PYROLYSIS OF CRUDE TALL OIL-DERIVED PRODUCTS

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Crude tall oil (CTO) soap, purified and neutralised CTO, and neutralised distilled tall oil (DTO) were pyrolysed (at 750ºC for 20 s) by pyrolysis gas chromatography with mass-selective and flame ionisation detection (Py-GC/MSD and FID) to clarify their thermochemical behaviour. In each case, the pyrolysates were characteristically dependent on the feedstock, and a wide range of volatile aliphatic and aromatic compounds with some chemically bound oxygen formed. The CTO soap pyrolysate was typically composed of initial extractives-type compounds together with a significant amount of unsaturated aliphatic hydrocarbons and aromatics, whereas the DTO pyrolysate contained mostly just unsaturated aliphatic hydrocarbons and aromatics. These data are of importance when considering the suitability of various extractives-derived resources for producing bioliquids and chemicals.

Keywords: Pyrolysis; Crude tall oil soap; Distilled tall oil; Extractives; Fatty acids; Resin acids; Biofuels

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INTRODUCTION

The pulping industry has traditionally evolved as a reasonably efficient wood biorefinery process yielding pulp (cellulose and hemicelluloses), by-product extractives, such as volatile crude turpentine and non-volatile crude tall oil (CTO) soap, and mainly lignin- and aliphatic carboxylic acids-containing black liquor (Alén 2000, 2011; Lee et al. 2006; Holmbom 2011). Black liquor is then burned after evaporation in the recovery furnace to recover energy and inorganic cooking chemicals. However, in spite of this already versatile product spectrum, to increase further the competitiveness of kraft mills, they should diversify even more to become integrated wood biorefiners which are able to produce, for example, transport fuels and renewable chemicals (Diesen 2007).

During kraft pulping, extractives-based fats and waxes in the wood feedstock are saponified and converted into the sodium salts of fatty and resin acids (Alén 2000). These sodium salts are removed as the main components of CTO soap during the evaporation process of the black liquor by skimming and are liberated by adding sulphuric acid to yield CTO. The average yield of CTO (oxygen content about 11% (Sharma and Bakhshi 1991a)) is in the range of 30-50 kg/t of pulp, corresponding to 50-70% of the initial amount in the raw material used for pulping. CTO is normally fractionated (Gullichsen and Lindeberg 2000) by vacuum distillation (3 to 30 mbar, 170 to 290^{o}C) to several commercial fractions including tall oil fatty acids (TOFA, 20 to 40% of the total) and tall oil resin (TOR, 25 to 35%) together with light oil (“head”, 10 to 15%), distilled tall oil (DTO, about 10%), and tall oil pitch (TPO, 20 to 30%) (Alén 2000; Coll et al. 2001).

In terms of its composition, CTO resembles hydrolysed triglyceride-based vegetable oils which have potential as suitable sources of diesel-type fuels and/or their additives. The use of CTO for such purposes is supported by its huge worldwide production volume and the fact that the market price of diesel fuel is significantly greater than the heat value of CTO (Lee et al. 2006). In addition, CTO is about 60% cheaper than common vegetable oils (Keskin et al. 2007).

Fast pyrolysis is one of the most promising technologies applied to biomass and offers a potential way of converting biomass into liquid products at high yields (70-80%) (Bridgwater et al. 2002). This rather complex thermochemical process comprises a severe form of thermal cracking in the almost total absence of oxygen (air) with the subsequent reactions of some primary products. In general, the chemical composition of pyrolysis products from vegetable oils is highly dependent on the chemical composition of the raw material, and the elemental compositions of pyrolysis-produced biofuels are rather similar to those of feedstocks. For this reason, in contrast to fossil fuels, they also contain chemically bound oxygen. However, it is obvious that oxygen-poor extractives can be more effectively converted into high-energy bioliquids than carbohydrate-rich biomasses having high oxygen content (Huber and Corma 2007; Maher et al. 2008).

Pyrolysis of triglycerides has been investigated for more than 100 years, especially in countries lacking an adequate supply of petroleum sources (Demirbas 2009). There have also been earlier studies conducted on the thermal cracking of various vegetable oil soaps (Chang and Wan 1947; Fortes and Baugh 1994), whereas research reports on the pyrolysis of CTO soap or neutralised tall oil products are not commonly available. In general, when producing CTO-based biodiesel, CTO must first be fractionated by vacuum distillation, and the fraction of TOFA must then be converted into liquid fuels by esterification (Altiparmak et al. 2007; Keskin et al. 2007; Demirbas 2008). Another common approach has been the straightforward catalytic upgrading of CTO to fuels (Sharma and Bakhshi 1991a,b). In addition, Coll et al. (2006) have studied the conversion of CTO and TOR into fuels and chemicals by catalytic hydrotreatment, and Liu et al. (1998) have investigated the possibility of producing a cetane enhancer from the depitched tall oil by catalytic hydrogenation and cracking.

The primary purpose of this study was to clarify the pyrolysis chemistry of CTO soap (containing some black liquor impurities), washed CTO after neutralisation (as reference), and DTO by use of a laboratory-scale apparatus, rather than to make mass balances over the full-scale application. For this purpose, the versatile liquefiable volatile compounds were analysed in detail by gas chromatography (GC). The pyrolysis was mainly done with soap (i.e., as sodium salts of acids), since, for example, the thermal cracking of vegetable oils as such, compared to that of metal fatty acid salts, is much more difficult to control. It should also be pointed out that when applying pyrolysis to CTO soap, the chemically bound sodium can be recovered as Na_2CO_3, thus replacing the need for external sulphuric acid.

The study reported in this paper is a part of a larger project aiming at the clarification of the thermochemical behaviour of various extractives-based raw materials. This investigation continued our earlier reports on the pyrolysis of fatty acid sodium salts (Lappi and Alén 2009a) and vegetable oil soaps (Lappi and Alén in press). In forthcoming investigations, varying mixtures of fatty and resin acids will be pyrolysed.

EXPERIMENTAL

Chemicals and Tall Oil Samples

The solvents used in the sample preparation of extractives were analytical grade acetone (BDH), methyl *tert*-butyl ether (MTBE, Lab-Scan), and pyridine (BDH). The silylation reagents bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) were from Regis Technologies.

The compounds used as internal standards in the GC analysis of extractives were heneicosanoic acid (99%, Sigma) and betulinol (≥98%, Sigma). The external standard used in the quantitative pyrolysis experiments was adamantane (>99%, Fluka) in benzene (>99%, Fluka).

The chemicals used in the determination of saponification values were potassium hydroxide (≥85%, Riedel de Haën), sodium hydroxide (≥99%, Fluka), hydrochloric acid (≥37%, Riedel de Haën), denatured alcohol BA (99.5%, Altia), and phenolphthalein (Merck). Water was obtained from a Millipore Milli-Q water system.

The CTO soap with a dry solids content of 60.8% was obtained from a full-scale pine kraft pulping facility (Oy Metsä-Botnia Ab). Washed CTO (containing 10 to 20% neutral compounds) and DTO were both from Forchem Oy.

