

UNIVERSITY OF JYVÄSKYLÄ
DEPARTMENT OF CHEMISTRY
RESEARCH REPORT NO. 158

HANNA LAPPI

**PRODUCTION OF HYDROCARBON-RICH
BIOFUELS FROM EXTRACTIVES-DERIVED
MATERIALS**

Academic Dissertation for
the Degree of Doctor of Philosophy



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BY

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LIST OF ORIGINAL PUBLICATIONS

This thesis consists of an overview. The following four publications are referenced throughout the paper using Roman numerals (I-IV).

- I Lappi, H. and Alén, R. (2009). Production of vegetable oil-based biofuels - Thermochemical behavior of fatty acid sodium salts during pyrolysis, *Journal of Analytical and Applied Pyrolysis*, 86, 274-280.
<https://doi.org/10.1016/j.jaap.2009.07.005>
- II Lappi, H. and Alén, R. (2011). Pyrolysis of vegetable oil soaps - Palm, olive, rapeseed and castor oils, *Journal of Analytical and Applied Pyrolysis*, 91, 154-158.
<https://doi.org/10.1016/j.jaap.2011.02.003>
- III Lappi, H. and Alén, R. (2011). Pyrolysis of crude tall oil-derived products, *BioResources*, 6, 5121-5138.
<https://doi.org/10.15376/BIORES.6.4.5121-5138>
- IV Lappi, H. and Alén, R. (2012). Pyrolysis of tall oil-derived fatty and resin acid mixtures, *ISRN Renewable Energy*, 409157, 8p.
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The experimental work referenced above in publications I-IV was performed by the author and written by Hanna Lappi and Raimo Alén who served as a co-author. In publication II, Merja Rintala analyzed the extractives from vegetable oils. In publication IV, the analysis of extractives was performed by Maria Luhtala.

Other related publications by the author

Forssén, M., Lappi, H., Louhelainen, J., Alén, R., Hupa, M. (2007). Conversion routes from organic to inorganic nitrogen in burning single black liquor droplets, *International Chemical Recovery Conference*, Quebec, Canada, Vol. 2, p. 613.

Lappi, H., Alén, R. (2009). Production of bioliquids from extractives-derived materials, *15th International Symposium on Wood, Fibre and Pulping Chemistry*, Oslo, Norway, 2009.

Lappi, H., Alén, R. (2009). Production of bioliquids from extractives-based feedstocks by pyrolysis, *The 2nd Nordic Wood Biorefinery Conference*, Helsinki, Finland, 2009.

PREFACE

This doctoral thesis is based on experimental work that was carried out in the Laboratory of Applied Chemistry at the Department of Chemistry, University of Jyväskylä, from January of 2006 to March of 2011.

It would not have been possible to complete this dissertation without the help and support of a number of people. First and foremost, I thank my supervisor Professor Raimo Alén, for his encouragement, guidance and patience during this work. Thank you for all the efforts during these years. Your support was there whenever I needed it. I also wish to thank all my coworkers at the Laboratory of Applied Chemistry for the pleasant working atmosphere and skillful help. I am especially thankful to Arja Mäkelä and Marja Salo for all their help, encouragement and friendship. Special thanks also go to Piia Valto for her friendship and good company during the annual seminars of the International Doctoral Program in Bioproducts Technology (PaPSaT). Juhani Salovaara, thank you for all the help with the analytical equipment. I am deeply grateful for my friend Maija Hujala for her encouragement and peer support which I have had the pleasure of having since we first started our studies at the same time at LUT. Thanks are due also to my friends Heidi Ahkola and Pia Nekkula for their encouragement.

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Kannus, October 2012
Hanna Lappi

ABSTRACT

This research concentrated on the preliminary possibility of utilizing saponified extractive-based raw materials for the production of bioliquids through fast pyrolysis. The primary purpose of this study was to clarify the pyrolysis chemistry involved by a laboratory-scale apparatus, rather than to make mass balances over the full-scale application. For this purpose, the versatile liquefiable volatile compounds were analyzed in detail by gas chromatography (GC). The pyrolysis was mainly done with soap (i.e., as sodium salts of acids), since the thermal cracking of vegetable oils compared to that of metal acid salts, is much more difficult to control. The knowledge gained from this can be utilized for the planning of larger-scale experiments with a more technical approach to a wider range of raw materials.

In the first phase of the research, pyrolysis experiments with model compounds consisting of sodium salts from some commonly known fatty acids that have 18 carbon atoms and a varying degree of unsaturation were performed. The model compounds included sodium stearate ($C_{18:0}$), sodium oleate ($C_{18:1}$), and sodium linolate ($C_{18:2}$). The main purpose was to get an idea of the product profile under varying pyrolysis conditions and to verify the dominant reaction pathways. The formation of pyrolysis products clearly depended on its temperature and the time it took to form the unsaturation of the fatty acid carbon chain. The highest relative proportions of various alkenes and alkanes were obtained with saturated sodium $C_{18:0}$, whereas the lowest relative proportions of these compounds (and the highest proportions of aromatics and oxygen-containing compounds) were detected in sodium $C_{18:2}$ pyrolysate.

The primary aim of the second phase of the research was to further understand the pyrolysis chemistry of fatty acid soaps within natural matrices. Typical fragmentation patterns of the main product group were detected and the results were collected in accordance with the results of the model compounds, thus indicating only a slight matrix effect. The pyrolysis of the fatty acid sodium salts obtained from the alkaline hydrolysis of vegetable oils (palm, olive, and rapeseed oils) mainly resulted in the formation of volatile products. This similar to what is found within the boiling range of petroleum products like gasoline and diesel fuel. However, in this process, there were also some undesirable oxygen-containing products that were formed as well. Castor oil appeared to be an unsuitable raw material for the pyrolytic production of biofuels due its high content of ricinoleic acid.

The primary purpose of the third phase of this study was to further understand the pyrolysis chemistry of crude tall oil soap, which contained some black liquor impurities. The results of washed crude tall oil and distilled tall oil after neutralization, suggests that typical small amounts of black liquor that are normally found, had no significant effect on product quality. In these cases, the most important factor affecting the quality of bioliquid was the amount of resin

acids in the feedstock. Crude tall oil soap seemed to be suitable for feedstock when considering economically feasible processes for producing diesel fuel additives.

To gain further knowledge about the effect of different tall oil fractions on pyrolysis product formation, the pyrolysis of a neutralized tall oil fatty acid mixture as well as a neutralized tall oil resin acid mixture was performed. In the former case, the pronounced formation of different aliphatic hydrocarbons was obtained, whereas the pyrolysis of neutralized tall oil rosin led to the considerable formation of various aromatics. These aromatics were mainly resin acid-derived polyaromatics. However, monoaromatics (formed mainly from unsaturated fatty acids) were also present as well.

It could be concluded that the composition of this raw material had a particularly significant effect on the composition of liquefiable products. With respect to biodiesel production, the quality of a pyrolysate seemed to be better in the case of vegetable oils soaps than in various tall oil products. The best quality product was achieved with a raw material containing mostly saturated fatty acid (C_{18:0}) salts.

Keywords: pyrolysis, biofuel, vegetable oil, tall oil, extractives, fatty acid, resin acid

CONTENTS

| | |
|---|-----|
| LIST OF ORIGINAL PUBLICATIONS..... | i |
| PREFACE..... | iii |
| ABSTRACT..... | v |
| CONTENTS..... | vii |
| ABBREVIATIONS..... | ix |
| | |
| 1 INTRODUCTION | 1 |
| 1.1 Background..... | 1 |
| 1.2 Objectives of the study..... | 3 |
| 2 PLANT OILS..... | 4 |
| 2.1 Palm oil..... | 7 |
| 2.2 Olive oil..... | 10 |
| 2.3 Rapeseed oil..... | 12 |
| 2.4 Castor oil..... | 14 |
| 2.5 Tall oil products..... | 15 |
| 2.6 Fuel properties..... | 20 |
| 3 BIOMASS PYROLYSIS..... | 22 |
| 3.1 General approach..... | 22 |
| 3.2 Fast pyrolysis..... | 25 |
| 3.3 Analytical pyrolysis..... | 26 |
| 3.4 The chemistry of the pyrolytic process..... | 28 |
| 3.4.1 Fundamental reactions of free radicals in pyrolysis..... | 29 |
| 3.4.2 Thermal decomposition of triglycerides..... | 31 |
| 3.4.3 Thermal cracking of extractives-based soaps..... | 35 |
| 4 EXPERIMENTAL..... | 44 |
| 4.1 Chemicals and plant oil feedstocks..... | 44 |
| 4.2 Analytical determinations..... | 45 |
| 4.3 Pyrolysis experiments..... | 46 |
| 4.3.1 Model compounds..... | 47 |
| 4.3.2 Vegetable oil soaps and neutralized tall oil products..... | 47 |
| 5 RESULTS AND DISCUSSION..... | 50 |
| 5.1 Fatty acid sodium salts..... | 50 |
| 5.2 Vegetable oil soaps – Palm, olive, rapeseed, and castor oils..... | 55 |
| 5.2.1 Chemical composition..... | 55 |
| 5.2.2 Pyrolysis experiments..... | 56 |
| 5.3 Neutralized tall oil products..... | 66 |
| 5.3.1 Chemical composition..... | 66 |
| 5.3.2 Pyrolysis experiments..... | 68 |

| | | |
|-----|---------------------------------------|----|
| 5.4 | General considerations..... | 76 |
| 6 | CONCLUDING REMARKS..... | 77 |
| 6.1 | Summary of the results | 77 |
| 6.2 | Suggestions for future research | 78 |
| | REFERENCES..... | 80 |
| | APPENDICES..... | 95 |

ABBREVIATIONS

| | |
|-------------------|--|
| amu | Atomic mass unit |
| AN | Acid number |
| ANOVA | Analysis of variance |
| BSTFA | Bis(trimethylsilyl)trifluoroacetamide |
| CTO | Crude tall oil |
| CTOS | Crude tall oil soap |
| C _{18:0} | Stearic acid |
| C _{18:1} | Oleic acid |
| C _{18:2} | Linoleic acid |
| C _{18:3} | Linolenic acid |
| DG | Diglyceride |
| DGDG | Digalactosyldiacylglycerol |
| DS | Dry solids |
| DTO | Distilled tall oil |
| D2 | No. 2 diesel fuel |
| FA | Fatty acid |
| FFA | Free fatty acid |
| FIA | Fluorescence indicator adsorption method |
| FID | Flame ionization detector |
| GC | Gas chromatography |
| HHV | Higher heating value |
| HMM | High molecular mass |
| HP | Hewlett Packard |
| JYU | University of Jyväskylä |
| LLO | Linoleic-linoleic-oleic acid |
| LnLO | Linolenic-linoleic-oleic acid |
| LnOO | Linolenic-oleic-oleic acid |
| LOO | Linoleic-oleic-oleic acid |
| LOP | Linoleic-oleic-palmitic acid |
| MG | Monoglyceride |
| MGDG | Monogalactosyldiacylglycerol |
| MS | Mass spectrometry |
| MSD | Mass selective detector |
| MTBE | Methyl <i>tert</i> -butyl ether |
| m/z | Mass-to-charge ratio |
| N | Neutral compound |
| NaLi | Sodium linolate |
| NaOl | Sodium oleate |
| NaSt | Sodium stearate |
| ND | Not detected |
| OO | Oleic-oleic acid |
| OOO | Oleic-oleic-oleic acid |
| PAH | Polyaromatic hydrocarbon |

| | |
|-----------|--|
| PLO | Palmitic-linoleic-oleic acid |
| PLP | Palmitic-linoleic-palmitic acid |
| PO | Palmitic-oleic acid |
| POL | Palmitic-oleic-linoleic acid |
| POO | Palmitic-oleic-oleic acid |
| POP | Palmitic-oleic-palmitic acid |
| PP | Palmitic-palmitic acid |
| PPP | Palmitic-palmitic-palmitic acid |
| Py | Pyrolyzer |
| RA | Resin acid |
| RBD | Refined, bleached, and deodorized palm oil |
| RSD | Relative standard deviation |
| <i>sn</i> | substituent |
| TAG | Triacylglycerol |
| TAPPI | Technical Association of the Pulp and Paper Industry |
| TMAH | Tetramethylammonium hydroxide |
| TIC | Total ion current |
| TG | Triglyceride |
| TMCS | Trimethylchlorosilane |
| TOFA | Tall oil fatty acid |
| TOR | Tall oil resin acid |
| Tr | Traces |

1 INTRODUCTION

1.1 Background

Biofuels, which can be used as fuel or fuel additives have recently become more attractive because of their environmental benefits and the uncertainties concerning petroleum availability (Ma and Hanna 1999, Piel 2001, Demirbas 2003 a,b, Fortes and Baugh 2004). Instead of converting engines to run on alternative fuels (e.g., as in a fuel cell or in a methanol engine) in the future, the marketplace is more willing to convert alternative energy resources into synthetic liquid fuels that are similar to gasoline or diesel. Society can easily phase in liquid biofuels without costly upgrades and engine replacements. Among all of the different possible raw materials extractive-based triglycerides (TGs) esters of fatty acids with glycerol found in plants present the most promising source of hydrocarbon rich products that resemble petroleum. The diesel boiling range for material from plant oils is of particular interest because it has been shown to significantly reduce particulate emissions relative to petroleum diesel (Demirbas 2008a). Vegetable oils are high in energy content, regardless of the substantial amount of oxygen (average of 10-12% of the compound mass) that is bound to their structures. Besides the advantage of having a heating value similar to diesel fuels, these natural oils are low in sulfur and nitrogen (Dandik and Aksoy 1998). Additionally, they yield only a small net contribution of CO₂ throughout the process of their cultivation, production of oil, and conversion to biodiesel (Balat 2007).

The use of vegetable oils in diesel engines is nearly as old as the engine itself. The inventor of the diesel engine, Rudolf Diesel, reportedly used groundnut oil as a fuel for demonstration purposes in 1900 (Knothe et al. 1997). However, the direct use of vegetable oils and/or blends is generally considered to be unsatisfactory and impractical for both direct injection and indirect type diesel engines. While TGs can be directly used as a fuel for diesel engines, their high viscosities, low volatilities, poor cold flow properties, acid composition

(the reactivity of unsaturated hydrocarbon chains) and, free fatty acid content can lead to engine problems (Ma and Hanna 1999, Huber and Corma 2007, Demirbas 2008a). These problems require that vegetable oils are upgraded if they are to be used as a fuel in conventional diesel engines.

Considerable progress has been achieved with respect to converting TG-based vegetable oils to diesel-type fuels. It is evident that lessons learned from our knowledge of current biodiesel technology should be reviewed when considering the use of crude tall oil as a raw material for biodiesel production (Lee et al. 2006). The huge volumes of throughput in kraft pulping justify further work to maximize the value of various byproducts. With this in mind, the market price of diesel fuel can still be many times greater than the heat value of tall oil. Moreover, crude tall oil is about 60% cheaper than other vegetable oils (Keskin et al. 2007).

The main process that is needed for the conversion of vegetable oils into diesel-type fuels is known as alcoholysis (i.e., reaction with acidic methanol or ethanol) and pyrolysis to produce, respectively, fatty acid esters and hydrocarbons (Doll 2008). However, commonly practiced transesterification has some drawbacks including the requirement of a large amount of alcohol, typically methanol, which is usually derived from natural gas or other fossil fuel sources. The formation of a low value byproduct in the form of glycerol is also a problem, at least until there are enough facilities for its refining. Additionally, the heating values are lower than those of conventional diesel fuels and there are also stability issues with this kind of biodiesel (Junming et al. 2009).

Reactions from pyrolysis offer a promising option for the production of renewable fuels and chemicals from vegetable oils (Maher and Bressler 2007). The liquid fuel from pyrolysis has similar chemical components to conventional petroleum diesel fuel (Demirbas 2008a). Fast pyrolysis is one of the most promising technologies applied to biomass and it offers a potential way for the conversion of biomass into liquid products at high yields (70-80%) (Bridgwater et al. 2002). This rather complex process is comprised of a severe form of thermal cracking in the almost total absence of oxygen (air) with subsequent reactions from primary products. This option is especially promising in areas where the hydroprocessing industry is well established because the technology is very similar to that of conventional petroleum refining. In petroleum refineries, different types of fuels are obtained through the fractionation of crude oil by the distillation and subsequent processing of different fractions of it in downstream processes (Chew and Bhatia 2008). In a typical biorefinery, the further liquid product that is obtained from biomass processing and plant oil could be processed in an appropriate way to produce biofuels. The pyrolysis of TGs has been investigated for more than 100 years, especially in areas that lack deposits of petroleum (Demirbas 2009a).

Since the plant oil based pyrolysis products are highly dependent upon the chemical composition of the raw material, the elemental composition of biofuels typically resembles that of the raw material. It is obvious that extractives can be more easily converted into high-energy liquids with less oxygen than carbohydrate-rich biomass (Huber and Corma 2007, Maher et al. 2008). However, it should be pointed out that the pyrolysis of unsaponified vegetable oils produces not only desirable linear or cyclic paraffins and olefins, but also inconvenient oxygenated compounds such as aldehydes, ketones, and carboxylic acids (Dandik and Aksoy 1999, Fortes and Baugh 1999, Lima et al. 2004). Conversely, the saponification of TGs prior to pyrolysis offers a way to yield pyrolysates with a composition similar to that of diesel fuel (Fortes and Baugh 1994, Demirbas 2002, Jansson et al. 2007, Maher and Bressler 2007). For example, using sodium or calcium hydroxide treatment, facilitates, to some extent, the pyrolytic process and seems to produce pyrolysate containing less oxygen than the pyrolysis of neat TGs.

1.2 Objectives of the study

In order to develop an advanced pyrolysis process for various biomass-derived feedstocks and improve product quality and yield, in-depth investigations about the reaction mechanisms are needed. The main objective of this study was to produce useful data on the versatile chemistry dealing with the production of hydrocarbon-containing biofuels through pyrolysis.

Other objectives of this research included suitability tests of different extractive-derived materials for bio-oil production, since it was known that the compositions of bio-oils resemble those of the initial feedstock. The suitability of the pyrolysis process as potential biorefinery was also discussed. Obtaining information on various pyrolysis reactions and products is essential because the lack of basic information hinders the further development of biomass utilization via pyrolysis. The vegetable oils used in this research were all commercially available common vegetable oils.

