, grass, waste from food processing, aquatic plants and algae animal wastes, and a host of other materials. Wood residues, forest residues and bagasse are the most interesting short term biomass resources with the smallest ecological footprint. But also vegetable oils originating from algae seem to have high potential for replacing fossil resources. However, large-scale implementation of biomass technologies is hindered by a number of adverse biomass properties causing difficulties or excessive costs in its processing [1]. Such problems are its low annual yields, usually less than 10 ton per hectare (dry and ash-free), as well as in the wide variety in biomass structure and energy density [1]. For lingocellulosic biomass these disadvantages

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can be overcome by thermochemically converting the biomass into a uniform, liquid intermediate – so-called bio-oil – that is virtually ash-free and has a significantly increased energy density. Marsman and co-workers [2–4] were the first to recognise the potential of the GC × GC technique for the off-line analysis of thermochemically produced bio-oils. These authors focused on comparing the GC × GC data from the pyrolysis oil and the upgraded products to gain information on the chemical reactions taking place during upgrading. Moreover, the identification and quantification of complex mixtures of hydrocarbons and other heteroatom-containing compounds that range from small, volatile compounds to large, non-volatile ones is also important for crude-oil [5] or its fractions [6,7]. The advantages of GC × GC compared to conventional 1D-GC for these types of applications have been widely reported. The use of GC × GC results in enhanced peak capacity [8,9] and high sensitivity [10,11]. In particular the ordered retention of structurally related components is exceptionally useful, since it enables a more straightforward classification and identification of components based on their appearance in the two-dimensional separation space.

As stated previously triglyceride based biomass feedstocks and in particular microalgae are considered one of the long term alternatives for replacing fossil fuel because of their rapid growth and high oil content. Microalgae commonly double their biomass within 24 h. Biomass doubling times during exponential growth are commonly as short as 3.5 h, while the oil content in microalgae can exceed 80% by weight of dry biomass [12]. Conversion of algae, vegetable oils and animal fats composed predominantly of triglycerides using pyrolysis type reactions represents a promising option for the production of renewable fuels and chemicals [13]. Several GC × GC studies have been performed on the characterization of triglycerides, fatty acid methyl esters (FAME) and their mixtures [14–19]. However, none of them has looked at the pyrolysis liquid and gas fraction formed when using triglycerides or FAME's. Moreover, in all the previously discussed applications GC × GC is only used for off-line analysis of fractions, although its superior separation power makes it potentially one of the most suited analytical methods for on-line analysis of product streams originating from biomass. On-line sampling is in particular important when studying processes occurring at high temperatures because of the risk of secondary reactions (e.g. from dienes [20]) and unwanted transformations of the thermochemically produced product stream. This can lead to significant error bars on the measured composition, not to speak about sampling issues. Therefore in this work the thermochemical conversion of a rapeseed oil methyl ester, i.e. a FAME mixture produced by transesterification of rapeseed oil, has been investigated on a bench scale pyrolysis set-up. A dedicated on-line GC × GC set-up, equipped with both a time-of-flight mass spectrometer (TOF-MS) and a flame ionization detector (FID), has been incorporated into the analysis section of the pyrolysis set-up, enabling detailed characterization of the pyrolysis product.

2. Experimental

2.1. GC × GC-FID/TOF-MS setup

The GC × GC setup, shown schematically in Fig. 1, was built from a Thermo Scientific TRACE GC × GC, obtained from Interscience Belgium and has been discussed previously [21]. The columns, i.e. a typical non-polar/medium-polar column set, and the modulator, i.e. a two-stage cryogenic modulator (liquid CO_2) [22], are positioned together in a single oven. An overview of the GC × GC settings used in this work is given in Table 1.

The setup is equipped with both an FID and a TEMPUS TOF-MS (Thermo Scientific, Interscience Belgium). A built-in switching system, i.e. a 4 port 2 way valve (VICI AG International, Switzerland), allows to switch between FID and MS without the need to cool down and vent the TOF-MS [21].