Analysis of Tall Oil Products

For the analysis of CTO, it was separated from the CTO soap according to TAPPI standard T 635 om-93. Solids content was obtained after evaporation and drying about 5 g samples at 103ºC to a constant mass.

Saponification values for the CTO and DTO samples were determined according to the procedure described in TAPPI standard T 621 cm-01.

For the analysis of the CTO constituents, the samples were diluted in acetone (0.5 mg/mL), and this diluted sample was derivatised after drying with nitrogen stream for GC with a mixture of BSTFA and TMCS (99:1, respectively). Derivatisation of samples was performed by keeping them at 70ºC for one hour. For the “reference CTO” individual compounds after alkaline hydrolysis were also quantified, since according to the literature (Holmbom and Avela 1971) some esters are formed during the full-scale conversion of tall oil soap into crude tall oil and subsequent storage.

Quantitative analysis of the individual compounds was carried out on an Agilent 6850 Series GC System with an Equity-5 (30 m × 0.32 mm, film thickness 0.25 μm) column. The injector temperature was 290°C, injection volume 1 μL, injection mode pulsed slitless, and the detector temperature was 300°C. The GC oven temperature programme was 1.5 min at 100°C, followed by an increase of 6°C/min to 180°C, 10 min at 180°C, an increase of 4°C/min to 290°C and 20 min at 290°C. Qualitative analysis of the individual components was carried out with an Agilent 6890 Series GC System equipped with a 7683 injector and an Agilent 5973 mass selective detector (MSD). The MS full scan mode was used and the mass range was from m/z 50 to m/z 550. The capillary column used was an HP-5MS (30 m × 0.32 mm, film thickness 0.25 μm) and the GC oven temperature programme was the same as that used in the quantitative analyses.

Pyrolysis Experiments

For the pyrolysis experiments, the CTO soap was used as such, but the washed CTO and DTO were saponified with sodium hydroxide (the amount was 1.5 times the equivalent amount) prior to pyrolysis. Soap samples were pyrolysed in quartz tubes at a heating rate of 1000°C/s using a CDS Pyroprobe 1000 heated-filament pyrolyser coupled to an HP 5890 II gas chromatograph (Py-GC). The column was a ZB-5HT capillary GC column (30 m × 0.25 mm, film thickness 0.25 μm). Detection was carried out either with an HP 5972 mass selective detector (MSD, qualitative analyses, MS full scan mode, mass range m/z 45-700), or alternatively with an HP 5890 GC/flame ionisation detection (FID) (quantitative analyses). The sample size for qualitative analysis was about 3 mg and for quantitative analysis about 1 mg. Injection mode was splitless in both cases. The Py-GC interface temperature was 250°C and the injector temperature 280°C. Pyrolysis parameters were chosen according to the results of the previous research with model fatty acid salts (Lappi and Alén 2011). In each experiment, the pyrolysis temperature was 750°C and the temperature was kept constant for 20 s. The GC oven temperature was 5 min at 35°C, an increase of 5°C/min to 125°C, 3°C/min to 285°C, 5°C/min to 380°C, and finally 5 min at 360°C. Helium was used as the carrier gas and as an inert atmosphere in the pyrolysis interface. The carrier gas flow rate was kept at 1 mL/min during the gas chromatographic analysis.

Due to the multiplicity of pyrolysis products, the identification of all constituents in pyrolysates only by the retention time with respect to some internal standards appeared to be impossible. For this reason, a proper interpretation of the mass spectra of the pyrolysis products was based on a commercial database, Wiley 7n, together with the recognition of fragmentation patterns. Only quality matches of above 85% were included.

The calibration curve for quantitative determination of the pyrolysis products was determined by the pyrolysis of adamantane dissolved in benzene. The calibration was performed using a similar method to Bocchini et al. (1997) when adding the internal standard for pyrolysis. Solutions of adamantane in the 40-110 μg/mL range were carefully added to a quartz capillary tube, which was immediately inserted into the Py-GC interface. After an equilibration period of 30 s, pyrolysis was performed. Six different concentrations were pyrolysed using the same parameters as for the samples. Two replicates were made for each concentration. The coefficient of determination (R^2) of the calibration curve obtained was 0.990. Due to the multitude of peaks in the vegetable oil pyrolysates, adamantane was only used as an external standard. Quantification was used to calculate the product yields.

The precision of product formation in the pyrolysis experiments was evaluated by the method described by Destandau et al. (2005). Tall oil samples were analysed using four replicates (n = 4) over three days (n_1 = 3). The day-to-day repeatability and the intermediate precision were calculated from the results. The responses measured were the total ion current (TIC) peak areas. However, due to the multitude of different products formed in pyrolysis, the peaks were first grouped into various component classes and the relative peak area of each class was then calculated as a percentage of the total peak area of all detected products. Precision was evaluated for the relative proportions of the classes. An analysis of variance (ANOVA) was performed, and the results were used to calculate the different parameters of precision. The intraday (Equation (1)) and day-to-day (Equation (2)) precisions expressed as RSDs were evaluated from the residual error (σ_r) and from the error due to the day factor (σ_A). In Equation (2) x is the mean of response, q_A day factor mean square given by ANOVA and q_r residual mean square given by ANOVA. Intermediate precision was calculated as shown in Equation 3.

$$\mathrm{RSD}_{\mathrm{intraday}}(\%) = \frac{\sigma_r}{\bar{x}} \times 100 \tag{1}$$

$$\mathrm{RSD}_{\mathrm{day-to-day}}(\%) = \frac{\sigma_A}{\bar{x}} \times 100 \text{ with } \sigma_A^2 = \frac{q_A - q_r}{n} \tag{2}$$

$$\mathrm{RSD}_{\mathrm{intermediate\ precision}}(\%) = \frac{\sqrt{\sigma_A^2 + \sigma_r^2}}{\bar{x}} \times 100 \tag{3}$$

RESULTS AND DISCUSSION

Raw Materials

The amount of CTO recovered from the CTO soap (DS content 61%) was 54% (or 89% of the soap DS), which was slightly above the recommendations (>50%) for tall oil content in tall oil soap to be used for industrial refining (Gullichsen and Lindeberg 2000). The total amount of extractives detected in this “separated CTO” was 761 g/kg DS. In case of the “separated CTO”, thus also reflecting the composition of the initial CTO soap investigated, the content of fatty and resin acids was, respectively, about 58% and 34% of the compounds determined (Table 1).

The total content of extractives in the “reference CTO” was 847 g/kg DS and the fraction of esterified acids corresponding to 74 g/kg DS (containing only fatty acids), as earlier reported by Holmbom and Avela (1971). In this case, the content of fatty and resin acids was, respectively, about 53% and 27% of the compounds determined (Table 1). The highest content of extractives was obtained for DTO, and this sample consisted of about 67% of fatty acids and about 25% of resin acids.