2 PLANT OILS

One way to identify various oils is to distinguish them from oilseed crops and other vegetable oils that come from endosperm (soft fleshy fruit) (Gunstone 2002). Seed extraction is achieved through pressing and/or through solvent extraction, where oils from soft fruits are pressed out. Palm and olive oils belong to a group known as *endosperms* and, rapeseed as well as castor oils belong to a group known as *oilseed crops*. Commercial oils and fats are mixtures of lipids (Gunstone 2004). Vegetable oils are primarily composed of TGs (generally >95%), esters of glycerol and different fatty acids accompanied by diglycerides (DGs), monoglycerides (MGs), and free fatty acids (FFAs) (Hasenhuettl 1993, Stoker 2001, Gunstone 2004). Vegetable oils may also contain phospholipids, free sterols and sterol esters, tocopherols (tocopherols and tocotrienols), triterpene alcohols, hydrocarbons, and fat-soluble vitamins. The aforementioned refers to crude oils because during the refining process, some of the minor components are usually removed, either in their entirety or in part.

After refining, the content of the TGs rise to 97-99%, when almost all the FFAs and most MGs are removed. Other components which are removed in the refining process are phospholipids, colors and pigments, oxidized materials, flavor components, trace metals, and sulfur-containing compounds. Valuable minor components such as antioxidants and vitamins may also be removed. DGs tend to remain in the product and these are usually in the range of 0-2%. Molecular structures of the vegetable oil components are presented in Appendix I. Vegetable oil components can be classified into saponifiables, such as TGs, DGs, MGs, and phosphatides (i.e., fatty acid derivatives) through the use of alkaline hydroxide, and unsaponifiables. The unsaponifiable fraction includes sterols, higher aliphatic alcohols, pigments, and hydrocarbons.

FAs derived from vegetable sources generally contain an even number of carbon atoms (typically 12-22 carbon atoms, C₁₈ being the most common), have a straight carbon chain, and they may be saturated, monounsaturated or polyunsaturated (Gunstone 2004, Scrimgeour and Harwood 2007). Naturally

occurring double bonds are almost exclusively in the *cis* configuration. In general, the unsaturated centers appear at certain preferred positions. The most common positions are ω 9 as in oleic acid (ω 9-18:1) and erucic acid (ω 9-22:1), where ω indicates that with respect to the position of a double bond, the counting of the first carbon atoms involved is done from the methyl end of the chain instead of the carboxyl end. The most important polyunsaturated acids have methylene-interrupted patterns of unsaturation. The *n*-6 and *n*-3 family terms relate to the position of the first double bond with respect to the methyl end of the chain.

The most common saturated FAs in vegetable oils are palmitic (C_{16:0}) and stearic (C_{18:0}) acids and all oils contain at least small amounts of them (Appendix I) (Gunstone 2004, Demirbas 2008a). Saturated acids with more than 18 carbon atoms are rare. Similarly, oleic (C_{18:1}) and linoleic (C_{18:2}) acids are the most common unsaturated FAs. Many of the oils also contain some linolenic (C_{18:3}) acid. Other quite common FAs in vegetable oils are lauric (C_{12:0}), myristic (C_{14:0}), and erucic (C_{22:1}) acids. FAs seldom have functional groups beyond the carboxyl group and unsaturated centers, but examples of fatty acids with an oxygenated function (e.g., the hydroxyl group in ricinoleic acid in castor oil) include some of importance.

MGs exist in two forms depending on whether the primary (α) or secondary hydroxyl (β) is acylated (Gunstone 2004, Stoker 2006). The DGs exist in symmetrical (*sn*-1,3) and unsymmetrical forms (*sn*-1,2 and *sn*-2,3) with the 1,3-isomer as the most stable. TGs are fully acylated derivatives of glycerol. It is unusual for natural TGs to have only one kind of FA unless the single acid exceeds 70%. In vegetable oils, the *sn*-2 hydroxyl group is esterified almost entirely with unsaturated acids while saturated acids and the remaining unsaturated acids are at the *sn*-1(3) positions.

The phospholipid content of these oils varies widely, containing anywhere between 0.1% and 0.5% in most oils (Hasenhuettl 1993, Stoker 2006). Phospholipids are glycerides which are esterified by FAs at the 1,2-positions and a phosphoric acid residue at the 3-position. The identity of the moiety (other than glycerol) esterified to the phosphoric group determines the specific phospholipid compound. Most phospholipids have a saturated acyl chain at the *sn*-1 position and an unsaturated acyl chain at the *sn*-2 position. The major components of these are phosphatidylcholines (choline moiety), phosphatidylethanolamines (ethanolamine), and phosphatidylinositols (inositol) (Gunstone 2004). Glycolipids consist of various types of long chain sugar derivatives which may also contain DGs, a ceramide backbone or a phosphorylated polysaccharide-lipid complex.

Sterols (i.e., tetracyclic compounds derived from terpenes generally containing 27, 28 or 29 carbon atoms) are found in small quantities in plant oils

(Hasenhuettl 1993). Most vegetable oils contain 1000-5000 mg/kg of sterols, partly as free sterols and partly as esterified (the hydroxyl group esterified with fatty acid) sterols. The ratio of esterified to free sterol varies with the free sterols mostly predominating. Sitosterol is often known as a major phytosterol (50-80% of total sterols) with campesterol, stigmasterol, and Δ^5 -avenasterol are frequently obtained at significant levels.

Hydrocarbons of oils and fats include alkanes and alkenes (such as squalene and carotene), and polycyclic aromatic hydrocarbons (PAHs) (Gunstone 2004). More volatile alkanes (up to C₁₂) are not likely to be significant in refined oils. However, levels of C₁₃-C₃₃ alkanes in crude oils are usually between 40 mg/kg and 100 mg/kg with lower values for refined oils. Carotenoids, which are highly unsaturated tetraterpenes that are biosynthesized from eight isoprene units, can be divided into two main classes: carotenes, which are strictly polyene hydrocarbons, and xanthophylls, which contain oxygen. Xanthophylls are produced by hydroxylation of the carotenoid skeleton. Oxygen in xanthophylls can be in the form of a hydroxyl, keto, epoxy or carboxyl groups (Sambanthamurthi et al. 2000). β -Carotene is the best known component of carotenoids and also the precursor of vitamin A. Polycyclic aromatic hydrocarbons are present at levels of up to about 150 μ g/kg (ppb) in most crude oils and after refining, 80 ppb (Gunstone 2004).

Tocol extracts are mixtures of up to eight phenolic compounds. There are four tocopherols with a saturated branched C₁₆ side chain and four tocotrienols, which are analogous compounds that have three isolated double bonds in the branched alkyl side chain. Tocopherols are designated as vitamin E active. The concentrations of tocopherols in commercial vegetable oils vary widely, from 0.01% or less, up to 0.5%, depending on the raw material of the oil (Hasenhuettl 1993). The fat-soluble vitamins detected in vegetable oils include A (retinol), D (cholecalciferol), E (tocopherol), and K (menaquinones) (Gunstone 2004). Chlorophyll and its magnesium-free derivative (pheaphytin) are found in small concentrations in crude oils. Chlorophyll is composed of a porphyrin ring system where magnesium is the central metal atom of a phytol side chain (Hasenhuettl 1993).

Additionally, pure vegetable oils contain insignificant amounts of inorganic matter (Haga 2004). The oxygen content is the most important difference in the chemical composition of fossil and vegetable oils. Vegetable oils contain 10-12% of oxygen, whereas, fossil oils normally contain an insignificant amount of oxygen. On the other hand, vegetable oils typically do not contain any sulfur contrary to heavy fuel oil.

Data often found in the literature lacks mentioning detailed analytical information about the refining stage of oil upon the case. However, it is common knowledge that different refining stages/processes affect (remove

some components, including inorganics) the chemical composition of oils. Despite this shortcoming, it was concluded that the average chemical compositions of selected raw materials could be presented and enable a comparison of the raw materials' chemical properties (see Sections 2.1-2.4).

2.1 Palm oil

The oil palm (*Elaies guinensis*) grows in the tropical regions of Asia, Africa, and the Americas, and predominantly in Malaysia and Indonesia (Gunstone 2004, Sundram 2011). It is a perennial tree crop, which is unique in that it produces two types of oil. The fleshy mesocarp produces palm oil which is used mainly for edible purposes and the kernel produces palm kernel oil, which has a wide application in the oleochemical industry (Sambanthamurthi et al. 2000). Another species of oil palm (*Elaies oleifera*) originates from Central and South America (Lin 2002). However, its oil to bunch ratio is extremely low, making it uneconomical to plant on a commercial scale. In this thesis, only the chemical composition of palm oil (from *E. guinensis*) is considered. Oil yield from palm fruit is 45-50% (5950 L/ha) (Karmakar et al. 2010). Over 95% of palm oil consists of mixtures of TGs. It is mostly saturated oil which is solid at room temperature due to its FA composition (Pioch and Vaitilingom 2005). The oil contains almost equal proportions of saturated (44-45% palmitic and 4-5% stearic acids) and unsaturated acids (39-40% oleic and 10-11% linoleic acids) (Sambanthamurthi et al. 2000, Lin 2002, Gunstone 2004). In terms of FA composition and iodine value, there generally aren't any major differences between the oils from different locations.

Palm oil is unique among vegetable oils as it has a significant amount of saturated FAs (10-15%) at the 2-position of its TGs. However, as was stated earlier, the *sn*-2-position has specificity for unsaturated FAs. Therefore, more than 85% of the unsaturated FAs are located at the *sn*-2-position of glycerol (Lin 2002, Noor Lida et al. 2002). The major TGs in palm oil are disaturated POP (27-31%), monosaturated POO (20-26%), monosaturated PLO (9-11%) and disaturated PLP (6-11%), where P refers to palmitic acid, O to oleic acid, and L to linoleic acid (Gunstone 2004). The fully unsaturated TGs constitute a range of 6% to 12%, whereas the amount of fully saturated TGs is 7-10% (mainly PPP) (Sambanthamurthi et al. 2000, Sundram 2011).

Partial glycerides do not occur naturally in significant amounts except in palm oil from damaged fruits (Sambanthamurthi et al. 2000), although for example, different isomers of MGs and DGs are found in palm oil. According to Sambanthamurthi et al. (2000), the DG content of crude palm oil varies from 5.5% to 7.1% with a mean average of 4.9%. Pioch and Vaitilingom (2005) have reported the value of 8.4% of DGs for refined palm oil. More 1,3-DG than 1,2-DG isomers (in an approximate proportion of 2:1) are observed in all crude oils

(Sambanthamurthi et al. 2000, Gibon et al. 2007). Palm oil contains three main types of DGs - 12.6% of C₃₂ dipalmitoylglycerol (PP), 54.4% of C₃₄ palmitoyloleylglycerol (PO), and 33.0% of C₃₆ dioleylglycerol (OO). The MG content of palm oil is low, usually below 1%.

The major FAs in palm oil MGs are palmitic and oleic acids. While it is possible to obtain a crude palm oil with only 0.02% FFAs from fresh ripe fruit, the FFA content of commercial crude palm oils is, on average, about 3.5% (Gibon et al. 2007). The main phosphatide component in palm oil is phosphatidylcholine and the major glycolipid is galactosyldiacylglycerol. Lactones, which are cyclic esters produced from unsaturated acids, hydroxy acids or other FA derivatives, are major cyclic esters in palm oil (although classified as a minor component) (Sambanthamurthi et al. 2000). The amount of lactone is reported to be as much as 1 mg/kg in palm oil and δ -lactones (δ -C₁₁ and δ -C₁₅) were reported to be the most predominant type.

The total amount of sterols contained in crude palm oil is around 0.03% (Gibon et al. 2007, Sundram 2011). Sterols have been observed to be either free or esterified (50:50). Free and mainly acetylated sterol glucosides have also been detected (up to 300 ppm). Sitosterol is the most abundant sterol (up to 63%) in palm oil. Campesterol (~20%), stigmasterol (~20%), and cholesterol (~4%), Δ^5 -avenasterol (0-2.8%), Δ^7 -stigmasterol (0-2.8%), and Δ^7 -avenasterol (0-4%) have also been observed to exist in lower quantities (Sundram 2011). Methylsterols and triterpene alcohols (consisting mainly of five condensed cyclohexane rings with 30 carbon atoms) are present at a concentration of 800 ppm (Gibon et al. 2007). 4-Methylsterols, which have been identified in palm oil include obtusifoliol, cycloeucanol, gramisterol, and citostadienol (Sambanthamurthi et al. 2000). Triterpene alcohols identified in palm oil include cycloartenol, 24-methylenecycloartenol, cycloartanol, and β -amyrin. The content of isoprenoid alcohol in crude oil is about 80 ppm (Gibon et al. 2007).

The vitamin E content in crude palm oil ranges between 600-1000 ppm (after refining 350-630 ppm) and is a mixture of tocopherols (18-22%) and tocotrienols (78-82%) (Sambanthamurthi et al. 2000, Sundram 2011). The major tocotrienols in palm oil are α -tocotrienol (22%), γ -tocotrienol (46%), and δ -tocotrienol (12%). The content of vitamin E has been reported to be reduced in the refining process. Compared to other oils, palm oil has a high proportion of tocopherols and tocotrienols in relation to its unsaturation, which could explain its greater oxidative stability (Gibon et al. 2007).

Two classes of pigments occur in palm oil; carotenoids and chlorophylls (Sambanthamurthi et al. 2000). Crude palm oil has a high content of carotene (700-800 ppm), which causes its rich orange-red color. According to Gibon et al. (2007) the content of carotenoid compounds within crude oil might even be as high as 2000 ppm. The major carotenoids in palm oil are β - and α -carotenes

which account for 36% and 54% of the total carotenoids, respectively. Most of the carotenoids in palm oil are destroyed during the refining process. Carotenoids are the precursors of vitamin A, with β -carotene having the highest provitamin A activity (Sambanthamurthi et al. 2000). Another important group of pigment in palm oil is chlorophyll and includes the green chlorophyll *a* and chlorophyll *b* types (Fig. 1). Brown pheophytin *a* and pheophytin *b* are also present. Chlorophyll content in ripe fruits has been reported to be 80-90% smaller than in the green fruits. Also, according to some studies performed for physically refined oils, the chlorophyll content in crude oils has been reported to be about 800 $\mu\text{g}/\text{kg}$, but no residual chlorophyll has been found in refined palm products. In another study, it has been reported that the chlorophyll content in crude oil, expressed as pheophytin *a*, ranged from 250 $\mu\text{g}/\text{kg}$ to 1800 $\mu\text{g}/\text{kg}$ and the liquid (olein) fraction contained more chlorophyll because of the preferential partitioning of chlorophyll into it.

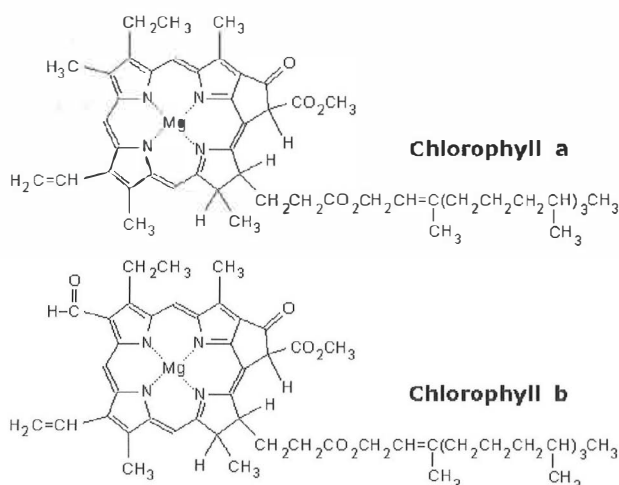


FIGURE 1 Structures of chlorophyll a and chlorophyll b (Anon. 2011).

In addition to neutral lipids (TGs), palm oil contains polar lipids such as glycolipids and phospholipids. Glycolipids are major polar lipids (1000-3000 ppm) (Sambanthamurthi et al. 2000). Monogalactosyldiacylglycerol (MGDG) is a major glycolipid (26.8% of total glycolipids), whereas digalactosyldiacylglycerol (DGDG) is the second major glycolipid (23.1%) in palm oil. Additionally, steryl glycoside and acylated steryl glycoside have been detected in Indian palm oil. Compared to other vegetable oils, palm oil includes relatively small quantities of phospholipids (5-30 ppm). The major phosphatide component in palm oil is phosphatidylcholine (Gibon et al. 2007). On the other hand, phospholipids form a relatively minor proportion of the total phosphorus content in crude palm oil. Typically, the inorganic phosphorus content is eight times that of the phospholipid phosphorus. Most of the phosphorus appears as inorganic orthophosphates and the major phosphorus compounds in refined

palm oil are the phosphoric acids, phosphorylated DGs such as phosphatidic acids, and possibly polyphosphates (Sambanthamurthi et al. 2000).

The flavor compounds in the natural (or fresh) palm oil include small amounts of aldehydes, with hydrocarbon terpenes and monooxygenated terpenes predominating (Sambanthamurthi et al. 2000). The terpenes include linalool, *trans*-allo-ocimene and β -cyclocitral. Additionally, naphthalene and its derivative 1,2,3,4-tetrahydronaphthalene have also been detected. The flavor compounds of rancid palm oil are mostly aldehydes and ketones.

The content of squalene, which is a hexaunsaturated hydrocarbon with 30 carbon atoms, in crude palm oil is 200-350 ppm (Sambanthamurthi et al. 2000). Other hydrocarbons present in small quantities are sesquiterpene and diterpene hydrocarbons. These hydrocarbons are removed during the refining of the crude oil. The content of non-terpene hydrocarbons is 30-50 ppm (Gibon et al. 2007). Crude palm oil also contains 10-80 ppm of ubiquinone-10 and 5 ppm of ubiquinone-5, which are related to vitamin K.

Trace metals can be present as complexes surrounded by proteins, phospholipids, and lipids or non-lipid carriers. They can also be present as suspended solid impurities in the oil. The average level of iron reported in crude palm oil is 4.4 ppm while for copper it is 0.06 ppm (after refining 1.0 ppm and <0.1 ppm, respectively). Other metals reported in palm oil are manganese (about 1 ppm), cadmium, and lead. Cadmium and lead are found at very low concentrations.