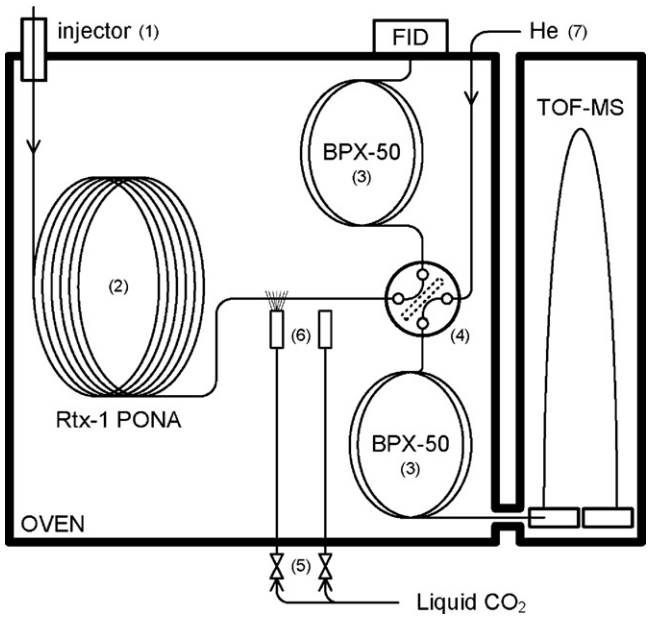

Fig. 1. Schematic overview of the GC × GC-FID/TOF-MS setup (1: split/splitless injector, 2: primary column, 3: secondary column, 4: manual 4-port 2-way valve, 5: solenoid valves, 6: two stage cryogenic modulator, 7: protective helium flow) [21].

2.2. Pyrolysis set-up

The bench scale pyrolysis set-up, shown schematically in Fig. 2, consists of three parts: the feed section, the furnace/reactor section and the analysis section [23,24].

2.2.1. Feed, furnace and reactor section

As shown in Fig. 2, the reactor feedstock, i.e. a FAME mixture in this work, is pumped towards an evaporator using a peristaltic pump (Heidolph, Germany). The constant flow rate of the feed is calibrated using an electronic balance. The diluent, i.e. N_2 in this work, is heated to the same temperature as the evaporated feed. Both the evaporators/heaters and the mixer are electrically heated quartz beads filled units, enabling a smooth evaporation of the feed and uniform mixing of feed and diluent. The flow rate of the latter is controlled by a coriolis mass flow controller (Bronkhorst, The Netherlands). For the experiments discussed here a dilution of 10 moles N_2 per mole FAME was used.

Table 1
GC × GC settings for off-line and on-line analysis.

Detector	FID, 300 °C	TOF-MS, 35–400 amu
Injection		
Off-line analysis	0.2 μl, split flow 150 ml/min, 250 °C	
On-line analysis	250 μl (gas), spiltless, 250 °C	
Carrier gas	He, constant flow (2.1 ml/min)	He, constant flow (1.6 ml/min)
Primary column	Rtx-1 PONA[a] (50 m × 0.25 mm × 0.5 μm)	
Secondary column	BPX-50[b] (2 m × 0.15 mm × 0.15 μm)	
Oven temperature		
Off-line analysis	50 → 340 °C (3 °C/min)	
On-line analysis	−40 (4 min hold) → 40 °C (5 °C/min) → 340 °C (4 °C/min)	
Modulation period		
Off-line analysis	4 s	
On-line analysis	5 s	

[a] Dimethyl polysiloxane (Restek).
[b] 50% Phenyl polysilphenylene-siloxane (SGE).