Due to chemical changes caused by kraft pulping and soap cooking, the chemical composition of the tall oil fraction is typically somewhat different from that in wood (Severson et al. 1972; Lappi and Alén 2009b). For example, in addition to the obvious alkaline hydrolysis of glycerides, some double bond rearrangements with the formation of conjugated di- and triunsaturated fatty acid systems occurred (Holmbom and Avela 1971). In practice, this could be seen by the formation of three isomers of conjugated $C_{18:2}$ acids (Table 1). Only two of them were detected in the “separated CTO” (CTO soap) and “reference CTO”, but all the three components were present in DTO. In addition, some less common fatty acids (i.e., 10-nonadecenoic and anteiso-heptadecanoic acid) were detected in all these samples. In general, the main fatty acid components were unsaturated linolenic ($C_{18:3}$), linoleic ($C_{18:2}$), and oleic ($C_{18:1}$) acids, whereas the main resin acid components were palustric, dehydroabietic, and abietic acids.

Table 1. Composition of the Extractives in the Samples Studied (% of the total compounds)*. Abbreviations: CTO soap is the original crude tall oil soap (analysis was based on the “separated CTO”), CTO the “reference CTO” and DTO distilled tall oil (for details, see the text).

Compound		CTO soap	CTO	DTO	Formula
FATTY ACIDS		57.8	53.2	66.8	
Myristic acid	$C_{14:0}$	+	0.1	-	$C_{14}H_{28}O_2$
Pentadecanoic acid	$C_{15:0}$	-	0.2	-	$C_{15}H_{30}O_2$
Palmitic acid	$C_{16:0}$	0.9	2.0	0.8	$C_{16}H_{32}O_2$
Palmitelaidic acid	$C_{16:1}$	0.2	0.2	+	$C_{16}H_{30}O_2$
Margaric acid	$C_{17:0}$	0.7	0.5	0.8	$C_{17}H_{34}O_2$
17:0 anteiso	-	-	-	0.1	$C_{17}H_{34}O_2$
Stearic acid	$C_{18:0}$	3.5	2.4	2.1	$C_{18}H_{36}O_2$
Oleic acid	$C_{18:1}$	15.0	11.3	17.6	$C_{18}H_{34}O_2$
Linoleic acid	$C_{18:2}$	20.3	23.5	33.3	$C_{18}H_{32}O_2$
$C_{18:2}$ (conjugated)		2.3	1.4	0.6	$C_{18}H_{32}O_2$
$C_{18:2}$ (conjugated)		2.3	1.7	1.8	$C_{18}H_{32}O_2$
$C_{18:2}$ (conjugated)		-	-	1.6	$C_{18}H_{32}O_2$
Linolenic acid	$C_{18:3}$	5.9	4.5	6.5	$C_{18}H_{30}O_2$
Nonadecanoic acid	$C_{19:0}$	-	+	-	$C_{19}H_{38}O_2$
10-Nonadecenoic acid	$C_{19:1}$	0.8	0.6	0.6	$C_{19}H_{36}O_2$
Arachidic acid	$C_{20:0}$	0.4	0.7	0.2	$C_{20}H_{40}O_2$
Eicosadienoic acid	$C_{20:2}$	0.7	0.5	0.2	$C_{20}H_{36}O_2$
Eicosatrienoic acid	$C_{20:3}$	4.3	2.5	+	$C_{20}H_{34}O_2$
Behenic acid	$C_{22:0}$	0.5	0.7	0.6	$C_{22}H_{44}O_2$
Tricosanoic acid	$C_{23:0}$	-	0.1	-	$C_{23}H_{46}O_2$
Lignoceric acid	$C_{24:0}$	+	0.3	-	$C_{24}H_{48}O_2$
RESIN ACIDS		33.7	27.6	25.4	
Abietic acid		8.9	10.2	9.9	$C_{20}H_{30}O_2$
Neoabietic acid		5.3	3.9	1.0	$C_{20}H_{30}O_2$
Levopimaric acid		2.7	+	0.9	$C_{20}H_{30}O_2$
Palustric acid		5.7	4.3	3.3	$C_{20}H_{30}O_2$
Secodehydroabietic acid		-	+	+	$C_{20}H_{30}O_2$
Isodehydroabietic acid		+	+	-	$C_{20}H_{30}O_2$
Dehydroabietic acid		4.6	3.9	6.1	$C_{20}H_{28}O_2$
Abietatetraenoic acid		0.2	0.2	-	$C_{21}H_{26}O_2$
Hydroxydehydroabietic acid		-	0.2	-	$C_{20}H_{28}O_3$
7-Oxodehydroabietic acid		0.2	-	-	$C_{20}H_{26}O_3$
Pimaric acid		3.1	2.5	1.0	$C_{20}H_{30}O_2$
Isopimaric acid		2.2	1.8	1.1	$C_{20}H_{30}O_2$
Sandaracopimaric acid		0.8	0.6	0.3	$C_{20}H_{30}O_2$
Unidentified acids		+	+	1.8	-

Table 1. (Continued)

Compound	CTO soap	CTO	DTO	Formula
RESIN ALCOHOLS AND ALDEHYDES	0.8	0.3	-	
Thunbergol	0.2	-	-	$C_{20}H_{34}O$
Neoabienol	0.4	0.2	-	$C_{20}H_{34}O$
Isopimarol	+	-	-	$C_{20}H_{32}O$
Abietol	+	-	-	$C_{20}H_{32}O$
Neoabietol	+	-	-	$C_{20}H_{32}O$
Pimaral	0.2	0.1	-	$C_{20}H_{30}O$
STEROLS	4.7	5.9	-	
Sitosterol	3.2	2.9	-	$C_{29}H_{50}O$
Sitostanol	0.7	0.7	-	$C_{29}H_{52}O$
Campesterol	0.5	0.4	-	$C_{28}H_{48}O$
Cycloartenol	0.3	0.6	-	$C_{30}H_{50}O$
Methylene cycloartanol	-	0.6	-	$C_{31}H_{52}O$
Citrostadienol	-	0.7	-	$C_{30}H_{50}O$
MISCELLANEOUS (*e.g*. stilbenes and fatty alcohols)	3.0	13.0	7.8	-

* + indicates concentrations below 0.1%, - indicates not detected.

Pyrolysis Experiments

The characteristic feature for all the pyrolysates was a prominent amount of volatile products “C_3-C_5 compounds” (Figs. 1-3), primarily containing both alkenes and alkanes, but other highly volatile compounds were also present in minor amounts. However, due to the low resolution of these numerous low molecular- mass compounds, their proper identification was not possible.

Significant amounts of aromatics could be detected in all pyrolysates. This was due to the fact that not only unsaturated fatty acids form these compounds, but their formation from cyclic resin acids is also possible (Severson et al. 1972; Hartgers et al. 1995; Lappi and Alén 2009a). Various naphthalene derivatives were found to be the most abundant aromatics formed at a high temperature (800°C). It was assumed that a high yield of these naphthalene-related components arose from A-ring cleavage in the parent resin acid molecule before aromatisation occurred. According to Severson et al. (1972) this cleavage is most likely facilitated by the ease with which the resin acids undergo decarboxylation.