2.2 Olive oil

Olive oil is obtained from the mesocarp in the fruits of olive trees (*Olea europaea*) (Gunstone 2004). The oil yield is 25-30% (about 1200 L/ha) (Karmakar et al. 2010). Commercial growth of the tree is confined almost entirely to the Mediterranean countries of Italy, Greece, Spain, Turkey, and Tunisia. Virgin olive oil is produced from the first pressing and then other grades of lower quality are produced (Ramirez-Tortosa et al. 2006). Virgin olive oils are classified according to their maximum free acidity in terms of oleic acid, to extra virgin olive oil (1.0 g/100 g oil), virgin olive oil (2.0 g/100 g), ordinary virgin olive oil (3.3 g/100 g), and lampante virgin olive oil (more than 3.3 g/100 g). Refined olive oil has free acid content of no more than 0.5 g/100 g (expressed as oleic acid). Olive oil obtained through the blending of refined olive oil and virgin olive oil has free acid content of no more than 1.5 g/100 g. Olive oil is primarily a mixture of TGs, with some FFAs, DGs, and MGs, together with non-glyceride constituents (0.5-1.5%) (Boskou 2002). Major saponifiable components are composed of TGs. Minor components, which are present in very low

amounts, include more than 230 chemical compounds (Ramirez-Tortosa et al. 2006).

Olive oil is characterized by a high level of oleic acid (Gunstone 2004). The FA composition of olive oil varies (Boskou 2002); typically 7.5-20% palmitic acid, 0.5-5% stearic acid, 0.3-3.5% palmitoleic acid, 55-85% oleic acid, 7.5-20% linoleic acid, and 0.0-1.5% linolenic acid. Myristic, heptadecanoic, and eicosanoic acids are only found in trace amounts. FA compositions differ from sample to sample, depending on where they were produced, the latitude, the climate, the variety, and the stage of maturity of the fruit. Greek, Italian, and Spanish olive oils are low in linoleic and palmitic acids and have a high percentage of oleic acid. Tunisian olive oils are higher in linoleic and palmitic acids and lower in oleic acid. The major TGs are (Boskou 2002): OOO (40-59%), LOO (12-20%), POO (12-20%), and POL (6-7%). In virgin olive oil, the concentration of DGs is 1-2.8% and MGs are present in much smaller quantities (less than 0.25%).

The tocopherol content of olive oil is highly variable (5-300 mg/kg) although usual values for good quality oils are between 100 mg/kg and 300 mg/kg (Boskou 2002). The main component of the tocopherol mixture is α -tocopherol which accounts for up to 95% of the total. The other 5% of the mixture consists of β - and γ -tocopherols. Two hydrocarbons, squalene and β -carotene, are present in olive oil in considerable amounts. Another abundant carotenoid in olive oil is lutein. Total carotenoids generally range between 1 mg/kg and 20 mg/kg, but values do not usually exceed 10 mg/kg. Squalene, found in virgin olive oil at concentrations of 0.7-12 g/kg accounts for more than 50% of the unsaponifiable fraction of crude oil.

Chlorophylls *a* and *b* and their oxidation products, pheophytins *a* and *b*, are naturally present in olive oils and are responsible for the greenish color of the oils (Ramirez-Tortosa et al. 2006). In virgin olive oil that comes from mature olives, the levels of chlorophyll are from 1 mg/kg to 10 mg/kg and those of pheophytins are from 0.2 mg/kg to 24 mg/kg.

Four classes of sterols occur in olive oil, common sterols (4- α -desmethylsterols), 4- α -methylsterols, 4,4-dimethylsterols (triterpene alcohols), and triterpene dialcohols (Boskou 2002). The major class of sterols is desmethylsterols which are present at levels of up to 100-200 mg/kg. Some of the total sterols are esterified. Sitosterol makes up 75-90% of the total sterol fraction. Sterols found in considerable amounts are Δ^5 -avenasterol (5-36%) and campesterol (~3%). Other desmethylsterols found in olive oil (trace amounts) are cholesterol, campestanol, stigmasterol, Δ^7 -campesterol, chlerosterol, sitostanol, $\Delta^{5,24}$ -stigmastadienol, Δ^7 -stigmasterol, and Δ^7 -avenasterol. Salvador et al. (1998, 2001) have also found small amounts of 24-metilencholesterol and $\Delta^{5,23}$ -stigmastadienol from virgin olive oil. The amount of monomethylsterols in olive oil is in a range of 20-70 mg/100 g oil. The predominant methylsterols are

obtusifoliol, cycloeucanol, gramisterol, and citrostadienol. Triterpene alcohols are present at concentrations of 100-150 mg/100 g oil, with the most major ones containing β -amyirin, butyrospermol, cycloartenol, and 24-methylene-cycloartanol. The absolute amount of the two main triterpene dialcohols, erythrodiol, and uvaol, is 1-20 mg/100 g.

Fatty alcohols form an important class of olive oil's minor components because they can be used to differentiate between various olive oil types (Boskou 2002). The main linear alcohols include docosanol, tetracosanol, hexacosanol, and octacosanol. The total content of fatty alcohols does not usually exceed 35 mg/100 g oil. The content of waxes (i.e., the esters of fatty alcohols with FAs) are very low and do not exceed 35 mg/100 g. Additionally, two different diterpene alcohols, phytol (120-180 mg/kg) and geranylgeraniol, have been reported to be present in olive oil.

Phenolic compounds present in olive oil are conventionally characterized as "polyphenols", though not all of them are polyhydroxy aromatic compounds. The most important classes of phenolic compounds in virgin olive oil include phenyl acids (e.g., *p*-coumaric, vanillic, and ferulic acids), phenyl alcohols (e.g., 3,4-(dihydroxyphenyl)ethanol), flavonoids (e.g., luteolin), secoiridoids (e.g., oleuropein), and lignans (e.g., pinoresinol) (Garcia et al. 2001, Servili et al. 2004). Wide ranges of polyphenol content have been reported, ranging from 50 mg/kg to 1000 mg/kg, but usually values are between 100 mg/kg and 300 mg/kg. Olive oil also contains volatile flavor components which include hydrocarbons, alcohols, and furan derivatives (Torres et al. 2005). Saturated and unsaturated aldehydes are the major components representing 58% to 71% of the total volatile compounds.

2.3 Rapeseed oil

The seed oil of *Brassica napus* or *B. campestris* is grown primarily in Western Europe, China, India, and Canada (Gunstone 2004). The oil yield is 1190 L/ha (38.6%) (Gunstone 2002, Karmakar et al. 2010). Typically, the content of TGs in rapeseed oil is 91.8-99.0% (Przybylski and Mag 2002). The amount of FFAs in crude rapeseed oil is 1.35% and considerably less in refined rapeseed oil (0.018%) (Karaosmanoğlu et al. 1997, Jeong et al. 2004, Jeong, Park 2006).

Typical chemical composition of rapeseed oil according to multiple references is presented in Appendix II. It should be pointed out that there are specialty rapeseed oils (e.g., high-erucic-acid and low-erucic-acid oils) whose compositions differ remarkably from each other. Early rapeseed cultivars had high levels of erucic acid in the oil (Przybylski and Mag 2002, Gunstone 2004). The presence of erucic acid was considered to be a health concern and thus low-erucic-acid rapeseed oil was developed. In 1977, a low-erucic-acid trait was

made mandatory in Europe. However, high-erucic-acid (content 40-64% of FAs) oils are still predominant in India and China.

The fall in the level of erucic acid in rapeseed oil resulted in a marked increase in C₁₈ acids and they make up around 95% of all FAs present (Gunstone 2004). Typically, rapeseed oil contains palmitic (4%), stearic (2%), oleic (62%), linoleic (22%), and linolenic (10%) acids and have less saturated acids than any other commodity oil. Plant breeders have also developed varieties with low-linolenic-acid content (2%) and varieties with high-oleic-acid content (85%) (Przybylski and Mag 2002). Furthermore, canola oils, with a high content of lauric acid (39%) or stearic acid (40%) have been developed as well as oils containing up to 40% of γ -linolenic acid. Minor acids present in oils differ from other major components by the location of their double bonds. Generally, the content of these acids is in a range of 0.01-0.1%, except for 16:1 *n*-7, which is around 0.3%. Most of the minor acids are from the *n*-7-series, rather than the more common *n*-9-isomers. Conjugated C_{18:2} acids have also been found in canola oils. Some of these fatty acids are the by-product of refining and deodorization.

According to one example, its major TGs were LnLO (8%), LLO (9%), LnOO (10%), LOO (22%), LOP (6%), OOO (22%), and POO (5%). High-oleic-acid rapeseed oil resembles the composition of olive oil more closely than that of the regular canola oil (Przybylski and Mag 2002). In addition, rapeseed oils contain a few minor FAs (Przybylski and Mag 2002, Ratnayake and Daun 2004). Most of the minor FAs present in rapeseed oils differ from the usual common FAs in the form of a double bond. Generally, these FAs are present in the 0.01-0.1% range, except 16:1*n*-t FA which is around 0.3%. A few other minor FAs may have an unusual combination of some common structural features (Ratnayake and Daun 2004). The possible presence of trace amounts (<0.01% of total FAs) of sulfur-containing FAs have been found. Rapeseed oil is the only known edible oil that contains sulfur-containing FAs.

Sterols and sterol esters of FAs predominate among the non-acylglycerol lipids of vegetable oils (Przybylski and Mag 2002, Ratnayake and Daun 2004). The total amount of sterols (the sum of esterified and non-esterified sterols) in rapeseed oil ranges from 0.7% to 1.0%. The sterol content of refined oils is usually lower than that of crude oil. All the different varieties of rapeseed oil contain moderate amounts of brassicasterol (5.0-13.0% of total sterols). The other major sterols are sitosterol (45.1-57.9% of total sterols) and campesterol (24.7-38.6% of total sterols). Cholesterol, stigmasterol, Δ^5 -avenasterol, Δ^7 -stigmastanol, 24-methylene cholesterol, campestanol, $\Delta^{5,23}$ -stigmastadienol, sitostanol, $\Delta^{5,24}$ -stigmastanol, and Δ^7 -avenosterol are also present, but at lower levels.

Rapeseed oil contains mostly α -tocopherol (63-74% of total tocopherols) and γ -tocopherol (26-35% of total tocopherols), with γ -tocopherol usually present in higher amounts (Ratnayake and Daun 2004). β - and δ -tocopherols are usually present only in trace amounts. Crude rapeseed oil can contain as much as 95 mg/kg total carotenoids, which are predominantly xanthophylls (85-90%). Approximately 7-10% of carotenoids are present as carotene. Additionally, rapeseed lipids contain about 3% of phospholipids and about 1% of glycolipids. Phospholipids are generally divided into two classes, non-hydratable (phosphatidic acid and phosphatidylinositol) and hydratable phospholipids.

Rapeseed, and in particular, *B. napus* varieties grown in short-season areas (Canada and Scandinavia), contain a significant amount of chlorophyll (usually the amount varies within a range of 5-55 ppm). However, top-grade crude oil is expected to have less than 30 mg/kg of chlorophyll pigments. The amount of sulfur in rapeseed oil is relatively high, (5-35 ppm) depending on the processing stage of oil and determination method. Lastly, rapeseed oil contains inorganic elements (Cu, Fe, Pb, Ni, P, Zn, Na, K, Ca, and Mg) in trace amounts.

2.4 Castor oil

Castor oil, also known as ricinus oil, is derived from the plant *Ricinus communis*, grown mainly in India, Brazil, and China (Naughton 1993, Gunstone 2004, Karmakar et al. 2010). The seeds contain up to 60% oil which is rich in TGs, mainly ricinolein (Figueiredo et al. 2009). The oil yield is about 1400 L/ha. The FAs of castor oil consist of 80-90% ricinoleic acid, 3-6% linoleic acid, 2-4% oleic acid, and 1-5% saturated FAs (palmitic, stearic, dihydroxystearic, and eicosanoic acids) (Naughton 1974, Scholz and da Silva 2008). The maximum amount of FFAs that can be found is in a range of 0.75-3.0% depending on oil quality (according to specifications of by the International Castor Oil Association) (Naughton 1993). The amount of unsaponifiable matter (max.) is from 0.7% to 0.8%.

Compared with other vegetable oils, castor oil has a very high proportion of monounsaturated FAs ($C_{18:1}$). The chemistry of castor oil is centered on its high content of ricinoleic acid and the three points of functionality; carboxyl group, olefinic linkage, and hydroxyl group (Ogunniyi 2006). The predominating FA gives this vegetable oil many unique properties. Castor oil is odorless, viscous, and is non-drying oil (iodine number less than 90) which in its natural state is yellow-green to yellow-brown in color. Unlike other vegetable oils it is characterized by its indigestibility, solubility in alcohol, high hygroscopicity, and extraordinarily high viscosity. It is also less soluble in hexane. According Lechner et al. (1999) the tocopherol content in castor oil is 0.052% and the most abundant tocopherols were γ -tocopherol (260 $\mu\text{g/g}$) and δ -tocopherol (244 $\mu\text{g/g}$). The content of free sterols is 0.244%. The most abundant

sterols are sitosterol (1171 $\mu\text{g/g}$), stigmasterol (543 $\mu\text{g/g}$), and Δ^5 -avenasterol (435 $\mu\text{g/g}$). Additionally, brassicasterol, Δ^7 -stigmasterol, and Δ^7 -avenasterol have been detected in castor oil (fraction of free sterols) (Chakrabarti and Ali 2009).

2.5 Tall oil products

The main by-products of softwood kraft pulping are crude sulfate turpentine and crude tall oil soap (CTOS) (Alén 2000, Gullichsen and Lindeberg 2000). This soap is formed from the non-volatile extractives fraction and it is composed of sodium and calcium salts of FAs and resin acids (RAs), together with some neutral substances ("non-saponifiables") (Alén 2000). RAs are monocarboxylic diterpene acids, the most common of which have the molecular formula $\text{C}_{20}\text{H}_{30}\text{O}_2$ (Soltes and Zinkel 1989). With very few exceptions, the pine resin acids belong to four basic skeletal classes: abietane, pimarane, isopimarane, and labdane (Fig. 2). It should be pointed out that several new FA components are formed in the sulfate pulping process via isomerization (Holmbom 1977). The dienoic and trienoic acids are isomerized to acids with conjugated double bonds having mainly a *cis-trans* configuration. These isomerization products are evidently formed from linoleic and pinolenic acids (Holmbom and Ekman 1978).

RAs also undergo double bond isomerization during pulping (Holmbom and Ekman 1978). The principal change has been proved to be the partial isomerization of levopimaric acid. By concentrating the cooking liquor ("black liquor"), soap floats to the surface where it can be skimmed off (as crude soap) (Gullichsen and Lindeberg 2000). The main impurity in soap is entrained black liquor containing several compound groups. For many reasons, CTO content in soap should be above 50%. The extractives composition of CTOS from pine (100% pine) pulping is presented in Appendix III. The low amount of non-saponifiables, 8.4%, depends on the wood raw material used for pulping. The amount of neutral components increases with the use of spruce or birch in a pulping furnish. The content of sterols was found to be 56.0-56.5% of the non-saponifiables in soap originating from Scots pine pulping (Holmbom and Ekman 1978). Main sterols were sitosterol (34-35% of the non-saponifiables), stigmasterol (6.8-8.0%), and cycloartenol (4.4-4.6%). The major alcohols (14.5-16.0%) in non-saponifiables fraction included pimarol (6.4-6.8%), thunbergol (1.2-1.4%), and isopimarol (1.2-1.6%). Major components in aldehyde fraction (12.0-12.5%) were pimaral (6.0-6.6%) and isopimaral (2.2-2.4%). Some fatty alcohols (5.2-6.5%) were also present in the non-saponifiables fraction. Additionally, small amounts of hydrocarbons (thunbergene and pimaradiene) as well as squalene, were detected.

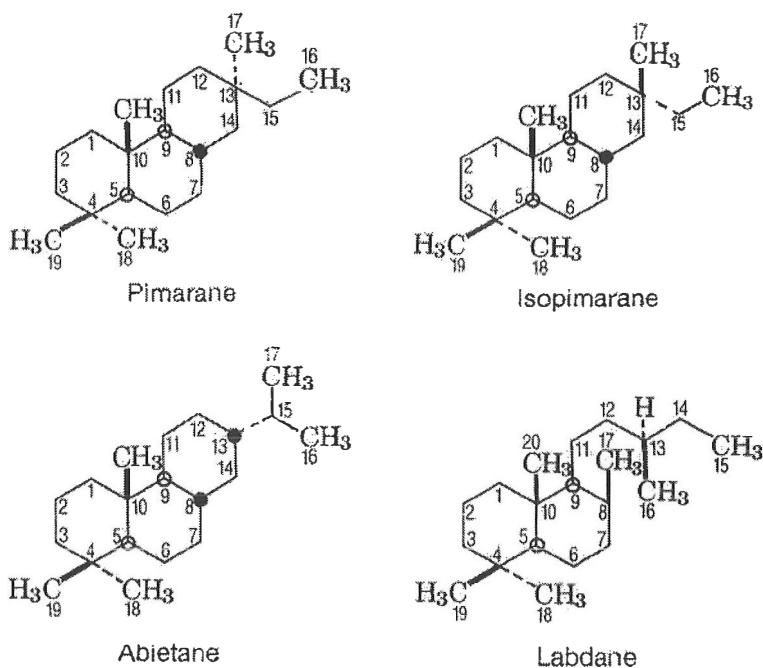


FIGURE 2 The principal diterpene hydrocarbon skeletons on which pine resin acids are based (Soltes and Zinkel 1989).

The tall oil soap is removed during the evaporation process of the black liquor by skimming, and then the resin and fatty acids are liberated by adding sulfuric acid to yield crude tall oil (CTO) (Alén 2000). The average yield of CTO is in the range of 30-50 kg/t of pulp. The rest is lost during woodyard operations, pulping, black liquor recovery, and acidulation (Huibers 1997). In the sulfate soap acidulation process the main component changes are isomerizations of RAs and conjugated FAs (Holmbom 1977). In tall oil cooking, a shift in the FA composition towards a lower degree of unsaturation and a notable isomerization of palustric, levopimaric, and neoabietic acids to abietic acid have been seen to occur (Holmbom and Avela 1971a, Holmbom 1978a). The tall oil quality deteriorated (observed as a decreased acid number) during soap acidification, CTO washing, and drying processes as well as during storage. The principal reason for deterioration is that esterification takes place. All FAs take an equal part in esterification but RAs are not esterified. Primary alcohols like tricyclic diterpene alcohols and fatty alcohols are almost completely esterified in the stored CTO from pine, whereas only about half of secondary alcohols, i.e., sterols and triterpene alcohols, occur in ester form. The composition of CTO varies considerably, depending on the location of the mill and the wood furnish used. Pulping process variations further affect CTO composition (Huibers 1997).