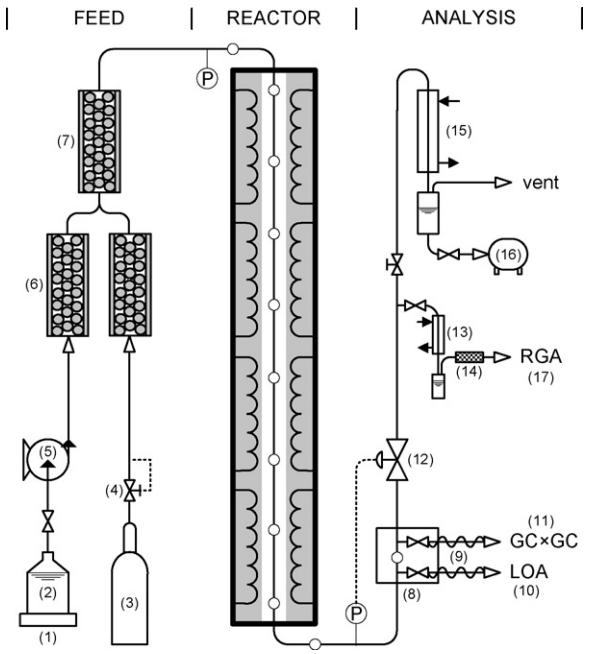

Fig. 2. Schematic of the experimental pyrolysis set-up, indicating the most important process gas temperature (◯) and pressure measurements (P) (1: electronic balance, 2: liquid feed reservoir (FAME), 3: gaseous diluent (N_2), 4: coriolis mass flow controller, 5: peristaltic pump, 6: quartz beads filled evaporator/heater, 7: quartz beads filled mixer, 8: heated sampling oven, 9: heated transfer lines, 10: GC × GC-FID/(TOF-MS), 11: light oxygenates analyzer, 12: COP regulation valve, 13: water cooled heat exchanger, 14: dehydrator, 15: water cooled heat exchanger, 16: condensate drum, 17: refinery gas analyzer).

The feed/diluent mixture enters the reactor, which is a 1.475-m long, 6-mm internal diameter tube, made of Incoloy 800HT (Ni, 30–35; Cr, 19–23; and Fe, >39.5 wt.%). There are eight thermocouples along the reactor, measuring the process gas temperature at different positions. The reactor is heated electrically and placed vertically in a rectangular furnace. The furnace is divided into four separate sections which can be controlled independently to set a specific temperature profile. During the currently discussed set of experiments the reactor is operated near isothermally. To compensate for heat losses near the outlet of the reactor, an extra heater is placed at the bottom of the furnace, so that the temperature will only drop at the outlet of the reactor. The pressure in the reactor is controlled by a back pressure regulator downstream from the outlet of the reactor. Two manometers, situated at the inlet and outlet of the reactor, allow to measure the coil inlet pressure (CIP) and the coil outlet pressure (COP) respectively. The pressure drop over the reactor was found to be negligible.

2.2.2. On-line effluent analysis section

The analysis section of the pyrolysis set-up enables on-line qualification and quantification of the entire product stream, i.e. a wide boiling mixture containing H_2, CO, CO_2, alcohols (methanol, ethanol and heavier), aldehydes and ketones (formaldehyde, acetaldehyde, acetone, etc.), esters, and hydrocarbons ranging from methane to polyaromatic hydrocarbons (PAH). The wide boiling range of the product constituents makes a complete and accurate analysis of pyrolysis reactor effluents a difficult task. Three different gas chromatographs are required: a refinery gas analyzer (RGA), a light oxygenates analyzer (LOA) and the GC × GC-FID/(TOF-MS) described above. The analytical equipment is positioned at different positions on the reactor effluent line, as illustrated in Fig. 2. Their specifications are summarized in Tables 1 and 2.

The reactor effluent is sampled on-line, i.e. during operation, and at high temperature (350 °C). The heated sampling system consists of a high temperature 6-port 2-way valve, kept at 300 °C in the so-called sampling oven to prevent condensation of high molecular weight components. As shown by Van Geem et al. [25], the temperature at which sampling occurs is well above the dew point of the effluent sample. Furthermore, since the reactor effluent is diluted with N_2, component partial pressures, and therefore chances of condensation, are reduced. Using this valve-based sampling system [21,26] and uniformly heated transfer lines a gaseous sample of the reactor effluent is injected onto the GC × GC or onto the LOA. This approach allows analysis of the entire product stream, from methane to PAHs and heavy methyl esters, in a single run of the GC × GC.

The LOA is used for the analysis of formaldehyde, water and methanol. This additional GC is necessary because of the limited response of these components on a FID and difficulties in separating them chromatographically from light C_2 and C_3 hydrocarbons. This GC is therefore equipped with a TCD and the separation is performed on 2 consecutive columns, i.e. a Rt-U-BOND capillary column (Restek, 1 m × 0.32 mm × 10 μm) followed by a Rt-Q-BOND capillary column (Restek, 1 m × 0.32 mm × 10 μm). On the first column, a primary separation between heavier components and the components of interest takes place. At a programmed time, this first column is back-flushed directing the heavier components to the vent, while lighter components (i.e. CO, CO_2, CH_4, C_2 and C_3

Table 2
Pyrolysis analysis section: refinery gas analyzer (RGA) and light oxygenates analyzer (LOA) GC settings.