It has been found (Moldoveanu 2010b) that besides fragmentation and decarboxylation reactions, dehydrogenation also comprises to an important reaction taking place in resin acids. Actually, the main products were found to be molecules showing less fragmentation of the decahydrophenanthrene ring system (i.e., the formation of phenanthrenes), although traces of various substituted cyclopentanes, cyclopentenes, cyclohexanes, cyclohexenes, cyclohexadienes, benzenes and naphthalenes could also be detected in the pyrolysates. In general, the main reactions seemed to include only the basic elimination of carbon monoxide and water. However, the diterpenoid structures that contain carboxyl and hydroxyl groups or carbonyl groups were still relatively stable in pyrolysis. In addition, several other aromatics, such as indenes and anthracenes, were formed in the pyrolysis of our tall oil-derived samples.

The pyrolysate of the CTO soap consisted mostly of the initial extractives-type, often oxygen-free compounds together with significant amounts of aliphatic hydrocarbons and aromatic compounds (Fig. 1). Most of the aliphatic compounds (Table 2) were unsaturated alkenes or alkadienes and a major part of the detected aromatics (Table 3) contained one benzene ring. It should be pointed out that, as indicated in our separate experiments with black liquor (Lappi and Alén 2009b), in this case, only a very low amount of sulphur-containing pyrolysis products was present. This finding suggested that a small amount of black liquor impurities in the CTO soap did not have a substantial effect on product quality.

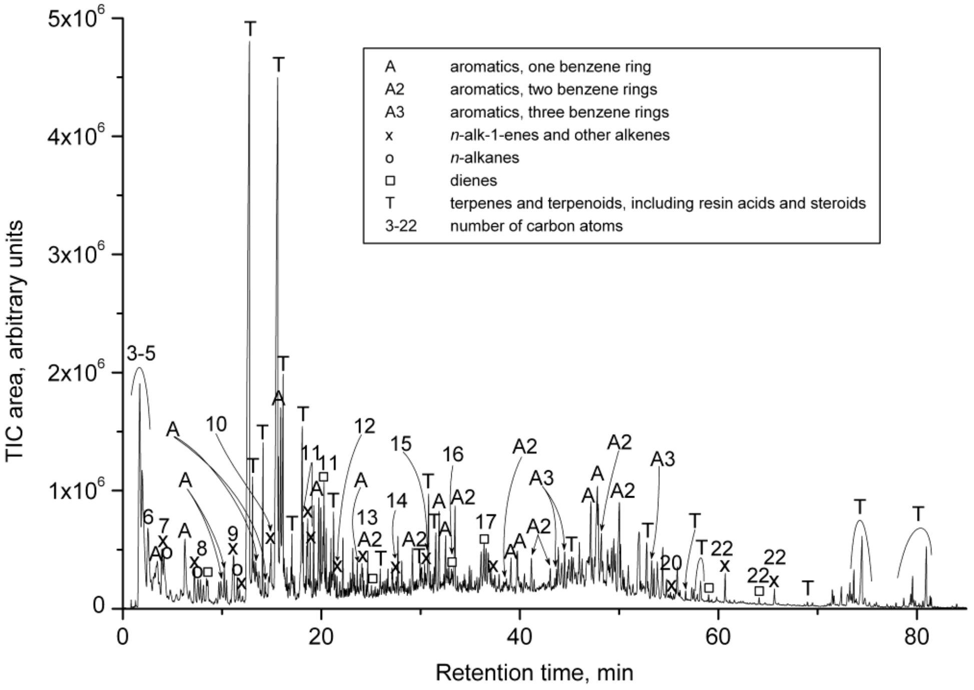

Fig. 1. The main products formed in the pyrolysis experiments (750°C and 20 s) with the CTO soap. Numbers indicate the number of carbon atoms in a molecule.

Although the chemical composition of the neutralised "reference CTO" was rather similar to that of the CTO soap, the total amount of the initial extractives-type pyrolysis products was clearly lower (Fig. 2 and Table 2). In addition, no significant differences caused by black liquor impurities (i.e., pyrolysis of CTO soap vs. neutralised "reference CTO") could be found. The pyrolysis products of DTO after neutralisation also contained mainly aliphatic hydrocarbons and aromatics, rather than extractives-type compounds (Fig. 3 and Tables 2 and 3). As in the previous cases, the amount of phenolics was very low and the aliphatic hydrocarbons were primarily unsaturated alkenes. The difference in the amounts of initial extractives-based compounds in different pyrolysates was due to the initial moisture content of raw material. The CTO soap received from the pulp mill was pyrolysed as such without drying prior to its pyrolysis. The wet feedstock decomposition was dominated by the reaction mechanisms similar to those taken place in dry pyrolysis, including hydrolysis, dehydration, decarboxylation, aromatization, and recondensation (Minkova et al. 2001). The main effect of water during pyrolysis is hydrolysis (Moldoveanu 2010a). The hydrolysis reaction exhibits lower activation energy than most of the pyrolytic decomposition reactions (Libra et al. 2011). This finding has also been shown by calorimetric measurements. Therefore, the principle biomass components are less stable under hydrothermal conditions, and this leads to lower decomposition temperatures. Water vapour has the ability to penetrate the solid material and to help desorption, distillation, and the efficient removal of the volatile products from it (Minkova et al. 2001). In addition, water vapour is a reactive agent, which reacts with the pyrolysis products. It may stabilise the radicals obtained in the thermal decomposition of the fuel increasing the yield of volatiles.