The best CTO is produced from pine wood, whereas the composition of extractives in hardwoods such as birch can have detrimental effects on the quality of the CTO end products (Gullichsen, Lindeberg 2000). The usage of spruce in the pulping wood furnish makes the yield decrease. The increased use of hardwood lowers the yield further (as well as the quality). The composition of crude tall oil from Scots pine generally varies in the range of 45-60% FAs, 35-50% RAs, and 8-12% non-saponifiables (Appendix III) (Holmbom 1978b). The content of sterols (sitosterol, sitostanol, and campesterol) in CTO from pine is about 40% of the unsaponifiables, i.e., about 3% of the tall oil (Holmbom and Avela 1971b). Sitosterol is the most dominant component. Usually the Scandinavian CTO contains 43% of FAs, 29% RAs, and 28% neutral components (Huibers 1997). Tall oil is produced mainly in North America (~250 0000 tons) and Scandinavia (~90 000 tonnes) (Gunstone 2004). Crude tall oil is a dark oily liquid and is also an excellent source of oleic/linoleic FAs and RAs or rosin. Elemental analysis has shown that tall oil contains 11.0% oxygen, 79.1% carbon, and 9.9% hydrogen (Sharma and Bakhshi 1991b, Altiparmak et al. 2007).

CTO is purified and fractioned through vacuum distillation (see Fig. 3 for distillation process) (Alén 2000). Extensive distillation is required, not only to separate desired products, but also to remove the neutrals (Huibers 1997). Extensive reactions of tall oil components take place at higher temperatures, up to 280-290 °C during tall oil distillation (Holmbom 1978a). RA reactions giving other RAs include double bond isomerization, disproportionation, and dehydrogenation (Holmbom 1978). Artifact RAs are formed both from abietane-type and pimarane-type acids. For example, the double bond isomerization of pimaric acid yields 8,15-pimaradienoic acid. Reactions causing losses of RAs (and the formation of non-saponifiables) are decarboxylation (results in the formation of hydrocarbons), dehydration (RA anhydrides), and polymerization (e.g., dimers and trimers). The losses of FAs during distillation are less than RA losses. The saturated FA losses have been observed for the C₂₀-C₂₄ acids but not for the C₁₆-C₁₈ acids. Monoenoic, dienoic, and trienoic acids are subject to reactions attacking the double bonds. Conjugated acids have a tendency to undergo the Diels-Alder condensation effect which results in the formation of dimers and cyclic fatty acids (e.g., cyclopinenic).

Various commercial FA products from tall oils (TOFAs) are available varying in both purity and composition (Alén 2000). The rosin content in these products is usually in a range of 1-10% (Lee et al. 2006). Oleic and linoleic acids are the most common in TOFA products. The predominating RAs in commercial rosins (TORs) are abietane (e.g., abietic and dehydroabietic acids) and pimarane types (e.g., pimaric, palustric, and levopimaric acids), but lesser amounts of the labdane-type can also be present in some TORs. The RA compositions of tall oil rosin have been found to differ significantly from that of corresponding CTO feeds (Holmbom 1978a,b). Several RAs (artifact RAs) present in rosins have been formed in the distillation process. Neutral fractions

of tall oil are typically the most prominent in the heads fraction of tall oil (the part which distills first) before the RAs and FAs (Lee et al. 2006). Main species in the head fraction consist of resin alcohols, steroids (especially sitosterol), fatty alcohols, diterpenes, sesquiterpenes, and resin aldehydes.

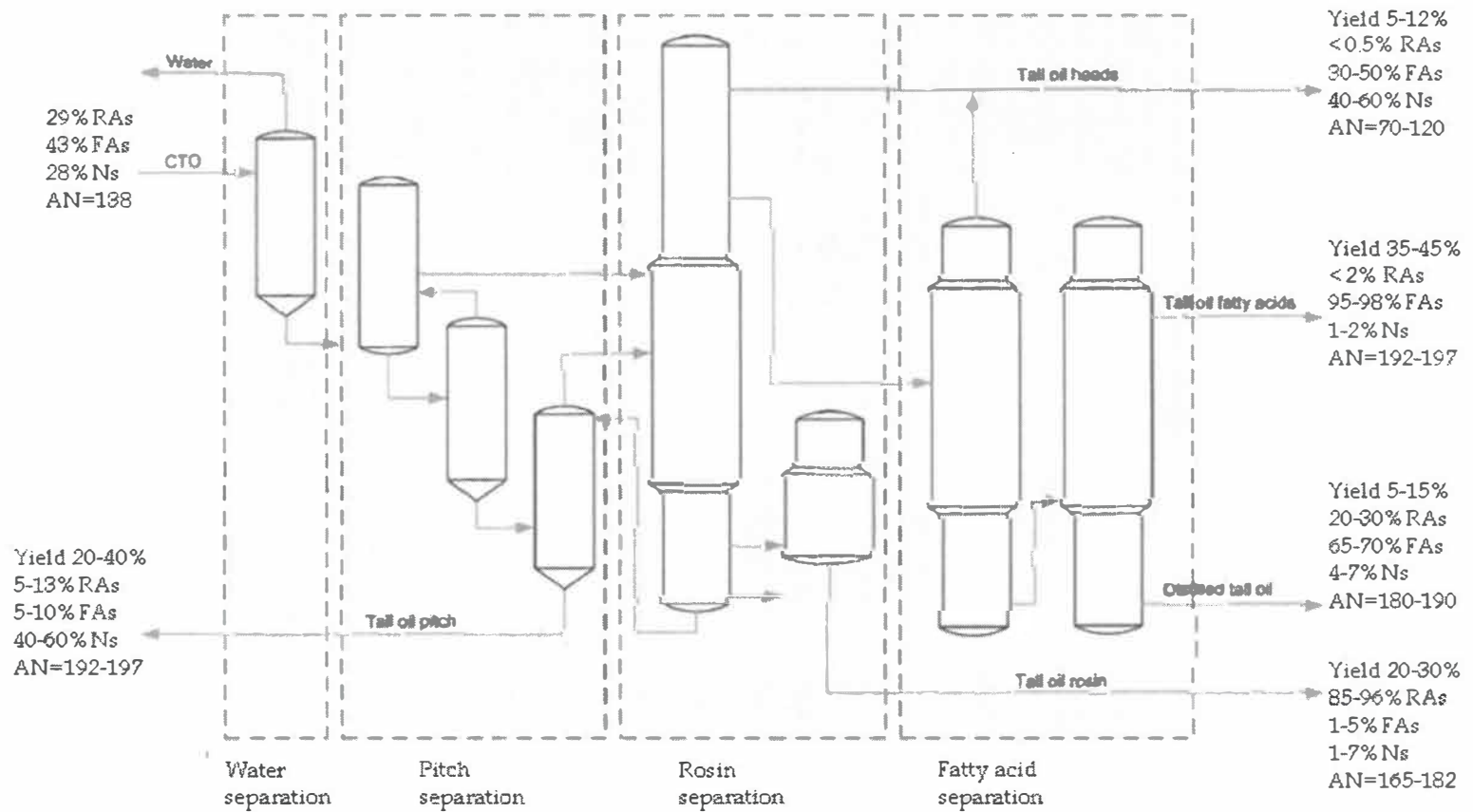


FIGURE 3 Composition of incoming and outgoing streams in the tall oil distillation process. CTO = crude tall oil, RA = resin acid, FA = fatty acid, N = neutral component, and AN= acid number (modified from Refs. (Niemelä 2000, Koski 2008)).

2.6 Fuel properties

Chemical and physical properties of diesel fuel

Diesel fuel is a very complex mixture of thousands of individual compounds, mostly with carbon numbers between 10 and 22 (Bacha et al. 1998). The hydrocarbons present in the diesel fuels include paraffins, naphthenes, olefins, and aromatics (Srivastava and Prasad 2000). While carbon and hydrogen are the predominant elements in crude oil, small amounts of sulfur, nitrogen, and oxygen are also present (Bacha et al. 1998). Typical examples of non-hydrocarbon compounds found in diesel include dibenzothiophene and carbazole. Although these compounds are present in small amounts, they play a significant role in determining certain fuel properties. According to one example, the Swedish commercial summer diesel fuel contained 26.1 vol-% of aromatics (20.2% monoaromatics, 4.8% diaromatics, and 1.1% triaromatics), 1 vol-% (measured with fluorescence indicator adsorption method, FIA) olefins, 25.9 wt-% naphthenes and 46.9 wt-% paraffins (Westerholm and Li 1994, Sjögren et al. 1995). The amount of sulfur detected was 0.16 wt-%. For diesel fuel physical properties, see Appendix II.

Properties of vegetable oils vs. properties of diesel fuels

In 1898, Rudolph Diesel used peanut oil in the first demonstration of his compression ignition engine at the World's Exhibition in Paris (Luque 2008, Lin et al. 2011). Vegetable oils were used in a diesel engine until the 1920's when the engine was altered significantly, enabling it to use the residue of petroleum products (nowadays know as diesel No. 2, D2). D2 is a diesel engine fuel that has hydrocarbons of 10 to 20 carbon atoms. The major problems associated with the use of pure vegetable oils as fuels in diesel engines are caused by a high amount of fuel viscosity in the compression ignition (Ma and Hanna 1999, Srivastava and Prasad 2000, Demirbas 2003a,2008a). The high viscosity of these oils is due to large molecular mass (three or more times higher than that of diesel fuels) and its chemical structure. The vegetable oils are extremely viscous with viscosities ranging from 10 to 20 times greater than those of D2. Castor oil is in class by itself having a viscosity of more than 100 times that of D2.

Although vegetable oils contain chemically bound oxygen, their gross heat contents are approximately 88% of that of D2 (Demirbas 2008a). Castor oil has more oxygen so its higher heating (HHV) value is slightly lower than HHVs of other oils. Vegetable oils are better than diesel fuels in terms of sulfur content, flash point, aromatic content, and biodegradability. Additionally, they are portable and readily available. The disadvantages of using vegetable oils as a diesel fuel, in addition to having a higher viscosity, are lower volatility and

reactivity of unsaturated hydrocarbon chains. The problems in long-term engine tests include coking on injectors, more carbon deposits, oil ring sticking, and thickening as well as gelling of the engine lubricant oil. Comparison of the physical and chemical properties of vegetable oils to those of D2 fuel is presented in Appendix II. The direct use of tall oil is also not possible, since it produces excessive corrosion, has deficient rheological properties at low temperatures, and produces unacceptable contamination of lubrication oil and coking in the engine (Coll et al. 2001). These problems require that vegetable oils should be upgraded if they are to be used as a fuel in conventional diesel engines.

3 BIOMASS PYROLYSIS

3.1 General approach

“Biomass” is a generic term for all animate organic matter, excluding fossil fuels, where not only crops, forestry, and marine products but also organic wastes, such as municipal solid waste, sewage, and pulp-derived black liquor, are widely included (Demirbas 2000). Virtually all biomass products can be converted into commercial fuels (Ates et al. 2006). Biomass pyrolysis can be defined as the thermal decomposition of organic material without the use of an oxidizing agent, or with such a limited supply that extensive gasification does not occur (Walter et al. 2000, Demirbas 2008a). Gas, liquid, and char are produced as a result. The relative proportions of these are dependent on the pyrolysis method and reaction parameters, especially when it comes to the temperature and heating rate (Bridgwater and Cottam 1992, Encinar et al. 1996). Other parameters affecting the pyrolysis product distribution are vapor residence time and pressure (Azeez et al. 2010).

Pyrolysis is the simplest, and almost certainly, the oldest method of processing one fuel in order to produce a better one (Demirbas 2009b). Pyrolysis is a good option for conversion because it is relatively inexpensive and requires lower temperatures than gasification (Maher et al. 2008). It is also simple and inexpensive to construct and it has feedstock flexibility (Maher and Bressler 2007, Junming et al. 2009). The main objective of pyrolysis is to obtain products with a higher energy density and better properties compared to its initial biomass (Walter et al. 2000). With modern technologies, pyrolysis can be carried out under a variety of conditions in order to capture all of the necessary components that will maximize the output of a desired product, be it char, liquid or gas (Ates et al. 2006).

The direct production of liquids is of particular interest because of their much higher energy density, which reduces transport and handling costs, and

because of their possible use as a substitute for conventional fuels in many applications (Bridgwater and Cottam 1992, Demirbas 2007a). Additionally, they offer flexibility in production and marketing. The bio-oil can be used in engines and turbines and its use as a feedstock for refineries is also being considered (McKendry 2002). Nearly 100 different biomass types have been tested by many laboratories, including agricultural residues (Encinar et al. 1996, Oasmaa et al. 2010), municipal wastes (Demirbas 2007b), algal biomass (Peng et al. 2000), wood, bark, pulping wastes and forestry residues (Demirbas 2002a, 2007b Oasmaa et al. 2003, Luik et al. 2007, Zhang et al. 2007, Ingram et al. 2008, Oasmaa et al. 2010) nuts and seeds, like linseed (Acikgoz and Kockar 2007), to grasses (Boateng et al. 2006, Onay 2007, Uçar and Karagöz 2009). The need for further investigations into the chemistry of pyrolysis arises from the fact that the decomposition of biomass is complicated since it represents a large number of reactions in a parallel and in a series (Onay 2007). Different kinds of biomass possess different reactions in a pyrolytic process and that subsequently causes differences in the compositions of bio-oils from different feedstocks. The key properties of bio-oils for use as a diesel substitute are viscosity, heating value, density, and stability.

Though the oil yield can be maximized by changing the operating conditions, the oil quality is commonly not at a maximum (Peng et al. 2000). Pyrolysis oils from a carbohydrate-rich biomass contain hydroxyaldehydes, hydroxyketones, sugars, dehydrosugars, carboxylic acids, and phenolic compounds (Mohan et al. 2006). The presence of oxygen (45-50 wt-%) is the primary reason for differences between hydrocarbon fuels and biomass pyrolysis oils, which is immiscible with liquid hydrocarbons due to its high polarity and hydrophilic nature. Additionally, bio-oils are corrosive (McKendry 2002). The calorific values of the oils are about 55% of that of diesel fuel on a volumetric basis (Boateng et al. 2006). Although, it should be pointed out that pyrolysis oil produced from oilseeds has a heat content close to that of diesel fuel (Onay 2007).

The main focus in this study was on the pyrolysis of plant oils, or extracts, which are very important as biomass sources for the production of synthetic fuels and chemicals because of their suitable properties (i.e., high energy content and low content of sulfur and nitrogen) (Demirbas 2003a). The high viscosity of vegetable oils can be markedly reduced through thermal cracking (Megahed 2004). During this process, the TG molecules are broken into smaller fragments yielding a mixture of hydrocarbons that are much less viscous than the parent oil and that could potentially be used as a petrochemical replacement (Maher et al. 2008).

Plant oils have been pyrolyzed both with (Konwer et al. 1989, Idem et al. 1997, Dandik and Aksoy 1998, Dandik and Aksoy 1999, Demirbas 2003b, Sang 2003, Demirbas 2009c, Junming et al. 2009, Kirszensztejn 2009) and without a

catalyst (Alencar et al. 1983, Idem et al. 1996, Fortes and Baugh 2004, Lima et al. 2004, Sadrameli and Green 2007), as methyl esters (Billaud et al. 1995) and in the saponified form (Chang and Wan 1947, Fortes, Baugh 1994, Demirbas 2002b, 2003a, 2009c). Reports about the pyrolysis of neutralized tall oil products and crude tall oil soap were hard to find. This gave us reason to assume that this research topic is novel and less studied. In one Finnish study (Arpiainen 2001) the fast pyrolysis of pulverized crude tall oil soap to produce light fuel oil has been investigated. In earlier studies, CTO was mostly fractionated to the FA and RA fractions before the conversion was made of the FA fraction into biodiesel through transesterification (Altiparmak et al. 2007, Keskin et al. 2007, Demirbas 2008b). Fractionation was done because from the standpoint of conversional biodiesel production, the composition of tall oil is far from ideal (Lee et al. 2006). Another common approach was for direct catalytic upgrading of tall oil into fuels (Sharma and Bakhshi 1991a,b). Furthermore, Coll et al. (2001) studied the conversion of an RA fraction of CTO into fuels and chemicals by catalytic hydrotreatment and Liu (1998) has investigated the possibility of producing a cetane enhancer from depitched tall oil through a process of catalytic hydrogenation and cracking.

Pyrolysis of vegetable oils by these means produces not only the desirable linear and cyclic paraffins and olefins, but it also creates inconvenient oxygenated compounds such as aldehydes, ketones, and carboxylic acids together with water (Demirbas 2003b, 2009a,c, DeOliveira et al. 2006). It can therefore, be concluded, that thermal degradation alone is not a suitable method for the production of hydrocarbon fuels when the goal is to achieve complete deoxygenation (i.e., to obtain only hydrocarbons among liquid products) (Pioch and Vaitilingom 2005). However, high conversions and reasonable yields of diesel-like fuel can be obtained from direct thermal cracking of TGs. The focus of the research has shifted to catalytic cracking to increase conversion further (liquid yield) and to improve product quality. It has been observed that both catalytic cracking and pyrolysis of saponified plant oils improves the liquid product yield and results in the formation of petroleum like hydrocarbons with a lower oxygen content than the pyrolysis of plant oils. (Pioch and Vaitilingom 2005, Huber and Corma 2007, Junming et al. 2009). Saponification (i.e., the reaction of caustic with TG) prior pyrolysis results in a composition similar to diesel. For example, treatment with calcium hydroxide also facilitates the pyrolytic process (i.e., catalyzes the process) (Chang and Wan 1947, Fortes and Baugh 1994, Demirbas 2002b). Thermal cracking of vegetable oils as such (i.e., not as soap), is also more difficult to control.