	RGA		
	Channel 1	Channel 2	Channel 3
Injection	50 μl (gas), 80 °C	250 μl (gas), 80 °C	250 μl (gas), 80 °C
Carrier gas	He	He	N_2
Pre-column	Rtx-1[a] (15 m × 0.53 mm × 3 μm)	Hayesep Q (0.25 m × 1/8″)	Hayesep T (1 m × 1/8″)
Analytical column	Rt-Alumina BOND[b] (25 m × 0.53 mm × 15 μm)	Hayesep N (1 m × 1/8″), Molsieve 5A (1 m × 1/8″)	Carbosphere (2 m × 1/8″)
Oven temperature	50 → 120 °C (5 °C/min)	80 °C	80 °C
Detector	FID, 200 °C	TCD, 160 °C	TCD, 160 °C

LOA	
Injection	250 μl (gas), 190 °C
Carrier gas	He
Pre-column	Rt-U-BOND[b] (2 m × 0.32 mm × 10 μm)
Analytical column	Rt-Q-BOND[c] (2 m × 0.32 mm × 10 μm)
Oven temperature	100 °C (10 °C/min) → 150 °C (5 min)
Detector	TCD, 190 °C

[a] Dimethyl polysiloxane (Restek).
[b] Divinylbenzene ethylene glycol/dimethylacrylate (Restek).
[c] 100% Divinylbenzene (Restek).

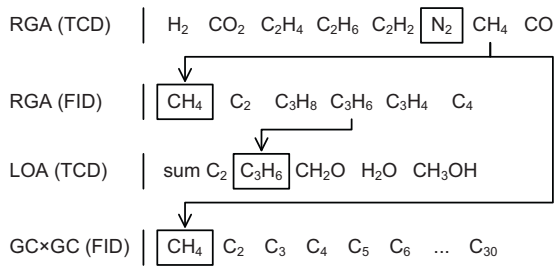

Fig. 3. Use of reference components for quantitative on-line effluent analysis.

hydrocarbons, methanol, water and formaldehyde) have already reached the second analytical column, where they are separated further.

Further downstream the reactor effluent is cooled to approximately 150 °C using a water cooled heat exchanger. Water and condensed products are removed in a liquid separator, while the remainder of the effluent stream is sent directly to the vent. Before reaching the vent a fraction of the effluent is withdrawn. After removal of all remaining water using a water cooled heat exchanger and dehydrator, this effluent fraction is injected automatically into the RGA using built-in gas sampling valves (80 °C). This analysis allows detection of all permanent gases, such as N_2, CO, CO_2 and H_2, present in the effluent and additional analysis of the lighter hydrocarbons, i.e. methane and C_2–C_4 hydrocarbons. For the experiments discussed here, the diluent (N_2) also acts as an internal standard, and the analyses on the RGA therefore permit to determine absolute flow rates of all effluent components, as will be discussed in Section 2.3.

2.3. Data acquisition and quantification

For all analog detectors, data acquisition and processing was performed using Thermo Scientific's Chrom-Card data system. The data obtained with TOF-MS was acquired using Thermo Scientific's Xcalibur software. The raw GC × GC data files were processed using HyperChrom and GC Image (Zoex Corporation, USA). Both packages allow automatic 3D peak quantification and identification. The latter is accomplished by cross referencing the measured mass spectra to the spectra in the available MS libraries.

2.3.1. Quantification of off-line analyses

Concerning the off-line GC × GC analysis of the reactor feed, i.e. a rapeseed oil derived FAME mixture, each peak is identified based on the ordered retention of components and MS confirmation. To each component a weight fraction was assigned by internal normalization [27]:

$$x_i = \frac{f_i \cdot A_i}{\sum_{i=1}^{n} f_i \cdot A_i} \tag{1}$$

where f_i is the relative response factor for component i, used to correct the corresponding total peak area A_i obtained with FID. The relative response factors f_i for all detected methyl esters were determined experimentally from calibration mixtures.

2.3.2. Quantification of on-line analyses

The mass flow rates of all reactor effluent components, ranging from H_2, CO and methane to PAHs, are calculated from the known mass flow rate of the diluents (N_2) which acts as an internal standard. The followed quantification approach is based on multiple reference components, as illustrated in Fig. 3, and allows to successfully combine the data from the different instruments. Using the TCD channel of the RGA, see Table 2, the amount of methane present in the effluent can be determined based on the known mass flow rate of N_2.

$$\dot{m}_{CH_4} = \frac{f_{CH_4} \cdot A_{CH_4}}{f_{N_2} \cdot A_{N_2}} \dot{m}_{N_2} \tag{2}$$

The response factor of methane is chosen to be unity ($f_{CH_4} = 1$). The relative response factor for nitrogen is determined by calibration. Subsequently, methane is used as a reference component for the analyses performed on the RGA-FID channel, and the GC × GC-FID.

$$\dot{m}_i = \frac{f_i \cdot A_i}{f_{CH_4} \cdot A_{CH_4}} \dot{m}_{CH_4} \tag{3}$$

For all major components, the relative response factors f_i on each FID detector were determined by calibration. The response factors for the minor components were calculated according to the following equation [27]:

$$f_i = \frac{M_i}{N_{C,i}} \cdot \frac{1}{M_{CH_4}} \tag{4}$$

where M_i is the molecular mass of component i with $N_{C,i}$ carbon atoms.