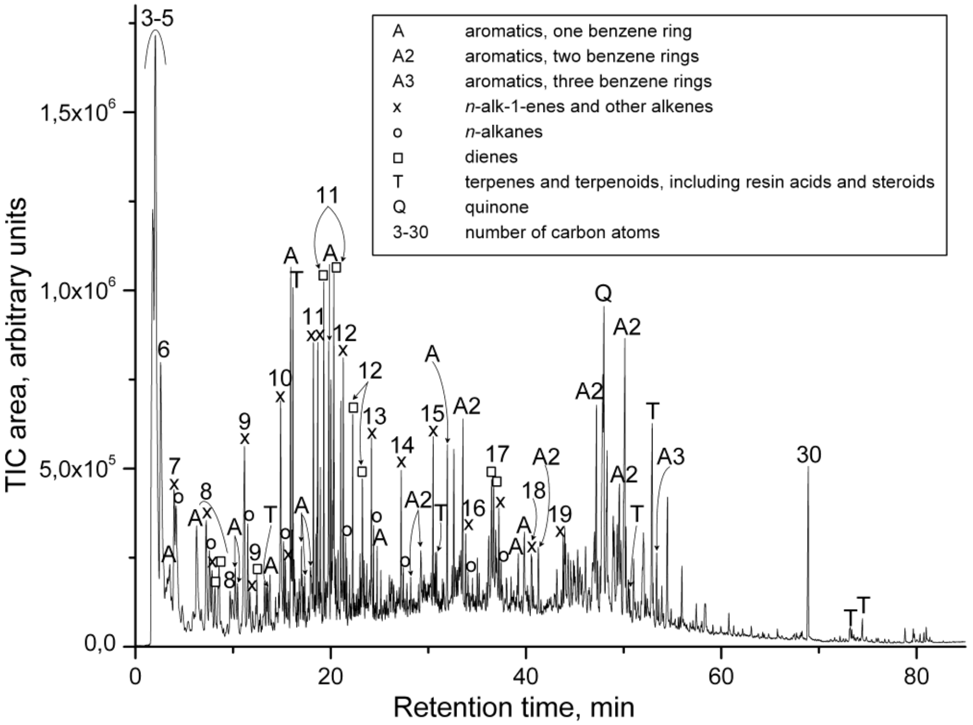

Fig. 2. The main products formed in the pyrolysis experiments (750°C and 20 s) with the neutralised “reference CTO”. Numbers indicate the number of carbon atoms in a molecule.

The total amount of pyrolysis products recovered from laboratory-scale pyrolysers is normally low, although these products can be considered to reflect well the main chemistry involved. In our experiments, quantitative analyses indicated that detectable amounts of liquefiable products were (expressed as % of the initial dry solids) 1.1% (for CTO soap and the neutralised “reference CTO”) and 0.9% (for the neutralised DTO).

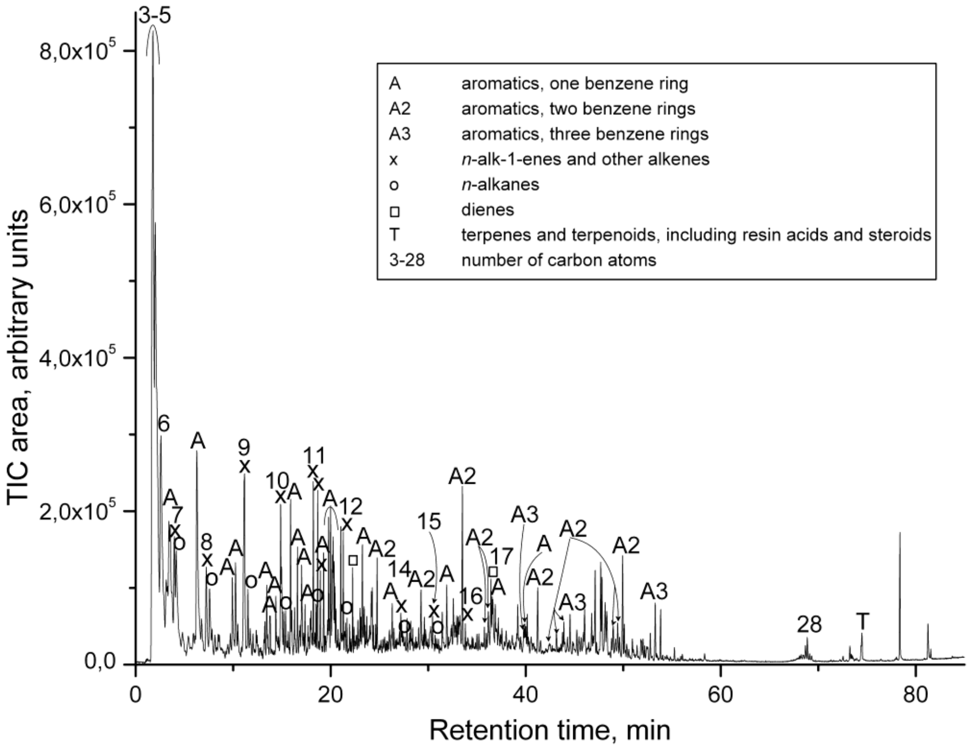

Fig. 3. The main products formed in the pyrolysis experiments (750°C and 20 s) with the neutralised DTO. Numbers indicate the number of carbon atoms in a molecule.

When comparing the results of this study with those of model compounds (Lappi and Alén 2009) and vegetable oils (Lappi and Alén 2011) it could be concluded that the composition of the raw material had a significant effect on pyrolysate composition. The characteristic fragmentation patterns for each feedstock material could be detected. The effects of the main constituents of the raw material on pyrolysis product distribution were clearly visible even in a case when the raw material was the complex mixture of various extractives-based compounds. The best product quality (i.e., less aromatics and oxygen-containing compounds) was achieved with the raw material containing mostly salts of the saturated FAs. The quality of the pyrolysate was better in the experiments performed with the vegetable oil soaps (excluding castor oil) than in those done with the tall oil products.

Precision of the pyrolysis results

As the results of Fortes and Baugh (1999) indicated, the critical problem with the Py-GC/MSD technique is the reproducibility of the pyrolysis experiments. There are several parameters that could possibly cause variations in the results, for example, small sample size (which causes unavoidable weighing errors) and the inhomogeneity of soap. In the case of the CTO soap, taking a representative sample was more challenging than with other samples because of the varying moisture content. Some samples might have a somewhat higher dry matter content than others. In addition, part of the devolatilised pyrolysis products was condensed before reaching the GC column. This problem, which was related to successive runs (i.e., the accumulation of "dirt" on the surfaces of the apparatus lines), might have also had some effect on product formation and could not be

Table 2. Classification[a] of Aliphatic Pyrolysis Products (including their formula) Detected in the Pyrolysates