Pyrolysis usually takes place within a 400-800 °C temperature range (Da Rocha Filho et al. 1992, Walter et al. 2000). Depending on the operating conditions, the pyrolysis process can be divided into subclasses. Lower process temperatures and longer vapor residence times favor the production of charcoal (Bridgwater and Maniatis 2004). Higher temperatures and longer residence

times increase the biomass conversion to a gas and moderate temperatures with a short vapor residence time are optimum for producing liquids. Pyrolysis methods and their parameters are presented in Table 1. Today, the term pyrolysis often describes a process where liquid oils, especially those with desirable chemical and physical attributes for liquid fuels, fuel supplements and chemical feedstock, are preferred products (Das and Ganesh 2003, Mohan et al. 2006).

TABLE 1 Pyrolysis methods, their variants, and products (modified from Refs. (Maniatis 2004, Balat 2008, Demirbas 2009b, Bridgwater))

| Method | Residence time | Temperature, [K] | Heating rate | Products |
|-------------------------------|----------------|------------------|-----------------------|-------------------------|
| Carbonation | Days | 675 | Very low | Charcoal |
| Conventional | 5-30 min | 550-950 | Low, 0.1-1 K/s | Oil, gas, char |
| Fast | 0.5-10 s | 850-1250 | Very high, 10-200 K/s | Bio-oil |
| Flash | < 1 s | 1050-1300 | High, > 1000 K/s | Bio-oil, chemicals, gas |
| Hydropyrolysis ^a | < 10 s | < 775 | High | Bio-oil |
| Methanopyrolysis ^b | < 10 s | > 975 | High | Chemicals |
| Ultra pyrolysis ^c | < 0.5 s | 1275 | Very high | Chemicals, gas |
| Vacuum pyrolysis | 2-30 s | 675 | Medium | Bio-oil |

^a) Hydropyrolysis: pyrolysis with water.

^b) Methanopyrolysis: pyrolysis with methanol.

^c) Ultra pyrolysis: pyrolysis with a very high degradation rate.

3.2 Fast pyrolysis

In the 1980's researchers found that the pyrolysis liquid yield could be increased using fast pyrolysis (Mohan et al. 2006). Fast pyrolysis is an advanced high temperature process where the biomass is rapidly heated in the absence of oxygen (Bridgwater et al. 1999). With carefully controlled parameters, bio-oil is obtained in yields of up to 75-80 wt-% on a dry-feed basis, together with by-product char (12%) and gas (13%) (Bridgwater et al. 1999,2002). There are four essential features of a fast pyrolysis process (Bridgwater et al. 1999,2002, Mohan et al. 2006). First, very high heating and heat transfer rates at the reaction interface are used, this usually requires a finely ground biomass feed. Secondly, the pyrolysis reaction temperature is carefully controlled (typically at relatively low temperatures, often in the range of 425-500 °C, but less than 650 °C, are used). Third, short vapor residence times are used (typically less than 2 seconds). Fourth, pyrolysis vapors and aerosols are rapidly cooled to give the bio-oil product. The longer residence time can cause secondary cracking of primary products, reducing yield, and adversely affecting bio-oil properties (Onay 2007). Additionally, a low heating rate and a long residence time may increase energy input.

The advantages of fast pyrolysis for the production of biofuels include a simple, efficient (high thermal efficiency), low fossil fuel input, and inexpensive technology (Mohan et al. 2006, Luque 2008). Compared to transesterification, its advantages include that the product has similar chemical components to conventional petroleum diesel fuel and can be used without major modification as an alternative engine fuel. The disadvantage of using the pyrolysis process is that the temperature must be kept rather high. Still it has been calculated that 85% of the initial energy content in starting oil would remain available as fuel by using pyrolysis (Pioch and Vaitilingom 2005). The by-products char and gas can be used within the process to provide process heat requirements (Bridgwater and Maniatis 2004). This way there are no waste streams other than from flue gas and ash.

3.3 Analytical pyrolysis

Analytical pyrolysis is the technique of studying molecules either by observing their behavior during pyrolysis or by studying the resulting molecular fragments (Wampler 2007a). The essential requirement in analytical pyrolysis is that of reproducibility (Irwin 1982). Replicate analyses should produce the same product profile and pyrolysis fragments should be transmitted efficiently to an analytical device. Overall a quantitative control of the pyrolysis system is necessary.

When a sample is subjected to pyrolysis, primary-bond-fission reactions are initiated (Irwin 1982). Processes proceed by several temperature dependent and competing reactions. This makes the final product distribution highly dependent upon the pyrolysis temperature. Thus, the first priority is to use a precisely controlled temperature (i.e., final pyrolysis temperature) for analysis. Generally, as the pyrolysis temperature increases, smaller and less characteristic fragments begin to dominate the pyrogram. Therefore, pyrolysis temperatures that range from 600 °C to 800 °C are preferred. The next concern is the temperature-time profile (i.e., heating rate) of the pyrolysis unit. Because of very rapid degradation reactions occurring during pyrolysis, the process may be essentially complete before the final pyrolysis temperature is reached. However, the situation may be even more complex. The temperature required for complete pyrolysis of the sample falls markedly as the total heating time increases (i.e., heating rate decreases). For the final temperature to have any significance, the heating rate should be rapid compared to the degradation rate of the sample. The rate of heating to the final temperature in the millisecond range is typical for analytical pyrolysis. If the energy parameters (temperature, heating rate, and time) are controlled in a reproducible way, the fragmentation is characteristic of the original molecule based on the relative strengths of the

bonds between its atoms (Wampler 2007a). The same distribution of smaller molecules will be produced each time in an identical sample as it is heated in the same manner.

It is important to heat the entire sample to the endpoint quickly, especially if one is studying the effects of the temperature from pyrolysis on the composition of the pyrolysate (Wampler 2007b). Samples slowly heated will undergo a considerable amount of degradation while the pyrolysis instrument is still heating to the final set point temperature, and a large sample will degrade according to the temperature distribution across the sample as it is heated. Consequently, reproducibility may depend heavily upon the ability of the pyrolysis instrument to heat the sample uniformly and to achieve the final temperature before the sample has already begun degradation.

To overcome differences in pyrolysis pathways caused by temperature-dependent effects, the whole sample should be subjected to the same temperature profile (Irwin 1982). To achieve this target, the sample should be in intimate contact with the pyrolysis heater in a way that the formation of a temperature gradient within the sample could be prevented. For this reason, very thin films are most appropriate for a high degree of reproducibility and an increasing sample-size will cause increased deviations from what is the ideal and may introduce variations due to temperature gradient effects. Sample size also has an effect on the fate of the primary pyrolysis products. Increasing amounts of samples also increase the amount of secondary reactions. Differences in quantitative recovery are also susceptible to variations in a sample load.

Resistively heated filament pyrolyzers operate by taking a small sample from an ambient to a pyrolysis temperature in a very short time (Wampler 2007b). Platinum filament pyrolyzers achieve very high temperatures and heating rate, so that they can reproduce the operating conditions of large scale plants (Biagini et al. 2006). Pyrolysis performed in a laboratory is frequently used to simulate different types of burning or industrial processes involving pyrolysis. (Moldoveanu 2010c). Azeez et al. (2010) have observed that there was close agreement in the composition of the volatile products from pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) and bench-scale pyrolysis. This proves further that Py-GC/MS is a reliable technique for qualifying pyrolysis products and offers the potential for studying their mechanisms of formation. It was concluded that analytical pyrolysis was a suitable method for gaining a better understanding of the pyrolysis chemistry of extractives-derived raw materials and to assess common trends throughout the process for these kinds of materials. However, when using a Py-GC, gaseous diffusion must be minimized and pyrolysis should be affected as near to the top of the column as possible. The amount of condensation onto cool surfaces should also be reduced

(Irwin 1982). Lack of control at the Py-GC interface will also disrupt pyrogram reproducibility

3.4 The chemistry of the pyrolytic process

The formation of pyrolysis products depends on the structure of the initial compound (parent compound) and also on pyrolysis conditions (Moldoveanu 2010a). In spite of the complexity of pyrolytic reactions, the pyrolysates are obtained through the cleavage of one or only a few bonds from the initial compound and of some initial pyrolysis fragments. Therefore, some resemblance between the initial molecule and the pyrolysis products is frequently obvious. The way in which a molecule fragments during pyrolysis and the identity of the fragments produced depend on the types of chemical bonds involved and the stability of the resulting smaller molecules (Wampler 2007a). The whole molecular structure as well as particular functional groups may contribute to the outcome of pyrolysis (Moldoveanu 2010a). In a molecule, where a specific moiety is more susceptible to thermal decomposition, the members of a homologous series may have a similar behavior (e.g., simple organic acids). As the complexity of the whole molecule increases (e.g., additional numbers of double bonds, aromatic rings, and more than one functional group), the outcome of the pyrolysis depends more and more on the whole molecular structure, and the role of one single functional group becomes less important.

The decomposition mechanism plays a major role regarding pyrolysis outcomes (Moldoveanu 2010a). Free-radical pathways dominate mechanisms for the pyrolysis of organic materials, although alternatives such as concerted molecular processes and ionic reactive intermediates do occur (Carey 2000, Poutsma 2000, Savage 2000). When the formation of free radicals occurs, the result is typically more complex than in cases where a concerted mechanism is responsible for the changes during pyrolysis (Moldoveanu 2010a). The most common types of reactions encountered in pyrolysis include elimination reactions (α -, β -, 1,3-, and 1,*n*-eliminations), fragmentation reactions (fragmentations, retro-ene reactions, retro-Diels-Alder and retro-aldol condensations, and extrusions), rearrangements (1,2-migrations, rearrangements in compounds with bent bonds, electrocyclic rearrangements, and sigmatropic rearrangements), other reaction types (oxidations/reductions, substitutions, and additions), and reactions in the presence of reactants or a catalyst.

When mixtures of compounds are pyrolyzed, more than one molecular species is subject to thermal degradation. Pyrolysis of compound mixtures is a complex problem as numerous parameters determine the outcome of the process. Both physical parameters (pyrolysis conditions) and chemical

parameters affect the pyrolytic outcome. However, each component can be considered as starting the pyrolytic process independently and this significantly reduces the complexity of the problem. However, this does not exclude the further interaction of the molecular fragments resulting from independent pyrolysis processes. The pyrolysate contains a mixture of a pyrolytic product of each compound that is generated from a combination of fragments from the initial components. Since free radical eliminations are the most dominant reaction mechanisms in hydrocarbon pyrolysis at temperatures between 600 °C and 900 °C, in this literature study, a substantial amount of emphasis is given to exploring these mechanisms.

3.4.1 Fundamental reactions of free radicals in pyrolysis

A free radical reaction is a chemical process that involves molecules having unpaired electrons (Carey 2000). Radical mechanisms combine, often in a chain like fashion, to accomplish an overall pyrolysis reaction. Chain mechanisms consist of a cycle of repetitive steps where they form many product molecules for each initial event. It is not uncommon for a radical mechanism of a moderately complex molecule, or a mixture of substrates, to contain tens or even hundreds of elementary steps in pyrolysis.

Hydrocarbon pyrolysis mechanisms usually comprise of a set of reversible free radical reactions that belong to a relatively small number of reaction families (Savage 2000). The main reaction families in hydrocarbon pyrolysis provide opportunities for both making and breaking chemical bonds. As shown in Figure 4, thermal hydrocarbon chemistry can involve both the degradation of large molecules into smaller ones and the molecular growth and production of heavier molecules (Carey 2000, Poutsma 2000, Savage 2000). The first two reaction families are usually the important initiation and termination events. They are the only ones where there is a net change in the number of radicals, which means that these are the steps that influence the total concentration of free radical intermediates. Hydrogen abstraction and β -scission steps often occur together in a chain propagation sequence. The thermochemistry of the above elementary reactions is dependent on the stability of the radicals involved.

The most common radical forming reaction is homolysis (unimolecular reaction), or the breaking of a covalent bond to form two radicals (Poutsma 2000). Homolysis is, out of all the elementary processes to be considered, the most kinetically sensitive to the stability of the radicals involved because of its highly exothermic reverse reaction, radical-radical combination. Another reaction producing free radicals is called molecular disproportionation. This bimolecular reaction and reverse reaction for radical disproportionation acts as a termination reaction. The usual disproportionation reaction of alkyl radicals involves the transfer of hydrogen from carbon β to the radical site leading to the

formation of alkane and alkene (Carey 2000). The most numerous classes of elementary radical reactions are those where one radical is consumed while another is formed, i.e., hydrogen abstraction, β -scission-addition, and rearrangement reactions.

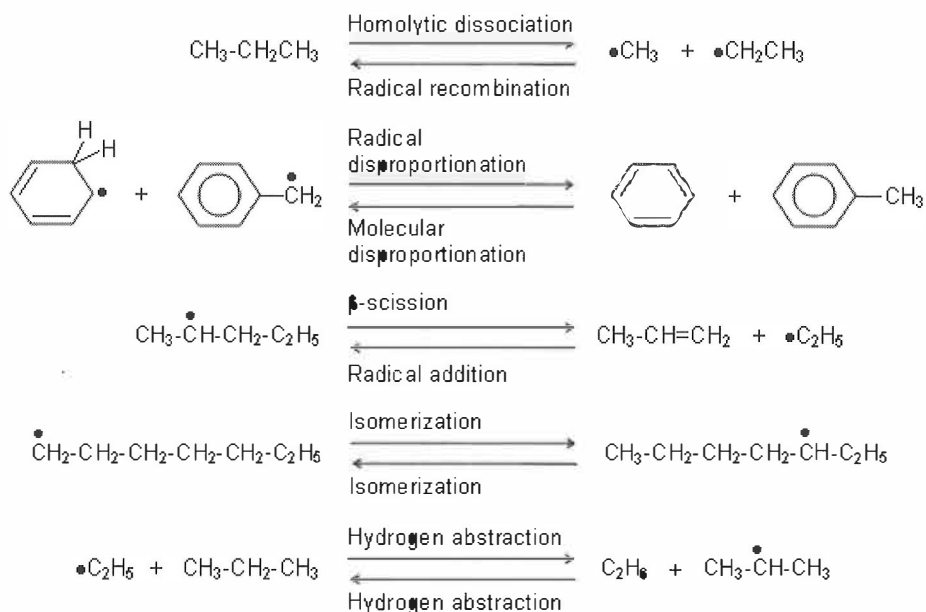


FIGURE 4 Reaction mechanisms for hydrocarbon pyrolysis involve elementary steps drawn from the five reaction families (Savage 2000).

In hydrogen abstraction reactions, the strength of the bond to the reacting hydrogen is a major determinant for how fast the reaction occurs (Carey 2000, Savage 2000). When multiple paths are available for a bond-breaking reaction, the path that involves cleavage of the weakest chemical bond is expected to be the fastest path. High reactivity correlates with low bond strength. C-H bonds are typically stronger than C-C bonds.

Some other major factors that determine the strength of a C-H bond in hydrocarbons are the hybridization state of the carbon and the opportunity for resonance delocalization of the unpaired electron in the resulting C-centered radical (Poutsma 2000). Increasing p-character compared to s-character at carbon weakens the C-H bond in the bond strength order: $sp > sp^2 > sp^3$. Less dramatic stabilization of alkyl radicals occurs as the extent of carbon branching at a radical center increases. Increased branching results in stabilizing interactions of an unpaired electron with the β -hydrogens and possibly releases some steric compression in going from a tetrahedral precursor to a trigonal radical. The effect of delocalization of the unpaired electron into an adjacent π -system results in significant bond weakening (Carey 2000, Poutsma 2000). The

C-H bond dissociation energies of the following compounds decrease in this order: $\text{CH}_3\text{CH}_2\text{-H} > \text{CH}_2=\text{CHCH}_2\text{-H} > \text{PhCH}_2\text{-H}$. Even further stability is offered by delocalization into larger polycyclic aromatic rings. Additional stabilization is offered by a second aryl substituent at the radical center.

Both electron-attracting groups such as the carbonyl and electron-donating groups such as the methoxyl groups have a stabilizing effect on a radical intermediate at an adjacent carbon (Poutsma 2000). The stabilization effect is caused by the delocalization of the unpaired radical onto the adjacent substituents and is particularly strong when both an electron-attracting and an electron-donating substituent are present at the radical site. Donor substituents, such as hydroxyl groups, are not as strongly stabilized as acceptor substituents, as with the carbonyl groups. A carbonyl substituent on a C-centered radical (e.g., $\text{RC(=O)CH}_2\cdot$ and $\text{ROC(=O)CH}_2\cdot$) provides only about half the resonance stabilization as does an olefinic substituent. Also, compared to strongly bound vinylic or aryl hydrogens, an aldehydic or formate hydrogen directly bonded to a carbonyl carbon, even though it is sp^2 -hybridized, is relatively weakly bonded and $\text{RC(=O)}\cdot$ and $\text{ROC(=O)}\cdot$ radicals are quite reactive.

According to Poutsma (2000), when comparing the kinetics of elementary reactions involving varying radicals within structurally similar families, it is common to note that the more 'stable' the radical becomes, the larger the rate constants will be for those elementary steps that produce it, and inversely, the smaller it will be for those steps that consume it. Only reactions with low activation energies are fast enough to sustain a chain process (Carey 2000). Most organic free radicals have very short lifetimes. Steric hindrance provided by the substituents stabilizes free radicals.

Radicals without special stabilization rapidly dimerize or disproportionate, while highly delocalized radicals show no tendency toward dimerization or disproportionation. Steric hindrance also greatly retards the rates of dimerization and disproportionation. The oxygen molecule is extremely reactive toward most free-radical intermediates with its two unpaired electrons (Carey 2000). The presence of oxygen can modify the course of a free-radical chain reaction. The product which is formed is a reactive peroxy radical ($\text{R}\cdot + \text{O}_2 \rightarrow \text{R-O-O}\cdot$) and can propagate a chain reaction leading to oxygen containing products. The rate of the reaction of oxygen with most radicals is very rapid because of the triplet character of molecular oxygen.

3.4.2 Thermal decomposition of triglycerides

Mechanisms for the thermal decomposition of TGs are complex because of its many structures and the multiplicity of possible reaction routes of mixed TGs. There have been studies conducted both on the thermal decomposition of saturated (Chang and Wan 1947, Nichols and Holman 1972, Alencar et al. 1983) and unsaturated TGs (Kitamura 1971) as well as TGs containing both saturated

and unsaturated moieties (Idem et al. 1996). According to Hsu et al. (1950) and Fortes and Baugh (1994) pyrolysis products show significant differences from different sources. The difference between the pyrolysates is associated with the composition of the original oil submitted to pyrolysis. According to Artok and Schobert (2000), the pyrolysis of complex material where a variety of structures and functional groups are present is likely to involve numerous reaction pathways even at a single temperature and a set of reaction conditions (e.g., temperature and other species in the reaction medium).