This approach requires the separation of methane from all other components on the GC × GC. Therefore, the imposed oven temperature of both GC's gradually increases starting from −40 °C. To achieve cryogenic temperatures in the GC oven a built-in solenoid valve opens automatically, allowing liquid nitrogen to enter the oven through tubing connecting a pressurized Dewar vessel (1.5 bar abs) with the GC.

On the LOA methane cannot be separated from N_2 and CO using the column combination shown in Table 2. Hence methane cannot be used as reference component. Therefore on the LOA propene is used as reference component, the mass flow rate of which is calculated from the peak area measured on the RGA FID channel and the calculated methane flow rate on the RGA TCD, as shown in Fig. 3. Hence the amounts of methanol, water and formaldehyde are calculated according to the following equation:

$$\dot{m}_i = \frac{f_i \cdot A_i}{f_{C_3H_6} \cdot A_{C_3H_6}} \dot{m}_{C_3H_6} \tag{5}$$

Relating the calculated mass flows to the known flow rate of the reactor feed, permits to calculate the yields, x_i, of all detected components.

$$x_i = \frac{\dot{m}_i}{\dot{m}_{feed}} \tag{6}$$

The resulting sum of yields should amount to 100% if all components are measured accurately and no significant amounts of coke or soot are formed.

2.4. Chemicals and standards

The FAME mixture was provided by CARGILL (Ghent, Belgium). Analytical gases (N_2, He, CO_2) were obtained from Air Liquide at a minimum purity of 99.999%. A Supelco® 37 component FAME Mix and mixture containing linolenic acid methyl ester (C18:3), linoleic acid methyl ester (C18:2) and oleic acid methyl ester (C18:1) was used for calibration of the FAME mixture.

3. Results and discussion

3.1. Off-line feedstock analysis

Many different GC × GC column sets have been studied and employed for the determination of fatty acids in vegetable oils, animal fats [28–31] and mixtures with petroleum [14,16,18]. Typically a 5% phenyl-dimethyl siloxane and polyethylene glycol phase set

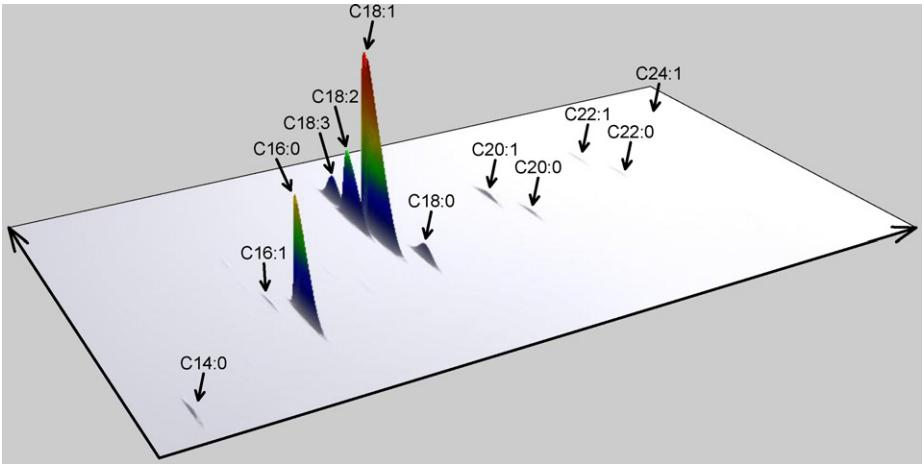

Fig. 4. Off-line GC × GC-FID chromatogram of the FAME mixture (e.g. C18:1 represents the methyl ester with 18 carbon atoms and 1 double bond in the fatty acid chain, i.e. $C_{19}H_{36}O_2$).

is chosen for the first and second column, respectively, representing a typical non-polar/medium-polar combination used in GC × GC analyses [14,18]. However, as reported by Seeley et al. [14] this column combination generates chromatograms where the fatty acid methyl esters (FAMEs) found in biodiesel occupy a region that is also populated by numerous cyclic alkanes and monoaromatics found in petroleum. According to Adam et al. [16] the combination of a Solgel Wax primary column and a DB-1 secondary column results in a superior separation compared to other column combinations, for mixtures containing FAME's, long branched aromatics, naphthenic compounds and paraffins. As the pyrolysis products contain a huge variety of these last type of components this column combination seems to be extremely suitable. However the very low temperatures needed in the GC × GC (−40 °C) for the on-line analysis makes the Solgel Wax ^{1}D not very suited for the present application.