***n*-Alk-1-enes and other alkenes**		**Alkanes**	
1-Hexene	C_6H_{12}	Heptane	C_7H_{16}
1-Heptene	C_7H_{14}	Octane	C_8H_{18}
1-Octene and other octenes	C_8H_{16}	Nonane	C_9H_{20}
1-Nonene and other nonenes	C_9H_{18}	Decane[c,d]	$C_{10}H_{22}$
1-Decene and other decenes[c,d]	$C_{10}H_{20}$	Undecane	$C_{11}H_{24}$
1-Undecene and other undecenes	$C_{11}H_{22}$	Dodecane[c,d]	$C_{12}H_{26}$
1-Dodecene and other dodecenes	$C_{12}H_{24}$	Tridecane	$C_{13}H_{28}$
1-Tridecene and other tridecenes[c]	$C_{13}H_{26}$	Tetradecane	$C_{14}H_{30}$
1-Tetradecene and other tetradecenes[b,d]	$C_{14}H_{28}$	Pentadecane[c,d]	$C_{15}H_{32}$
1-Pentadecene	$C_{15}H_{30}$	Hexadecane[c]	$C_{16}H_{34}$
1-Hexadecene	$C_{16}H_{32}$	Heptadecane[b,c]	$C_{17}H_{36}$
1-Heptadecene	$C_{17}H_{34}$		
1-Octadecene[c]	$C_{18}H_{36}$		
1-Nonadecene[c]	$C_{19}H_{38}$		
1-Eicosene[c]	$C_{20}H_{40}$		
1-Docosene[b]	$C_{22}H_{44}$		
9-Tricosene[d]	$C_{23}H_{46}$		
Dienes		**Trienes**	
1,4-Hexadiene and 2,4-hexadiene[b]	C_6H_{10}	1,3,5-Heptatriene[b]	C_7H_{10}
2,5-Dimethyl-2,4-hexadiene	C_8H_{14}	2-Methyl-1,3,5-hexatriene[b]	C_7H_{10}
1,3-Octadiene[b,c] and 2,4-octadiene[c]	C_8H_{14}	2,4,6-Octatriene[b,c]	C_8H_{12}
1,3-Nonadiene[c,d]	C_9H_{16}	Ocimene[b]	$C_{10}H_{16}$
1,4-Undecadiene[c] and 2,4-undecadiene	$C_{11}H_{20}$		
5,7-Dodecadiene[c,d] and 2,4-dodecadiene[c,d]	$C_{12}H_{22}$		
1,15-Hexadecadiene[b,c]	$C_{16}H_{30}$		
6,8-Heptadecadiene	$C_{17}H_{32}$		
1,21-Docosadiene[b]	$C_{22}H_{42}$		
Cycloalkenes		**Cycloalkanes**	
1,4-Cyclohexadiene[d]	C_6H_8	Nonylcyclopentane	$C_{14}H_{28}$
Cyclohexene[b]	C_6H_{10}		
1-Methyl-1,4-cyclohexadiene[b]	C_7H_{10}		
3-Ethenylcyclopentene	C_7H_{10}		
1,3-Cyclooctadiene[b]	C_8H_{12}		
3-Butyl-4-vinylcyclopentene[b]	$C_{11}H_{18}$		
Cyclododecene[b]	$C_{12}H_{22}$		
Terpenes and terpenoids			
α-Pinene[b], β-pinene[b]	$C_{10}H_{16}$	endo-Borneol[b]	$C_{10}H_{18}O$
Camphene[b]	$C_{10}H_{16}$	Fenchol[b]	$C_{10}H_{18}O$
β-Myrcene[b]	$C_{10}H_{16}$	1-Methyl-oestra-1,3,5(10)-trien-18-nor-17-ketone[b]	$C_{18}H_{22}O$
γ-Terpinene[b,c], α-terpinene[b,c]	$C_{10}H_{16}$	Dehydroabietic acid, methyl ester[b,c]	$C_{21}H_{30}O_2$
Δ^3-Carene[b]	$C_{10}H_{16}$	Methyl abietate[b]	$C_{21}H_{32}O_2$
Limonene[b,c]	$C_{10}H_{16}$	5-Ethenyl-(5β)-*A*-norcholestan-3-one[c]	$C_{28}H_{46}O$
α-Longipinene[b]	$C_{15}H_{24}$	4β-Methylcholesta-8,24-dien-3β-ol[b]	$C_{28}H_{46}O$
Ylangene[b]	$C_{15}H_{24}$	5α-Ergostan-3-one[b]	$C_{28}H_{48}O$
α-Copaene[b]	$C_{15}H_{24}$	4,4-Dimethylcholest-7-en-3-one[b]	$C_{29}H_{48}O$
Epizonarene[b]	$C_{15}H_{24}$	4-Ergosten-3-one[b]	$C_{28}H_{46}O$

Isolongifolene[b]	$C_{15}H_{24}$	5α-Stigmastan-3-one[b]	$C_{29}H_{50}O$
Isoledene[b]	$C_{15}H_{24}$	Stigmast-4-en-3-one[b,c]	$C_{29}H_{48}O$
α-Cadinene[b,c]	$C_{15}H_{24}$		
α-Amorphene[b]	$C_{15}H_{24}$		
α-Muurolene[c]	$C_{15}H_{24}$		
Germacrene-D[b,c]	$C_{15}H_{24}$		
Terpenes and terpenoids			
Δ-Cadinene[b,c]	$C_{15}H_{24}$		
1,4-Dimethyl-7-(1-methylethyl)azulene	$C_{15}H_{18}$		
Cembrene[b]	$C_{20}H_{32}$		
5α-Ergost-8(14)-ene[b]	$C_{28}H_{48}$		
Stigmastan-3,5-dien	$C_{29}H_{48}$		
Ketones		**Other oxygen-containing compounds**	
2-Heptadecanone[c]	$C_{17}H_{34}O$	2,4-Hexadienal[b,c]	$C_{6}H_{8}O$
Others		4-Methyl-1-(1-methylethyl)-3-cyclohexen-1-ol[b]	$C_{10}H_{18}O$
Thiobismethane	$C_{2}H_{6}S$	1-Tetracosanol[d]	$C_{24}H_{50}O$
1,2-Dimethylenecyclohexane[d]	$C_{8}H_{12}$	Hexahydro-7α-isopropyl-4*a*β,8*a*β-dimethyl-2(1*H*)-naphthalenone[c]	$C_{15}H_{24}O$
1,4-Bis(methylene)cyclohexane[c,d]	$C_{8}H_{12}$	Retinol[b]	$C_{20}H_{30}O$
1-(2'-Methyl-1'-propenyl)-7-[1'-propynyl]tricyclo[3.1.0.0(2,6)]hexane	$C_{14}H_{18}$	10-Pentadecen-1-ol[c]	$C_{15}H_{30}O$
10-Demethylsqualene[c,d]	$C_{19}H_{48}$	1-Eicosanol[c]	$C_{20}H_{42}O$

a) Compounds are listed within each substance group according to their GC retention times.

b) Only in the pyrolysate of the CTO soap.

c) Only in the pyrolysate of the neutralised CTO.

d) Only in the pyrolysate of the neutralised DTO.

Table 3. Classification[a] of Aromatic Pyrolysis Products (including their formula) Detected in the Pyrolysates