The mechanisms involved in the thermal cracking of saturated TGs

Based on a reaction scheme proposed by Chang and Wan (1947) Alencar et al. (1983) have proposed a reaction scheme for the thermal cracking of saturated TGs (Fig. 5). According to this scheme, the formation of a complete series of *n*-alkanes and 1-alkenes is consistent with the generation of the radicals RCOO· and RCH₂CO· from the saturated moieties of a TG molecule. Decarboxylation of RCOO· leads to the formation of R·, where on the disproportionation and successive eliminations of ethylene produces the odd series of *n*-alkanes and 1-alkenes. Radical RCH₂CO·, by loss of ketene, disproportionation, and successive elimination of ethylene molecules, generates the *n*-alkanes and 1-alkenes with an even number of carbon atoms.

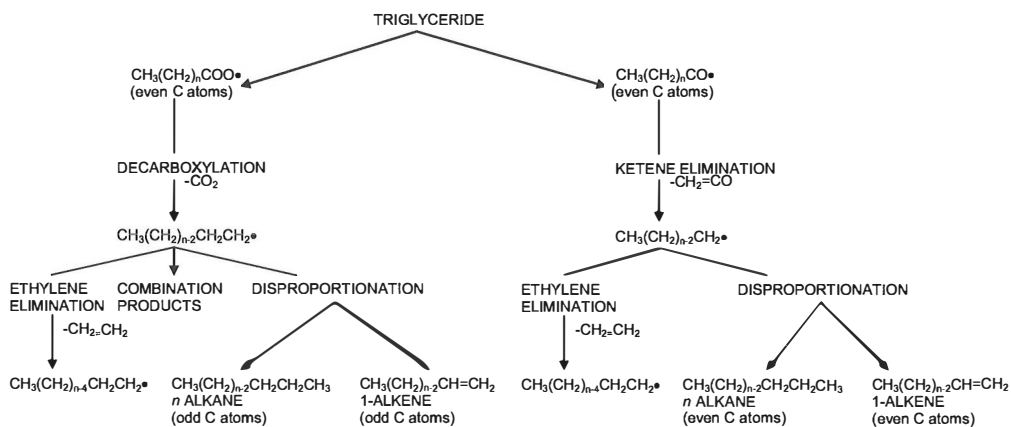


FIGURE 5 Thermal decomposition of saturated moieties of triglyceride molecule (Alencar et al. 1983).

The mechanisms involved in the thermal cracking of unsaturated TGs

Figure 6 outlines a schematic that accounts for the formation of alkanes, alkenes, alkadienes, aromatics, and carboxylic acids from the pyrolysis of unsaturated moieties of TGs. Unsaturated sites enhance the cleavage at the C-C double bond at position α,β to the unsaturation and this cleavage is the

dominant reaction (Idem et al. 1996, Ma and Hanna 1999, Srivastava and Prasad 2000, Maher and Bressler 2007).

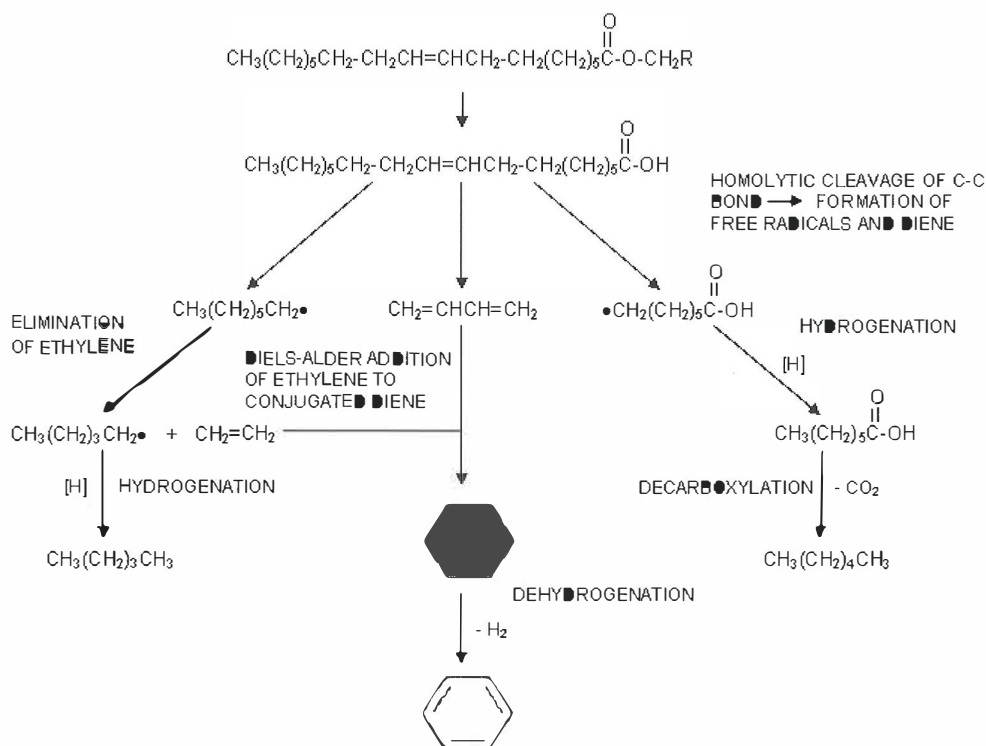


FIGURE 6 Thermal decomposition of unsaturated moieties of triglyceride (Ma and Hanna 1999, Srivastava and Prasad 2000).

Thermal decomposition of TGs consisting of both saturated and unsaturated moieties

In reality, vegetable and plant oils contain a complex mixture of saturated and unsaturated TGs (Maher and Bressler 2007). Idem et al. (1996) have further modified the reaction mechanisms presented above to explain both the decomposition of saturated and unsaturated moieties of the TG molecule and to account for the formation of other observed compounds. According to them, decarboxylation, decarbonylation, and ketene elimination (elimination of heavy oxygenated hydrocarbons such as esters, carboxylic acids, ketones, and aldehydes) are the most important steps when it comes to cracking a TG molecule in the absence of a catalyst. The result is the formation of hydrocarbon radicals. The initial decomposition of a TG molecule and the decomposition of FA molecules proceeds according to the following schemes (the primary reaction (1) and the secondary reactions (2) and (3)):





The initial decomposition of oils to heavy oxygenated hydrocarbons begins anywhere from 240 to 300 °C (Idem et al. 1996). The R in ketone and ester molecules indicates that each molecule may contain non-identical saturated and/or unsaturated hydrocarbon radicals in the form of $\text{C}_n\text{H}_{(2n\pm 1)}\cdot$, $\text{C}_n\text{H}_{(2n-3)}\cdot$ and $\text{C}_n\text{H}_{(2n-5)}\cdot$. The degree of unsaturation of the TG has a significant effect on the cracking behavior.

After these initial decomposition reactions, possible reaction routes include: (i) decarbonylation of saturated oxygenated hydrocarbons (loss of CO) followed by a C-C bond cleavage of the resulting hydrocarbon radicals, (ii) decarboxylation of saturated oxygenated hydrocarbons (loss of CO_2) followed by the C-C bond cleavage of the resulting hydrocarbon radicals, or (iii) C-C bond cleavage of unsaturated oxygenated hydrocarbons followed by the decarboxylation and decarbonylation of the resulting short-chain molecule (Idem et al. 1996). Radicals that are formed this way undergo various reactions such as; disproportionation, β -scission, isomerization, hydrogen abstraction, and aromatization.

Some direct cracking of oil itself (if still present) may happen by the C-C bond cleavage and yield straight- and branched-chain hydrocarbons (Idem et al. 1996). Various cracking reactions of the TG molecules containing both saturated and unsaturated acid moieties are presented in Figure 7.

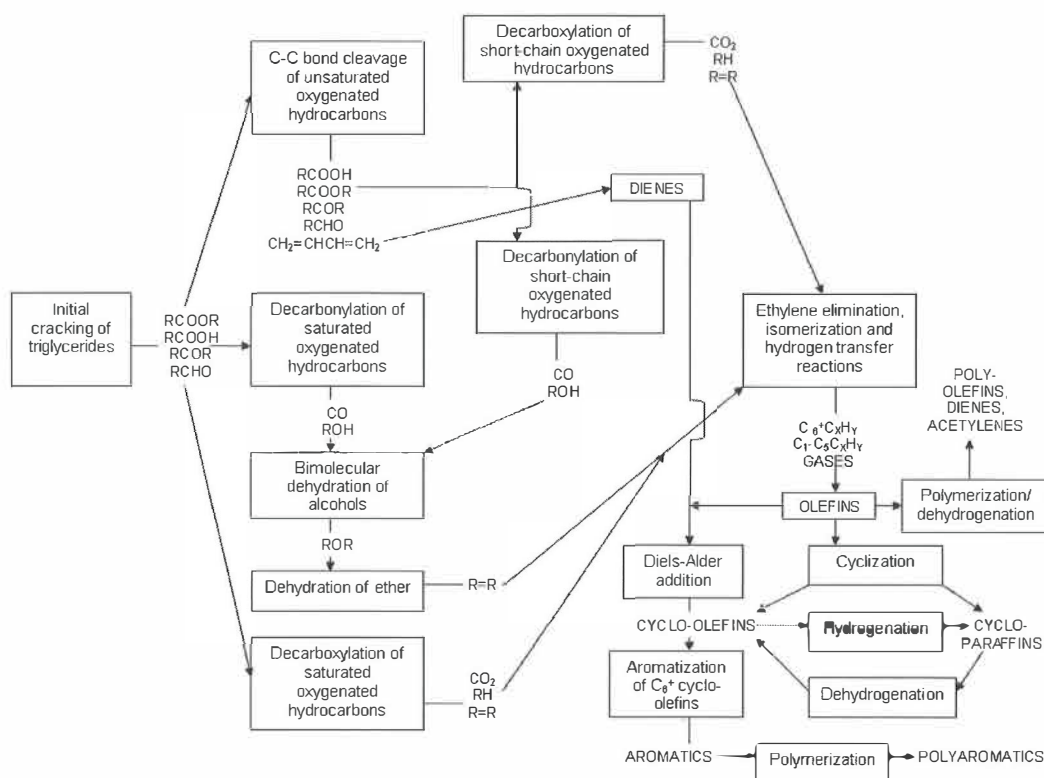


FIGURE 7 Thermal decomposition of the triglyceride containing both saturated and unsaturated acid moieties (Idem et al. 1996).

The thermal cracking of hydrocarbons is always accompanied by the coke formation (Towfighi et al. 2002). Many factors, such as feedstock, partial pressure of the hydrocarbon, temperature, conversion reactor construction material, and residence time, affect this phenomenon. Reactions which are responsible for the coke formation in pyrolysis are (Idem et al. 1996):

- polycondensation of TG,
- polycondensation of heavy oxygenated hydrocarbons,
- decomposition of long-chain hydrocarbon radicals,
- polymerization of olefins, and
- polymerization of aromatics.

3.4.3 Thermal cracking of extractives-based soaps

The pyrolysis of saponified vegetable oils results in the formation of complex mixtures where either thermal decomposition or thermal polymerization can occur (Fortes and Baugh 1994). Thermal decomposition produces low-molecular-mass types of compounds, while thermal polymerization produces compounds with a high molecular mass. Often both

reactions can occur simultaneously or in sequence. Vegetable oil soaps consist mainly of salty fatty acids and a glycerol residue (unless it is separated from other products). The saponification process is illustrated in Equation 4 (Demirbas 2002b).



Thus, in the pyrolysis process (if some oxygen is present), those salts are pyrolyzed and the pyrolysis of vegetable oil soaps proceeds according to Equation (5)



In 1974, Chang and Wan (1947) have reported a large-scale thermal cracking of tung oil calcium soap which yielded diesel-like fuel and small amounts of gasoline and kerosene. Fortes and Baugh (1994) have made a product with a similar composition to diesel fuel where, aside from the presence of some ketones, pyrolysis was achieved with the calcium soap of a Macauba fruit vegetable oil. Demirbas (2002b, 2003a) has pyrolyzed soaps of sunflower oil, corn oil, cottonseed oil, and soybean oil to hydrocarbon-rich products. In order to have a better understanding of vegetable oil soap pyrolysis, the mechanisms used for individual oil components should be clarified.

Fatty acid salts

Mechanisms involving the recombination of free radical fragments or free radical chains have been favored in explaining product formation in the pyrolysis of salts (Jones and Schmeltz 1969). A carbonium ion mechanism has also been used as an explanation for the product formation (Lee and Spinks 1953, Srivastava and Prasad 2000). Lee and Spinks (1953) have also proposed an intermolecular concerted process for its decarboxylation where the reaction may involve either the heterolytic or homolytic cleavage of the bond concerned. The plurality of these products makes an interpretation based on one or two common mechanisms difficult. According to Jones and Schmeltz (1969), different types of mechanisms can predominate at different temperatures.

Synthesis of symmetrical aliphatic ketones from the pyrolysis of metal salts of simple aliphatic acids is well known. According to Raven et al. (1997) ketones are formed by ketonic decarboxylation (i.e., a type of head to head condensation reaction) (Fig. 8). However, various other compounds, simple or complex, are generated along with the ketones (Lee and Spinks 1953, Chaudhuri et al. 1979).

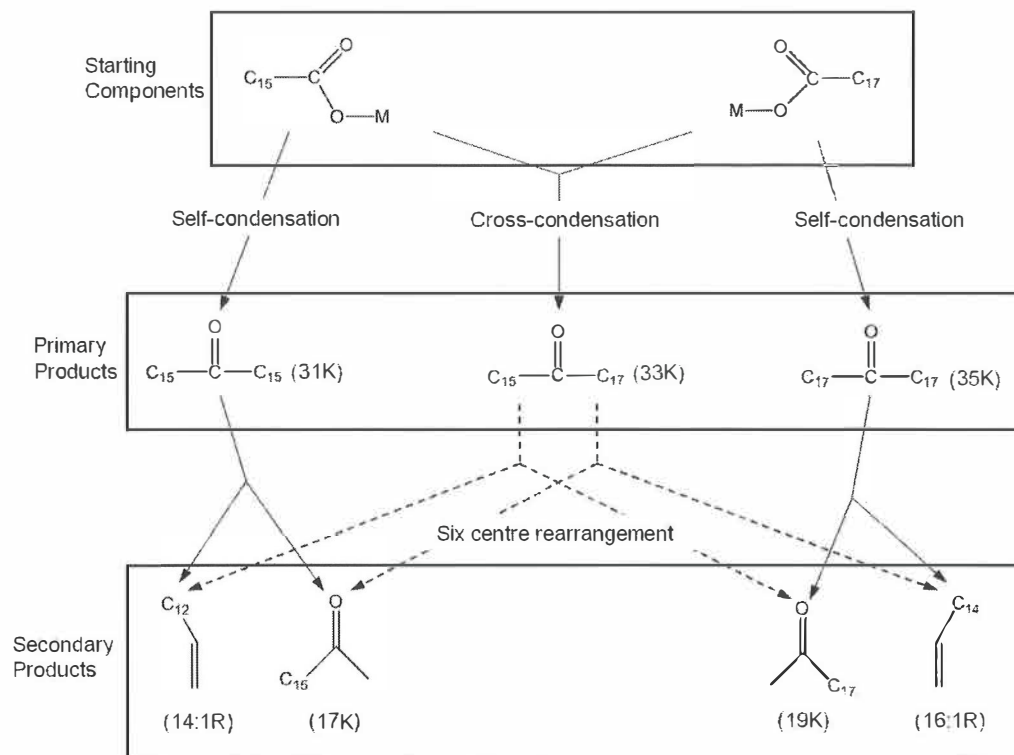


FIGURE 8 Proposed pathways leading to the formation of the primary and secondary pyrolysis products (Raven et al. 1997).

Hsu et al. (1950) used in their studies saponified tung oil and calcium stearate. Tung oil consists of about 80% eleostearic acid which has three conjugated double bonds. The results indicated that ketones decompose at once by splitting off carbon monoxide to give saturated and unsaturated hydrocarbons. The hydrocarbons obtained in this first stage of cracking can also undergo further reactions, such as; further decomposition, polymerization, condensation, cyclization, and aromatization. The three conjugated double bonds form resonance structures and a rupture of the carbon-carbon chain between them requires much more heat energy. Furthermore, the possibility of a rupture of another carbon-carbon chain is much greater. Thus, trienes are formed as a result of the decomposition of ketones. The cyclization of active trienes results in the formation of cyclic diolefins that then dehydrogenate to aromatics. Cracking reactions of calcium tungate proposed by Hsu et al. (1950) are shown in Figure 9.

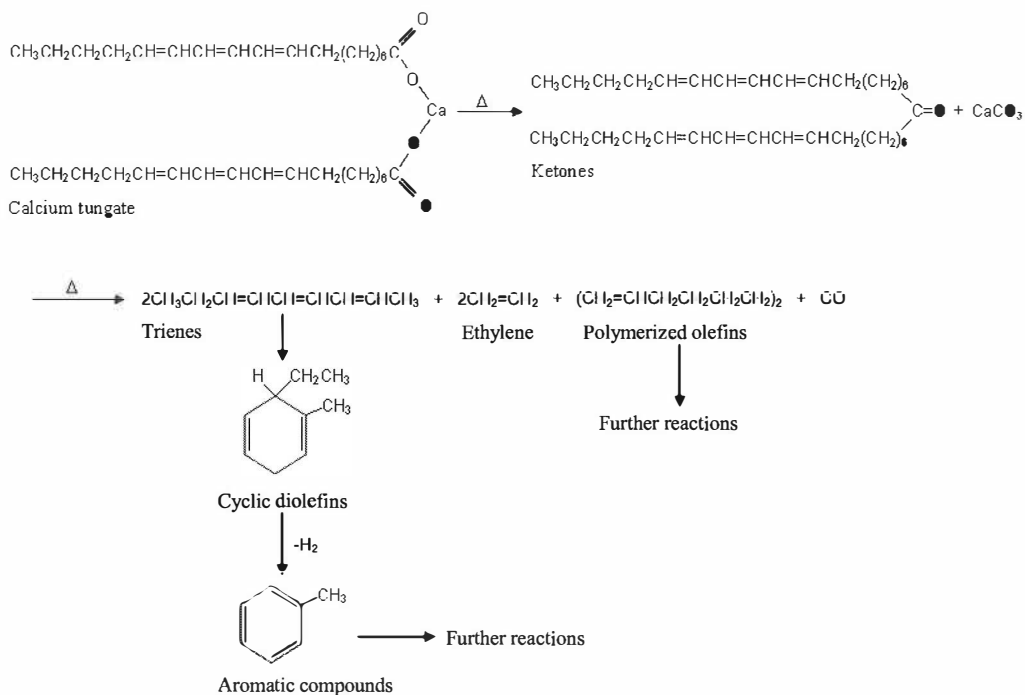


FIGURE 9 Thermal decomposition of calcium tungstate according to Hsu et al. (1950).