On the other hand for petrochemical applications usually a typical non-polar/medium polar is used [32]. For the diesel/FAME mixtures studied by Adam et al. [16] this configuration was shown to be far from optimal, but for petrochemical applications it has proven to be extremely robust for a huge variety of mixtures.

The FAME mixture used as reactor feed was analyzed using the GC × GC setup discussed above. Fig. 4 shows a 3D representation of the resulting chromatogram. FAME compounds exhibited a non-distorted peak shape with the non-polar primary column, the medium-polar secondary column and two-stage cryogenic modulator (liquid CO_2) [22]. As was already observed by Tiyapongpattana et al. [18], the positions in the 2D plane are clearly related to the number of carbon atoms, degree of unsaturation and the position of the first double bond of the compound, resulting in the ordered elution of the FAME using this column combination. All individual components of the FAME mixture were identified and subsequently quantified according to the procedure discussed in Section 2.3. In Table 3 the weight fractions of the different methyl esters are given as function of the carbon chain length of the fatty acid and the number of double bonds.

Table 3
Detailed quantitative composition of the FAME mixture used as reactor feed [wt.%] (e.g. C18:1 represents the methyl ester with 18 carbon atoms and 1 double bond in the fatty acid chain, i.e. $C_{19}H_{36}O_2$) (see also Fig. 4).

	:0	:1	:2	:3	SUM
C14	0.48	–	–	–	0.48
C16	14.02	0.19	0.02	0.04	14.27
C18	2.69	57.77	16.51	5.62	82.59
C20	0.55	0.98	–	–	1.53
C22	0.27	0.36	–	–	0.63
C24	0.24	0.26	–	–	0.5
SUM	18.25	59.56	16.53	5.66	100

3.2. On-line effluent analysis

The FAME mixture discussed above was used in a series of pyrolysis experiments on the bench scale pyrolysis set-up discussed in Section 2.2. The aim of such experiments is to assess the influence of the imposed process conditions on the product composition. Key components formed during the thermochemical conversion of the FAME mixture are, apart from unreacted feedstock molecules, H_2, CO, CO_2, methanol, formaldehyde, H_2O, methane, ethene, propene, 1,3-butadiene, 1,3-cyclopentadiene, benzene, styrene, long chain linear alpha olefins and unsaturated methyl esters, naphthalene, and other PAHs.

As explained in Section 2.3, yields of all effluent components are determined using a reference component, i.e. methane for on-line GC × GC-FID analysis. In order to separate methane from all other hydrocarbons, the oven temperature is gradually increased from −40 °C to 300 °C. The use of the two-stage cryogenic modulator with liquid CO_2 [22] does not allow to trap and refocus the most volatile components. Hence, the modulation is started when the oven temperature reaches 40 °C, thus dividing the resulting chromatogram into a conventional 1D part and a comprehensive 2D part. Since the total area of a GC × GC peak is in fact the sum of all second dimension peak areas belonging to that GC × GC peak, and because of mass conservation in thermal modulation, peak areas obtained in the 1D part and those in the 2D part of a single analysis can be successfully combined.

Fig. 5a shows the GC × GC-FID chromatogram obtained when the FAME mixture is thermochemically converted at a reactor temperature of 600 °C. As indicated, the lightest hydrocarbons, i.e. typically those with 4 or less carbon atoms, elute before modulation starts. In Fig. 6, this unmodulated part is visualized as a conventional chromatogram. It is obvious that sufficient resolution is available for adequate quantification of these light hydrocarbons, including the reference component methane.