Aromatics, with one benzene ring			
Benzene	$C_{6}H_{6}$	Pentylbenzene[d]	$C_{11}H_{16}$
Toluene	$C_{7}H_{8}$	Tetrahydrocycloprop[*a*]indene[d]	$C_{10}H_{10}$
Ethylbenzene	$C_{8}H_{10}$	*p*-Isobutyltoluene[d]	$C_{11}H_{16}$
Styrene	$C_{8}H_{8}$	1,1-Dimethylindene, 2,3-dimethylindene[b], 1,3-Dimethylindene[b]	$C_{11}H_{12}$
o-Xylene[d] and *m*-xylene[b,c]	$C_{8}H_{10}$	Triethylbenzene[b]	$C_{12}H_{18}$
Cumene[c,d]	$C_{8}H_{12}$	Hexylbenzene[d]	$C_{12}H_{18}$
Propenylbenzene[d]	$C_{9}H_{12}$	Tetrahydrocyclopropa[*b*]naphthalene[b]	$C_{11}H_{12}$
Isocumene[c,d]	$C_{9}H_{12}$	1,2-Dihydro-3-methylnaphthalene[d]	$C_{11}H_{12}$
m-Ethyltoluene and *o*-ethyltoluene	$C_{9}H_{12}$	1,1,3-Trimethylindene	$C_{12}H_{14}$
α-Methylstyrol[b]	$C_{9}H_{10}$	1,1,6-Trimethyltetralin[b]	$C_{13}H_{18}$
m-Vinyltoluene[d]	$C_{9}H_{10}$	Heptylbenzene	$C_{13}H_{20}$
2-Isopropyltoluene	$C_{10}H_{14}$	(2,4,6-Trimethylphenyl)allene[5]	$C_{12}H_{14}$
Indane[d]	$C_{9}H_{10}$	Octylbenzene[3]	$C_{14}H_{22}$
Allylbenzene[d]	$C_{9}H_{10}$	Octahydro-7-methyl-4-methylene-1-(1-methylethyl)naphthalene[b]	$C_{15}H_{24}$
Indene	$C_{9}H_{8}$	[(Tetramethylcyclopropylidene)methyl]-benzene[c,d]	$C_{14}H_{18}$
m-Propyltoluene[d] and *o*-propyltoluene[c,d]	$C_{10}H_{14}$	Nonylbenzene[d]	$C_{15}H_{24}$
Butylbenzene[c,d]	$C_{10}H_{14}$	(4,5,5-Trimethyl-1,3-cyclopentadien-1-yl)	$C_{14}H_{16}$

		-benzene[b]	
β-Dimethylstyrene[c]	$C_{10}H_{12}$	Decylbenzene[d]	$C_{16}H_{26}$
2,5-Dimethylstyrene[d]	$C_{10}H_{12}$	9-Ethyl-octahydroanthracene[b]	$C_{16}H_{22}$
p-Methylcumene[c,d]	$C_{10}H_{14}$	1,7-Dimethyl-5-phenyltricyclo[4.1.0.0]-hept-3-ene[b]	$C_{15}H_{16}$
2-Butenylbenzene[d]	$C_{10}H_{12}$	4*a*-Methyl-1-methyleneoctahydro-phenanthrene	$C_{16}H_{20}$
p-Ethylcumene[b,c]	$C_{11}H_{16}$	Undecylbenzene[d]	$C_{17}H_{28}$
2,3-Dihydro-2,2-dimethylindene[b]	$C_{11}H_{14}$	(1-Methyldecyl)benzene[c]	$C_{17}H_{28}$
3-Methyl-3-phenylbutene[c,d]	$C_{11}H_{14}$	1,4-Dimethyl-7-isopropyl-hexahydrophenanthrene[b,c]	$C_{19}H_{26}$
1-Methylindene	$C_{10}H_{10}$	Octahydro-4*a*-methyl-1-methylene-7-(1-methylethyl)phenanthrene[b]	$C_{19}H_{26}$
Aromatics, with two benzene rings			
Naphthalene[d]	$C_{10}H_8$	1-Methyl-3-[(4-methylphenyl)methyl]-benzene[b]	$C_{15}H_{16}$
Methylnaphthalene	$C_{11}H_{10}$	3-(1-Methylethyl)-1,1'-biphenyl[d]	$C_{15}H_{16}$
Dimethylnaphthalene	$C_{12}H_{12}$	2,6-Dimethyl-1-(phenylmethyl)benzene[b,c]	$C_{15}H_{16}$
Ethylnaphthalene	$C_{12}H_{12}$	9,10-Dihydro-1-methylphenanthrene	$C_{15}H_{16}$
2-Ethenylnaphthalene[b,d]	$C_{12}H_{10}$	Tris(1-methylethyl)naphthalene[d]	$C_{19}H_{26}$
2-(1-Methylethyl)naphthalene	$C_{13}H_{14}$	1,2,3,4-Tetrahydro-9,10-dimethylanthracene[b]	$C_{16}H_{18}$
1,4,5-Trimethylnaphthalene	$C_{13}H_{14}$	2,6-Bis(1,1-dimethylethyl)naphthalene[c]	$C_{18}H_{24}$
1,2,3,4-Tetramethylnaphthalene[b,d]	$C_{14}H_{16}$	1,1-Diphenyl-1,3-pentadiene[d]	$C_{17}H_{16}$
1-Methyl-7-(1-methylethyl)naphthalene	$C_{14}H_{16}$	9-Butyl-9-methylfluorene[b]	$C_{18}H_{20}$
4,4'-Dimethyl-1,1'-biphenyl	$C_{14}H_{14}$	Bis(1-methylethyl)-1,1'-biphenyl	$C_{18}H_{22}$
1,6-Dimethyl-4-(1-methylethyl)naphthalene	$C_{15}H_{18}$		
Aromatics, with three benzene rings			
Phenanthrene[d]	$C_{14}H_{10}$	2,3,5-Trimethylphenanthrene[d]	$C_{17}H_{16}$
4-Methylphenanthrene[b] , 1-methylphenanthrene	$C_{15}H_{12}$	1-Methyl-7-(1-methylethyl)phenanthrene	$C_{18}H_{18}$
3,6-Dimethylphenanthrene[c]	$C_{16}H_{14}$		
Phenolics and other oxygen-containing aromatics			
2-Methylphenol[b,c]	C_7H_8O	5,8-Dihydroxy-3-methyl-1,2-dihydro-9,10-anthraquinone[c]	$C_{15}H_{12}O_4$
2,3,5-Trimethylphenol[d]	$C_9H_{12}O$	1,2,9,10-Tetrahydro-2,9-dimethyl-naphtho[2,1-*b*:7,8-*b*']difuran[c]	$C_{16}H_{16}O_2$
Methyleugenol[b]	$C_{11}H_{12}O_2$	1,2-Dihydro-2-methyl-5-(2-propenyl)-naphtho[2,1-*b*]furan-4-ol[d]	$C_{16}H_{16}O_2$
1,2-Dimethoxy-4-(1-propenyl)benzene[b]	$C_{11}H_{14}O_2$	1-[4-(2-*p*-Tolulvinyl)phenyl]ethanone[b,c]	$C_{17}H_{16}O$
[1,1`-Biphenyl]-4-methanol[b]	$C_{13}H_{12}O$	Octahydro-1,4*a*-dimethyl-7-(1-methylethyl)-1-phenanthrenecarboxaldehyde[b]	$C_{20}H_{28}O$
1-[1,1'-Biphenyl]-4-yl-ethanone[d]	$C_{14}H_{12}O$	Octahydro-1,4*a*-dimethyl-7-(1-methylethyl)-1-phenanthrenemethanol[b]	$C_{20}H_{30}O$
Isomaturnin[b]	$C_{16}H_{14}O_3$		
Sulphur-containing aromatics			
2-Methyldiphenylsulphone[b]	$C_{13}H_{12}O_2S$		
2,2-Bis-(methylthiophenyl)propane[b]	$C_{17}H_{20}S$		

[a] Compounds are listed within each substance group according to their GC retention times.
[b] Only in the pyrolysate of the CTO soap.
[c] Only in the pyrolysate of the neutralised CTO.
[d] Only in the pyrolysate of the neutralised DTO.