The more aromatics that are present in the cracking phase, the greater the tendency to produce coke (Hsu et al. 1950). According to Hites and Biemann (1972), the first step in the pyrolysis of carboxylic acid salt is the formation of both alkyl and acyl radicals. The mechanism they proposed is based on the combination of alkyl and acyl radicals. The combination of two identical radicals would result in the formation of a symmetrical ketone. However, Raven et al. (1997) have proved that this proposed mechanism results in some inconsistencies and does not explain pyrolysis products when different metals are utilized.

According to Hsu et al. (1950) the first step in the pyrolysis of calcium stearate is the formation of stearone, which then decomposes to give carbon monoxide, olefins, and paraffins. For this reason, the amount of aromatics formed in this reaction is comparatively small. Aromatics are probably produced through the dehydrogenation of naphthenes which are produced as a result of isomerization of olefins. Pyrolysis reactions of calcium stearate proceed according to the reaction scheme shown in Figure 10.

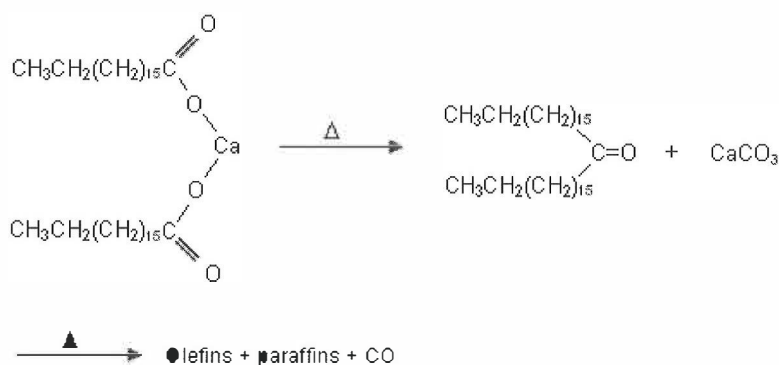


FIGURE 10 Thermal decomposition of calcium stearate (Hsu et al. 1950).

Hartgers et al. (1995) pyrolyzed salts of various functionalized fatty acids in order to achieve a better understanding of the thermal dissociation of lipid moieties. The proposed mechanisms of pyrolysis for the formation of *n*-alk-1-enes and *n*-alkanes from palmitic acid are presented in Figure 11. Initiation occurs by the homolysis of the weakest C-C bond adjacent to the carboxyl group which results in the formation of the pentadecyl radical. The pentadecyl radical is then propagated either as pentadecane by intermolecular H-radical transfer reactions or is stabilized as a secondary radical by random delocalization of the primary radical along the alkyl chain. The stabilization of the "free" secondary radicals can occur either via intermolecular H-radical transfer reactions or by β -scission reactions generating a homologous series of *n*-alk-1-enes and *n*-alkanes. The reaction starting a new chain cycle, i.e., hydrogen transfer, is competing with the β -scission reaction. β -Scission will be favored over H-radical abstraction at elevated temperatures and low H-radical concentrations. Intermolecular H-radical transfer processes can also lead to the formation of alkyl radicals that still contain the sodium salt functionality. Random delocalization of the alkyl radical along the alkyl chain and subsequent cleavages of the allylic C-C bonds generate a homologous series of *n*-alkenes. Also, primary radicals are formed in this process, which are then either stabilized by intermolecular H-radical transfer, or via the loss of hydrogen resulting in the formation of *n*-alkanes and *n*-alk-1-enes, respectively. The preference of the secondary radical for specific positions; i.e., α -, β -, and γ -carbon atoms, on the alkyl chain are controlled by the carboxyl functionality. These secondary radicals induce homolytic β -scission reactions.

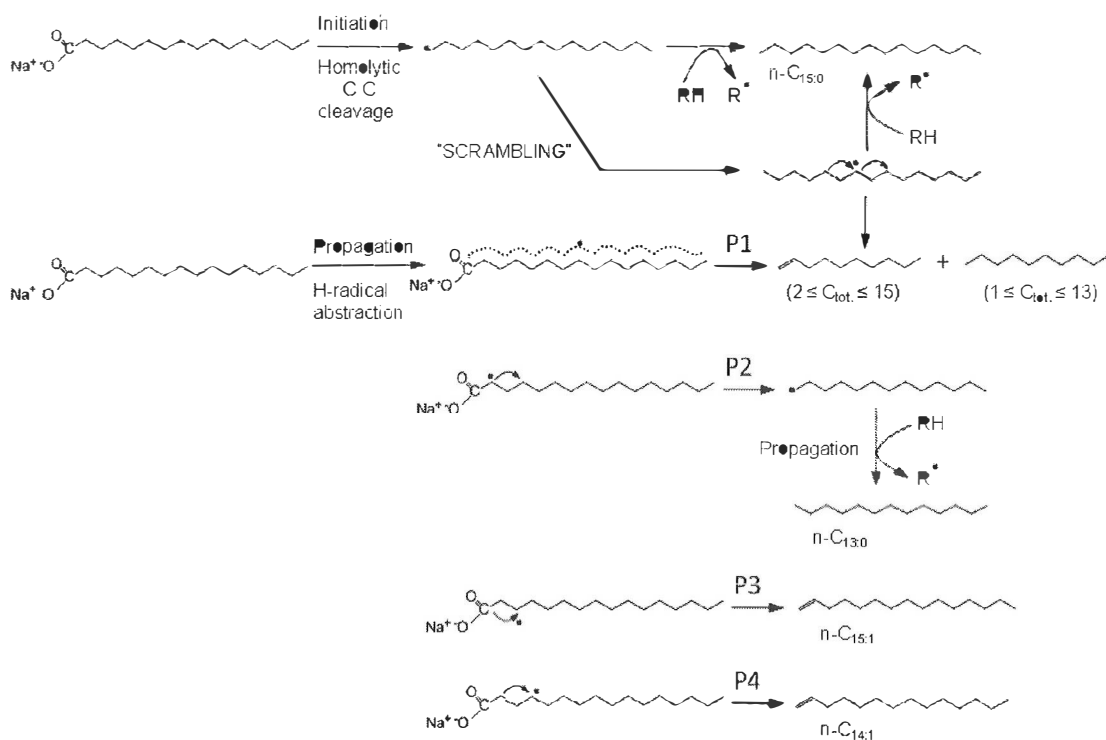


FIGURE 11 Thermal dissociation of sodium salt of palmitic acid (Hartgers et al. 1995).

Fragmentation mechanisms of sodium salt for (*Z*)-9-octadecenoic acid are analogous to those proposed for the sodium salt of hexadecanoic acid (Figs. 11 and 12) (Hartgers et al. 1995). The presence of the double bond in the alkyl chain, however, favors homolytic C-C cleavages at the allylic positions rather than homolytic C-C cleavages adjacent to the carboxyl group due to the lower bond dissociation energies of allylic C-C bonds. Additionally, it was observed that the double bond isomerization occurs readily; both *E* and *Z* isomers have been detected in pyrolysate. Also, the preference of secondary radicals, generated by intermolecular H-radical transfer reactions for specific carbon positions (i.e., α -, β -, and γ -carbon) in the alkyl chain was obvious as was seen in the case of sodium palmitate. The mid-chain double bond favors the formation of secondary radicals at the allylic positions, which induce homolytic β -scission.

In the case of sodium linolate, the additional double bond in the alkyl chain seems to favor cyclization and subsequent aromatization of the alkyl chain (Hartgers et al. 1995). Obviously, the presence of two conjugated double bonds in the alkyl chain triggers the cyclization at defined positions leading to the formation of aromatics. Otherwise, reaction mechanisms are analogous to sodium oleate dissociation.

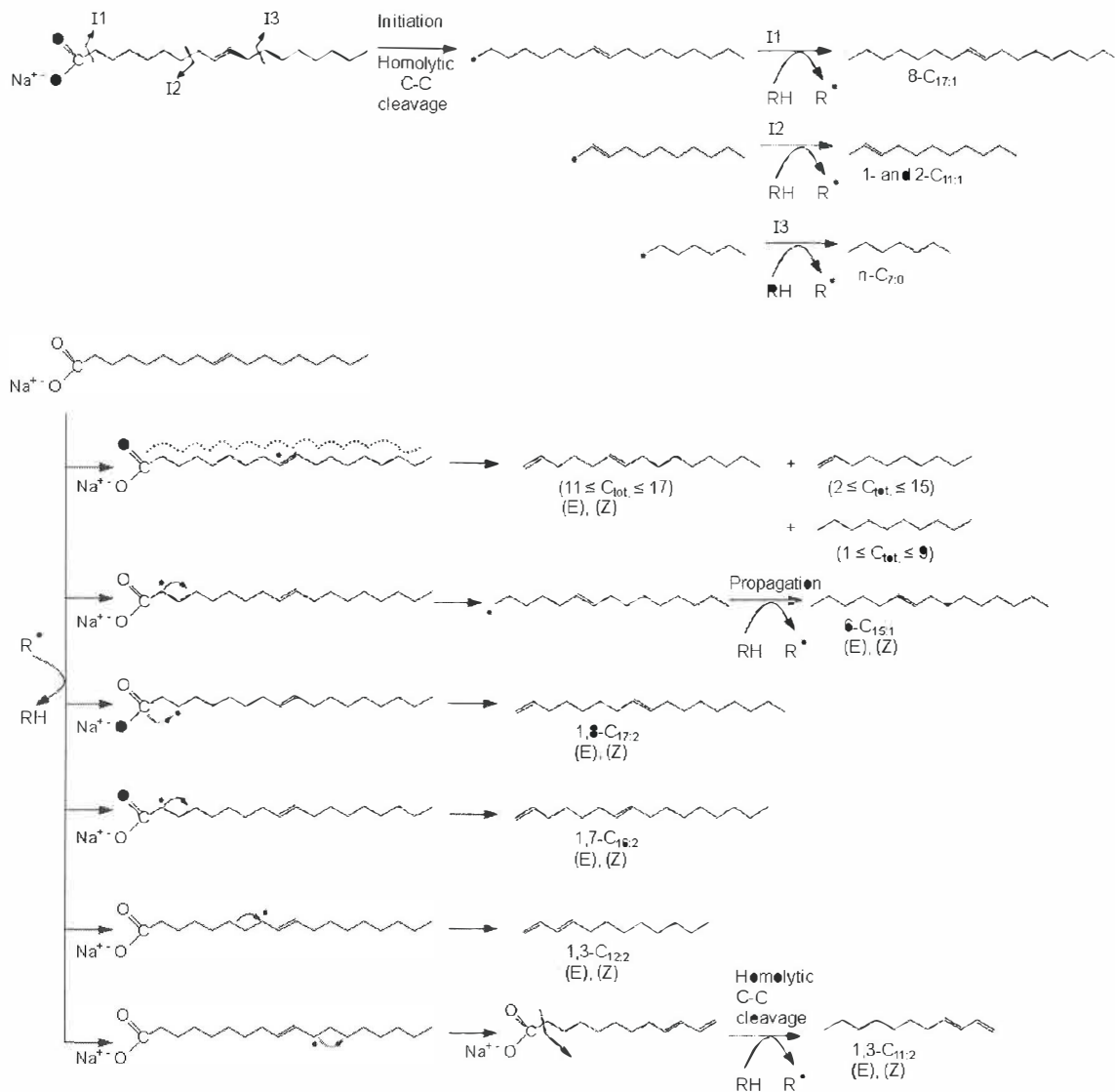


FIGURE 12 Thermal degradation of the sodium salt of oleic acid (Hartgers et al. 1995).

The major fragmentation pathways of sodium salt in 12-hydroxy-9-octadecenoic acid are mainly controlled by the hydroxyl group in the alkyl chain (Fig. 13) (Hartgers et al. 1995). The reaction mechanism first comprises of the formation of an unsaturated keto acid ($\text{NaO}_2\text{C}(\text{CH}_2)_7\text{CH}=\text{CHCH}_2\text{CO}(\text{CH}_2)_5\text{CH}_3$), which then further degrades via different reaction routes of various products. For example, octan-2-one is believed to result from a six-membered ring rearrangement. Homolytic C-C cleavage adjacent to the carboxyl group followed by intermolecular H-radical transfers and random cleavages of the alkyl chain is judged to be of less

importance, considering the relatively low amounts of a homologous series of alkenes and mid-chain ketones. Heptanal is formed by α -cleavage adjacent to the keto group, which is favored by the position of the double bond in the alkyl chain, weakening the allylic C-C bond relative to this double bond.

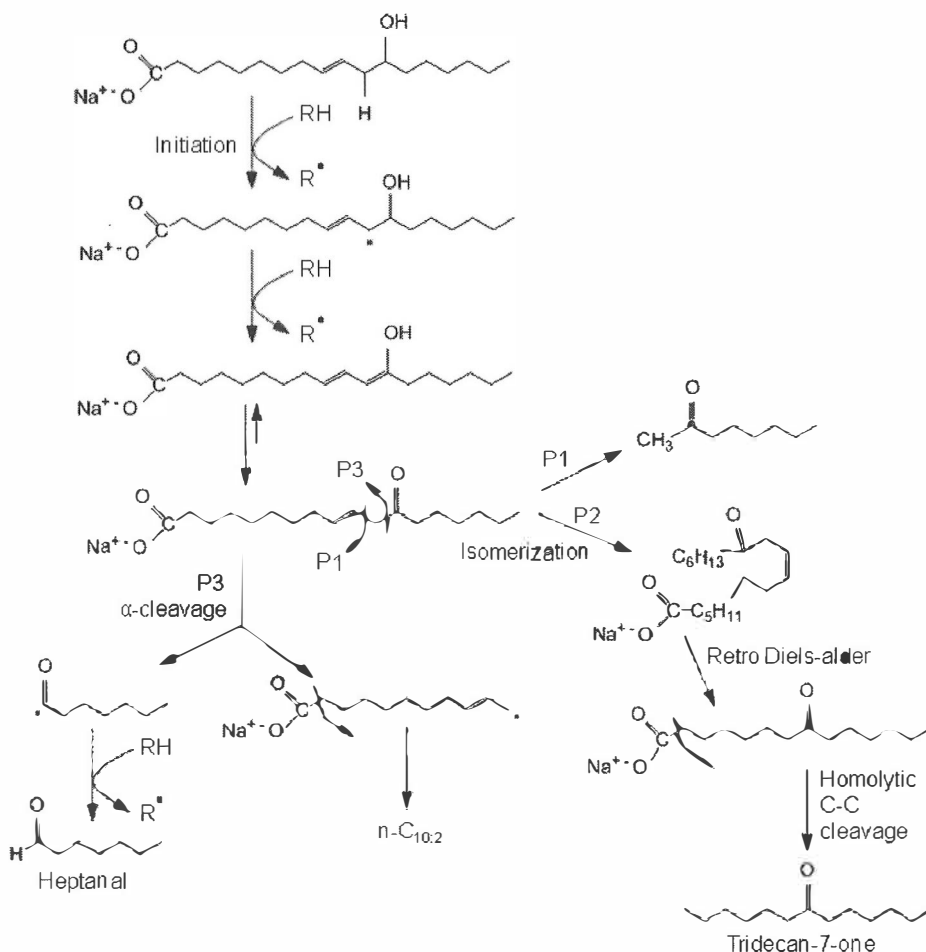


FIGURE 13 Thermal degradation of the sodium salt of ricinoleic acid (Hartgers et al. 1995).

Resin acid salts

The pyrolysis of RA salts seems to be a novel research area. No literature data concerning this application were found. However, literature dealing with the pyrolysis of RAs, as such, was available. More complex molecules, like acids of coniferous resin, can undergo, in parallel with decarboxylation, other reactions that will modify the expected outcome (Moldoveanu 2010d).

Various naphthalene derivatives have been found to be the most abundant kind of aromatics formed at a high temperature of (800 °C). It has been assumed that a high yield of these naphthalene-related components arises from an A-ring cleavage in the parent resin acid molecule before aromatization 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 2010d) that besides fragmentation and decarboxylation reactions, dehydrogenation is also an important reaction that takes place in RAs. Actually, the products that have been found are molecules that show less fragmentation of the decahydrophenanthrene ring system (i.e., the formation of phenanthrenes). In addition, traces of various substituted cyclopentanes, cyclopentenes, cyclohexanes, cyclohexenes, cyclohexadienes, benzenes, and naphthalenes have also been detected in the pyrolysates. In general, the main reactions seem to include only the basic elimination of carbon monoxide and water. However, the diterpenoid structures that contain carboxyl and hydroxyl groups or carbonyl groups are still relatively stable in pyrolysis. It is noteworthy that in pyrolysis experiments of abietic acid at 900 °C, a relatively high amount (about 43 %) of abietic acid did not decompose.

Other components

Many natural compounds with a terpenoid type of structure contain both COOH and OH groups; e.g., cholic acid, and ursolic acid (Moldoveanu 2010d). According to the literature, some of these structures like the perhydrocyclopentanophenanthrene basic structure of cholic acid and that of eicosahydro-picene in ursolic, asiatic, or madecassic acid are stable when undergoing pyrolysis. Pyrolysis of these compounds above 700-800 °C has been found to generate some intact parent molecules, some molecules generated by the elimination of H₂O from the hydroxyl groups, and also, numerous small fragment molecules including cyclohexane moieties. Also, aromatic compounds of alkylbenzenes, naphthalenes, indene and substituted indenenes, anthracene, phenanthrene, substituted phenanthrenes, and chrysene have been found. The elimination of H₂O from the cyclohexane cycle leads to the formation of double bonds, which increases the propensity for PAHs formation.