The added value of the second dimension separation becomes evident as the molecular mass of the eluting components increases. Not only does the ordered retention of components results in a straightforward interpretable chromatogram, but it also reduces peak overlap because of the increased separation power of the GC × GC. This analysis therefore allows a much more accurate quan-

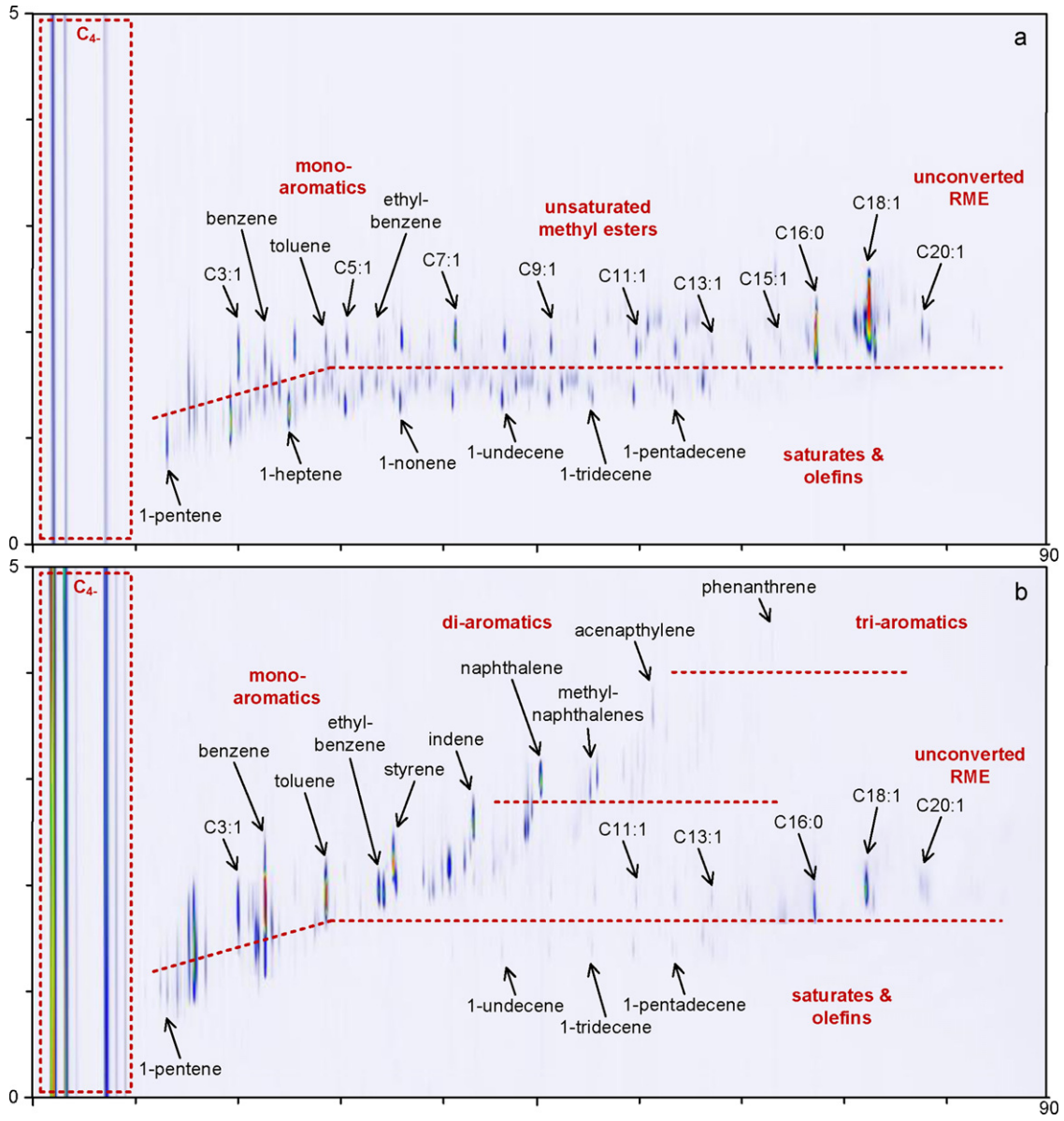

Fig. 5. On-line GC × GC-FID chromatogram of the rapeseed oil methyl ester (RME) pyrolysis product: (a) reactor $T = 600\,^{\circ}C$, (b) reactor $T = 800\,^{\circ}C$ (e.g. C18:1 represents the methyl ester with 18 carbon atoms and 1 double bond in the fatty acid chain, i.e. $C_{19}H_{36}O_2$).