Table 4. Percentage of Chromatographic TIC Peak Areas for Different Compound Classes in the Pyrolysis Experiments with the CTO Soaps and the Neutralised "Reference CTO" Including the Standard Deviations and Intraday (n=4), Day-to-day (n=3), and Intermediate Precision of the Results. For compounds, see Tables 2 and 3.

	CTO soap				Neutralised CTO			
Class of compounds	Average composition	RSD (%) Intraday	RSD (%) Day-to-day	RSD (%) Intermediate	Average composition	RSD (%) Intraday	RSD (%) Day-to-day	RSD (%) Intermediate
C_3-C_5 compounds	18.90 ± 3.47	18.4	1.2	18.4	21.98 ± 1.08	4.8	1.2	5.0
Aliphatic hydrocarbons	18.40 ± 3.66	20.4	5.3	21.1	21.69 ± 0.98	4.8	1.9	5.2
n-alk-1-enes and other alkenes	10.62 ± 2.05	19.7	4.6	20.3	13.40 ± 0.64	4.9	1.4	5.1
n-alkanes	2.49 ± 0.44	18.5	5.8	19.4	3.76 ± 0.22	6.6	3.3	7.3
dienes	4.53 ± 0.99	22.6	7.1	23.7	4.22 ± 0.16	4.1	1.7	4.4
trienes	0.76 ± 0.20	26.5	4.2	26.8	0.31 ± 0.02	6.4	1.5	6.6
Aromatics	15.61 ± 1.37	9.5	4.3	10.4	14.57 ± 0.35	2.5	1.0	2.7
with one benzene ring	9.18 ± 1.04	12.2	5.3	13.3	9.01 ± 0.26	3.0	0.7	3.1
with two benzene rings	4.16 ± 0.61	14.4	3.2	14.8	3.92 ± 0.13	3.7	1.7	4.0
with three benzene rings	0.46 ± 0.09	19.2	4.5	19.7	0.68 ± 0.04	6.2	0.5	6.3
phenolics and other oxygen-cont. aromatics	1.71 ± 0.32	17.3	7.6	18.9	0.96 ± 0.05	5.2	1.4	5.4
sulphur-cont. aromatics	0.10 ± 0.03	27.7	18.6	33.3	-	-	-	-
Cycloalkenes	1.26 ± 0.25	20.5	7.0	21.6	0.51 ± 0.05	10.1	2.5	10.4
Cycloalkanes	0.25 ± 0.03	12.7	5.7	13.9	0.10 ± 0.01	5.7	2.9	6.4
Ketones	-	-	-	-	0.18 ± 0.03	14.6	10.2	17.8
Other oxygen-containing compounds	0.64 ± 0.05	7.6	3.0	8.2	0.50 ± 0.02	4.7	2.2	5.2
Terpenes and terpenoids	21.01 ± 8.05	41.5	18.6	45.4	1.94 ± 0.16	8.3	2.9	8.8
containing oxygen	1.52 ± 0.33	14.2	19.2	23.9	0.14 ± 0.01	10.6	4.3	11.4
no oxygen present	19.49 ± 7.94	44.4	20.5	48.9	1.80 ± 0.17	10.0	3.5	10.6
Other identified compounds	0.61 ± 0.06	10.4	5.1	11.6	2.12 ± 0.16	7.7	2.2	8.0

Table 5. Percentage of Chromatographic TIC Peak Areas for Different Compound Classes in the Pyrolysis Experiments with the Neutralised DTO Including the Standard Deviations and Intraday (n=4), Day-to-day (n=3), and Intermediate Precisions of the Results. For compounds, see Tables 2 and 3.

	Neutralised DTO			
Class of compounds	Average composition	RSD (%) Intraday	RSD (%) Day-to-day	RSD (%) Intermediate
C_3-C_5 compounds	26.07 ± 2.28	7.6	5.1	9.1
Aliphatic hydrocarbons	21.25 ± 0.75	3.6	0.9	3.7
n-alk-1-enes and other alkenes	15.18 ± 0.57	3.3	2.2	4.0
n-alkanes	3.81 ± 0.31	7.3	3.8	8.2
dienes	2.26 ± 0.19	9.2	4.5	10.2
trienes	-			
Aromatics	19.83 ± 0.48	2.0	1.6	2.6
with one benzene ring	13.88 ± 0.40	3.1	1.4	3.4
with two benzene rings	5.15 ± 0.49	6.9	7.7	10.3
with three benzene rings	0.33 ± 0.06	15.6	7.8	17.4
phenolics and other oxygen-cont. aromatics	0.47 ± 0.05			
sulphur-cont. aromatics	-	-	-	-
Cycloalkenes	1.17 ± 0.08	7.0	2.4	7.4
Cycloalkanes	0.17 ± 0.04	19.0	14.6	24.0
Ketones	-	-	-	-
Other oxygen-cont. compounds	-	-	-	-
Terpenes and terpenoids	0.18 ± 0.06	35.0	15.2	38.2
containing oxygen	-	-	-	-
no oxygen present	0.18 ± 0.06			
Other identified compounds	1.11 ± 0.06	5.7	2.6	6.2

totally avoided by increasing the pyrolysis interface and injector temperatures. For this reason, the pyrolysis apparatus was regularly cleaned after a few runs. It was also noticed that analytical pyrolysis seemed to be rather sensitive to the sample position in the platinum coil filament.

The results (Tables 4 and 5) suggest that the intraday repeatability was rather poor in most cases. This trend was especially pronounced when the product groups with a low content of compounds were considered. The exception to this trend was “terpenes and terpenoids” in the CTO soap pyrolysate, which despite a high relative amount had a very poor intraday repeatability (41.5%). Intraday repeatability ranged from 7.6% to 44.4% (CTO soap), 2.6% to 14.6% (neutralised “reference CTO”) and 2.0% to 35.0% (neutralised DTO). The day-to-day repeatability was satisfactory, ranging from 1.2% to

18.6% (CTO soap) 0.7% to 10.2% (neutralised "reference CTO") and 0.9% to 15.2% (neutralised DTO).

In forthcoming studies, the pyrolysis of the crude hardwood oil soap with a higher relative amount of neutral compounds (and fatty acids) and without resin acids will be a topic of interest.

CONCLUSIONS

In this study, various samples of tall oil-based extractives were pyrolysed on the laboratory scale in order to clarify their thermochemical behaviour. The main findings can be summarised as follows:

1. Depending on the sample origin (crude tall oil soap, purified and neutralised crude tall oil or neutralised distilled tall oil) a wide range of liquefiable product groups in characteristic ratios could be obtained.
2. Normal amounts of black liquor impurities in the CTO soap did not seem to result in significant formation of environmentally harmful sulphur-containing pyrolysis products.
3. In general, the results suggest that this kind of extractives source might represent potential feedstocks when considering feasible alternatives for producing diesel fuel additives.

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