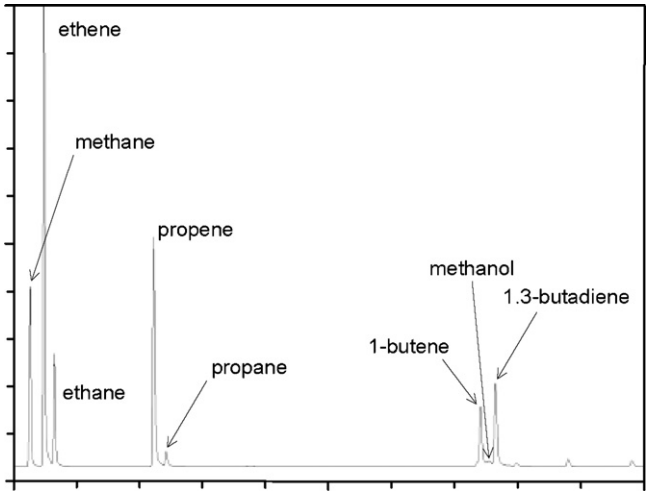

Fig. 6. 1D visualization of the C_4 part of the GC × GC-FID chromatogram in Fig. 5a.

tification of for example the olefinic components, as they are visibly separated from the aromatics and unsaturated methyl esters.

Fig. 5b shows the GC × GC-FID chromatograms of the on-line sampled effluent obtained at a reactor temperature of 800 °C. Again, a distinction can be made between several bands of components, which are indicated roughly by the red borders. These include olefinic and saturated components, followed by mono-aromatics with increasing alkyl substitution, starting with benzene, toluene, ethylbenzene, etc. Naphtheno-aromatics such as indene and alkyl substituted indenes have slightly higher second dimension retention. Di-aromatic components, i.e. naphthalene followed by C_1, C_2 and C_3 alkyl substituted naphthalenes, exhibit even higher second dimension retention. The next bands of components are made up of, respectively, naphtheno-diaromatics such as acenaphthylene and even traces of tri-aromatics such as phenanthrene. The GC × GC chromatograms in Fig. 5a and b clearly illustrate the effect of temperature on the conversion of the FAME mixture. At 600 °C a lot of methyl esters are still present, while at 800 °C the amount of methyl esters has reduced drastically.

Table 4
Overview of component yields [wt.%] for Effluents A and B (see also Fig. 5).

	Effluent A [T = 600 °C]	Effluent B [T = 800 °C]
CH_4	1.19	10.58
H_2	0.02	0.55
CO	0.81	9.60
CO_2	0.72	6.44
CH_2O	0.64	0.62
H_2O	0.11	0.14
Olefins		
C_1–C_4	6.74	45.05
C_5–C_{15}	20.55	5.56
C_{16}–C_{25}	1.33	0.20
Methyl esters		
C_1–C_4	2.67	0.85
C_5–C_{15}	8.25	0.15
C_{16}–C_{25}	50.76	1.10
Mono-aromatics	1.63	12.92
Poly-aromatics	0.01	1.04

On-line GC × GC–TOF-MS confirmation allowed to identify approximately 200 components in these effluents. Based on the quantification approach explained in Section 2.3, the FID chromatograms shown in Fig. 5 allowed to obtain a detailed composition of the entire product stream at each of the investigated process conditions. An overview of the component yields is given in Table 4. From Table 4 and the chromatograms, it is clear that higher temperatures result in increased conversion of the FAME components and also lead to a decreased amount of long chain olefins. The higher conversion mostly leads to higher ethylene yield, but also to increased amounts of CO, CO_2, mono-aromatics and PAHs such as naphthalene and acenaphthylene.

4. Conclusions

A GC × GC-FID/TOF-MS setup that enables both quantitative and qualitative analyses of complex mixtures using a single apparatus has been evaluated. A built-in 4-port 2-way valve allows to switch between FID and TOF-MS without the need to cool down and vent the MS.

The setup was used for the analysis of a rapeseed oil derived mixture of fatty acid methyl esters, as well as for the online analysis of the pyrolysis product of this mixture. A dedicated on-line sampling system makes it possible to analyze the entire reactor effluent from a single GC × GC chromatogram. The GC oven temperature gradually increases from −40 °C to 300 °C. The two-stage cryogenic modulation with liquid CO_2 starts when the oven temperature reaches 40 °C, thus dividing the GC × GC chromatogram into a 1D part and a comprehensive 2D part. This approach enables a complete and detailed on-line monitoring of thermal conversion processes, both qualitative and quantitative. Applied to pyrolysis of FAME mixtures, approximately 200 different components could be identified because of reduced peak overlap thanks to the increased separation power of the GC × GC.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2010.12.109.

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