A number of natural terpenoids contained within their molecular structure carboxyl and carbonyl groups (Moldoveanu 2010d). These compounds are also relatively stable in pyrolysis, and aside from the elimination of CO₂ that takes place from the carboxyl group, pyrolysis at temperatures above 650-700 °C leads to a multitude of fragments. The pyrolysis products contain fragments with one or more cyclohexane cycles and have various substituents and degrees of unsaturation. However, it is worth noting that the complexity of the pyrolysate is more dependent upon the whole molecular structure than just on its attached functionalities.

4 EXPERIMENTAL

4.1 Chemicals and plant oil feedstocks

The chemicals used in this study are listed in Table 2.

TABLE 2 Chemicals used in this study

| Chemical | Manufacturer/supplier | Grade, [%] | Purpose | Paper |
|--|-----------------------|------------------|--|--------|
| Heneicosanoic acid | Sigma | 99 | Internal standard | II-IV |
| Betulinol | Sigma | ≥98 | Internal standard | II-IV |
| Cholesteryl heptadecanoate | TCI | > 97 | Internal standard | II-IV |
| 1,3-Dipalmitoyl-2-oleylglycerol | Sigma | ~99 | Internal standard | II-IV |
| Adamantane | Fluka | >99 | External standard | III-IV |
| Benzene | Fluka | >99 | Solvent | III-IV |
| Acetone | BDH | analytical grade | Solvent | II-IV |
| Methyl <i>tert</i> -butyl ether (MTBE) | Lab-Scan | | Derivatization | II-IV |
| Trimethylchlorosilane (TCMS) | Regis Technologies | | Derivatization | II-IV |
| Potassium hydroxide | Riedel de Haën | ≥85 | Saponification values and alkaline hydrolysis of extractives | II-IV |
| Sodium hydroxide | Fluka | ≥99 | Saponification | II-IV |
| Hydrochloric acid | Riedel de Haën | ≥37 | Saponification values | II-IV |

TABLE 2 Continued

| Chemical | Manufacturer/supplier | Grade, [%] | Purpose | Paper |
|---|-----------------------|------------|--------------------------|-------|
| Denatured alcohol BA | Altia | 99.5 | Saponification values | II-IV |
| Phenolphthalein | Merck | | Saponification values | II-IV |
| Sulfuric acid | | | | II-IV |
| Diethyl ether | | | Solvent | II-IV |
| Pyridine | Fluka | > 99 | Solvent | II-IV |
| Bis(trimethylsilyl)- trifluoroacetamide (BSTFA) | Regis Technologies | > 99 | Derivatization | II-IV |
| Sodium sulfate | | | Drying agent | II-IV |

The model compounds (I) used were commercially available as: (Sigma Aldrich) sodium stearate ($\geq 98\%$), sodium oleate ($\geq 99\%$), and sodium linolate ($\geq 99\%$). The vegetable oils (II) selected for this research were refined, bleached, and deodorized palm oil (RBD), water-degummed crude rapeseed oil (Raisio Chemicals), olive oil (Sigma-Aldrich), and castor oil (Sigma-Aldrich). The crude tall oil soap (CTOS) (III) originated from full-scale softwood kraft-pulping consisting of 80% pine chips and 20% pine sawdust. The content of the dry matter in CTOS was 60.8%. CTO (III) containing 10-20 wt-% neutral components and distilled tall oil (DTO) (III) were the products of Forchem Oy. Tall oil fatty acids (TOFAs) (IV) contained about 1.4% unsaponifiables and tall oil resin acids (TORs) (IV) contained 3.5% unsaponifiables. These were also Forchem Oy products. Water was obtained from a Millipore Milli-Q water system.

4.2 Analytical determinations

A gas chromatography (GC) instrument was equipped with a mass selective detector (MSD) and used for the identification of individual extractives (II-IV). After qualitative analysis, quantitative determination was done with a GC equipped flame ionization detector (FID). FID was used for quantitative analysis since it is sensitive, reliable, and has a wide linear range. It also gives nearly the same response for different organic compounds (Holmbom 1999).

For the analysis of vegetable oils (lipophilic fractions and individual compounds after alkaline hydrolysis), the samples were diluted in acetone (0.5 mg/mL) and derivatized for GC analysis with a mixture of BSTFA and TMCS (99:1, respectively). The derivatization of the samples was achieved by keeping them at 70 °C for one hour.

For the analysis of the tall oil products, the samples were diluted in acetone (0.5 mg/mL) and derivatized for GC analysis with a mixture of BSTFA and TMCS (99:1, respectively). This was similarly done for vegetable oils. Only individual compounds were quantified for CTOS, DTO, TOFAs, and TORs. Also, for CTO, individual compounds were quantified after alkaline hydrolysis since, according to the literature, (Holmbom and Avela 1971a) esters are formed during the processing of soap into crude oil. Tall oil was first separated for analysis from CTOS according to the TAPPI-standard method T 635 om-89. The only exception from the standard method was that the amount of stock soap solution prepared was smaller (100 mL instead of 500 mL).

Quantitative component group determination was performed with a short capillary column and with a method which was modified in the JYU Laboratory of Applied Chemistry from the method first represented by Örså and Holmbom (1994) (Table 3). For the analysis of individual compounds, a longer column and longer lasting analysis time was introduced (Table 3).

TABLE 3 GC-systems, columns, and methods used in the extractives analyses (II-IV)

| | Agilent 6890 GC/MSD | HP5890 GC/FID | Agilent 6850 GC/FID |
|----------------------------|--|---|--|
| Column | HP-5MS | HP-1SIMDIS | Equity-5 |
| Length, [m] | 30 | 7.5 | 30 |
| Inner diameter, [mm] | 0.32 | 0.53 | 0.32 |
| Film thickness, [μ m] | 0.25 | 0.15 | 0.25 |
| Detector temperature, [°C] | 280 | 290 | 290 |
| Injector, [°C] | | On-column | |
| Initial temperature | 290 | 90 | 290 |
| Heating rate, [°C/min] | | 200 | |
| Final temperature | 290 | 320 | 290 |
| Carrier gas | He | N ₂ | N ₂ |
| Temperature program | 100 °C (1.5 min) → 6 °C/min → 180 °C (10 min) → 4 °C/min → 290 °C (20 min) | 90 °C → 12 °C/min → 320 °C (10 min) | 100 °C (1.5 min) → 6 °C/min → 180 °C (10 min) → 4 °C/min → 290 °C (20 min) |

4.3 Pyrolysis experiments

The pyrolyzer used in pyrolysis experiments was a CDS Instruments Pyroprobe 1000 and is a resistively heated platinum filament pyrolyzer. The coil element, which heats samples held in quartz tubes, was used. The pyrolyser was coupled to an HP 5890 II gas chromatograph (Py-GC). Detection was carried out either with an HP 5972 MSD (qualitative analyses) or alternatively with an HP 5890 GC/FID (semi-quantitative analyses). Helium was used as a

carrier gas and as an inert atmosphere in the pyrolysis interface. Due to the multiplicity of pyrolysis products, the identification of all of the 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 (based on a commercial database, Wiley 7n, together with recognition of fragmentation patterns) was used. Only quality matches of 85% or above were included.

4.3.1 Model compounds

The first phase of the pyrolysis research was to develop the pyrolysis method and the GC-oven temperature program for extractive-based saponified feedstocks (Table 4). This was done with the aid of model compounds that represented the most common plant-derived FAs in the saponified form. However, the primary purpose of the model compound study (I) was to obtain comparable data on the versatile formation of liquefiable volatile compounds by the laboratory-scale pyrolysis of sodium salts from the common 18 carbon atoms-containing and straight-chained aliphatic carboxylic acids. These are composed of; fully saturated stearic (C_{18}), monounsaturated ($C_{18:1(9)}$), and diunsaturated linoleic ($C_{18:2(9,12)}$) acids. The idea of this first research phase was to give an idea of the product profile at varying pyrolysis conditions and verify the dominant reaction pathways (i.e., the effect of unsaturation of FAs to product formation). Additionally, since one of the ultimate goals was the utilization of tall oil soap together with vegetable oil soaps for this purpose, our main interest was to study sodium salts of carboxylic acids rather than the free or esterified acids (i.e., TGs).

4.3.2 Vegetable oil soaps and neutralized tall oil products

Saponification values for the vegetable oils were determined according to the procedure described in TAPPI standard T621 cm-01. Two replicate analyses were performed for all of the oils. Each plant oil was saponified with sodium hydroxide (the amount was 1.5 times the equivalent molar amount, as calculated from saponification values) prior to its pyrolysis. An excess amount of alkali was used in order to achieve complete saponification. The pyrolysis conditions and the GC-oven temperature program are presented in Table 4. It should be pointed out that the HP-5MS column had a similar stationary phase to the ZB-5HT column. The difference was that with the ZB-5HT column, higher temperatures (enabling the detection of less volatile pyrolysis products) could be used in the GC oven.

TABLE 4 Experimental conditions in the pyrolysis experiments. "Model compounds" refer to sodium salts of the model FAs and "plant oils" include all of the vegetable oils and tall oil products

| | Model compound pyrolysis | Plant oil pyrolysis |
|-----------------------------------|---|---|
| Heating rate, [°C/s] | 1000 | 1000 |
| Py-GC-interface temperature, [°C] | 300 | 250 |
| Pyrolysis temperature, [°C] | 450-750 | 750 |
| Pyrolysis time, [s] | 20 and 80 | 20 |
| Column | HP-5MS | ZB-5HT |
| Length, [m] | 30 | 30 |
| Inner diameter, [mm] | 0.25 | 0.25 |
| Film thickness, [µm] | 0.25 | 0.25 |
| Detector temperature, [°C] | | |
| FID | 300 | 300 |
| MSD | 280 | 280 |
| Injector, [°C] | 280 | 280 |
| Carrier gas, He, [mL/min] | 1 | 1 |
| GC-oven temperature program | 35 °C (5 min) → 5 °C/min → 125 °C → 3 °C/min → 285 °C → 5 °C/min → 310 °C (5 min) | 35 °C (5 min) → 5 °C/min → 125 °C → 3 °C/min → 285 °C → 5 °C/min → 360 °C (5 min) |

The calibration curve for the quantitative determination of the pyrolysis products was determined through 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 that was immediately inserted into the Py-GC interface. After an equilibration period of 30 seconds, pyrolysis was performed. Six different concentrations were pyrolyzed using the same parameters as the samples. Two replicates were made for each concentration. The correlation coefficient (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.

The precisions of product formation in the pyrolysis experiments were evaluated by the method described by Destandau et al. (2005). All of the plant oil soaps were analyzed 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 response factors 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. Precisions were 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 (6)) and day-to-day (Equation (7)) precisions expressed as RSDs were evaluated from the residual error (σ_r) and from the error due to the day factor (σ_a). Intermediate precision was calculated as shown in Equation 8.

$$\text{RSD}_{\text{intraday}} (\%) = \frac{\sigma_r}{x} \times 100 \quad (6)$$

$$\text{RSD}_{\text{day-to-day}} (\%) = \frac{\sigma_A}{x} \times 100 \quad \text{with} \quad \sigma_A^2 = \frac{q_A - q_r}{n} \quad (7)$$

$$\text{RSD}_{\text{intermediate precision}} (\%) = \frac{\sqrt{\sigma_A^2 + \sigma_r^2}}{x} \times 100 \quad (8)$$

The total amount of pyrolysis products recovered from laboratory-scale pyrolyzers is normally low. However, those products can be considered to reflect well the situation in which the main chemistry is involved. The primary aims for vegetable oil pyrolysis (II) were to clarify the pyrolysis chemistry of FA soaps in natural matrices and to verify earlier findings obtained from model substances. The tall oil products (III and IV) that underwent pyrolyses were aimed at further understanding the thermochemical behavior of various extractive-based raw materials. Particular emphasis was paid to the effect resin acids have on pyrolysis product formation. The degree of precision that was conducted in the pyrolysis experiments was also evaluated since it is a known fact that the reproducibility of the pyrolysis experiments is often problematic (Fortes and Baugh 1999, Moldoveanu 2010c). Nevertheless, due the diversity of various pyrolysis systems, as well as the diversity of samples investigated through pyrolysis, it can be concluded that an intermediate amount of precision is satisfying for most applications within the field of analytical and applied pyrolysis (Ji 2009).

5 RESULTS AND DISCUSSION

5.1 Fatty acid sodium salts

A peak of (m/z 44) at the beginning of each GC run (with all of the model compounds) indicated the presence of carbon dioxide originating from the decarboxylation of FAs (Fortes and Baugh 1999). Compounds marked as C₃-C₇ hydrocarbons (Figs. 14-16) corresponded to both alkenes and alkanes, but other compounds were also present in minor amounts. However, the resolution of these low-molecular-mass compounds was not sufficient for their proper identification.

The pyrolysis of sodium stearate resulted in the formation of linear alkanes (up to C₁₇) and linear alkenes (up to C₁₈) as major products (Fig. 14 and Appendix IV). Besides alk-1-enes other linear alkenes with double bonds in different positions appeared in the pyrolysate. Some alkadienes, aromatics, and oxygen-containing compounds were also detected. Additionally, high-molecular-mass (308-506 amu) compounds were detected. However, these compounds could not be unambiguously identified. The mass spectral analysis, as well as literature research, suggested that these oxygen-containing compounds probably belonged to a series of long-chain ketones.

The main pyrolysis product, 1-heptadecene, could be considered as being formed via the homolysis of the weakest C-C bond adjacent to the carboxylic group that functions as an initial reaction for the reaction chain producing homologous series of *n*-alk-1-enes and *n*-alkanes (Hartgers et al. 1995). After the homolysis of the C-C bond adjacent to carboxylic groups was finished, the heptadecyl radical was formed. This radical was propagated either as heptadecane by intermolecular H-radical transfer reactions or was stabilized as a secondary radical by random delocalization of the primary radical along the alkyl chain. The stabilization of free secondary radicals proceeded via intermolecular H-radical transfer reactions, yielding heptadecane, or through β -

scission reactions generating a homologous series of alkenes and alkanes. At elevated temperatures and low H-radical concentrations, β -scission was favored. This was also obvious based on the low amount of heptadecane present in the pyrolysate. According to Hartgers et al. (Hartgers et al. 1995) intermolecular H-radical transfer processes can also lead to the formation of alkyl radicals that still contain sodium functionality. Random delocalization of the radical along the alkyl chain and subsequent cleavages of the allylic C-C bond also lead to the formation of a homologous alkene series. Similarly, as in the case of sodium palmitate, the relative abundances of pentadecane, 1-hexadecene, and 1-heptadecene were enhanced. This could be explained by a preference for the secondary radical of specific positions on the alkyl chain controlled by the carboxyl functionality. Secondary radicals at positions; α -, β -, and γ -carbon atoms were favored and induced the homolytic β -scissions. This also explained the enhanced abundance of the aforementioned compounds. The low abundance of heptadecane and hexadecane were a result of fragmented pathways. Heptadecane and hexadecane were formed only by the homolytic cleavage of the C_α - C_β and C_β - C_γ bonds relative to the carboxylic group, respectively, and through subsequent intermolecular H-radical transfer.

The main route for the formation of "high-molecular-mass" ketones was probably the thermal decarboxylation of fatty acid salts (i.e., the reaction of the metal salts of aliphatic acids with the simultaneous formation of metal carbonate) (Hsu et al. 1950, Raven et al. 1997). In this case, only part of the primary product (a symmetrical ketone) formed in the first phase was directly cracked to smaller molecules. This assumption was supported by the presence of 18-pentatriacontanone (Appendix IV). According to the literature (Hites and Biemann 1972) these high-molecular-mass ketones might belong to a homologous series of alken-18-ones. Another possible route for the formation of high-molecular-mass ketones with varying chain lengths was based on the partial cracking of sodium stearate first to shorter-carbon-chain acid salts, and then followed by their reaction with the sodium stearate.

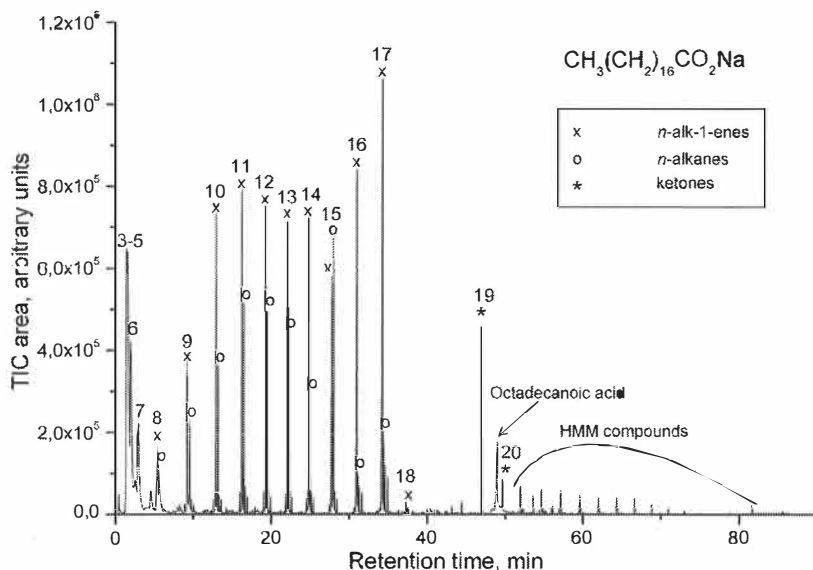


FIGURE 14 Main products formed in pyrolysis experiments (750 °C and 20 s) with sodium stearate (octadecanoate). Numbers indicate the amount of carbon atoms in a molecule (I).

The pyrolysate of sodium oleate was mainly characterized by linear alkenes up to C₁₈, linear alkanes up to C₁₃, and aromatics (Fig. 15 and Appendix IV). Besides alk-1-enes, other linear alkenes with double bonds in different positions appeared in the pyrolysate. Furthermore, trace amounts of high-molecular-mass (oxygen-containing) compounds were detected.

As suggested by Hartgers et al. (1995) the presence of the double bond in the alkyl chain favored homolytic C-C cleavages at the allylic positions leading to the formation of high amounts of compounds with 11 carbon atoms (i.e., the formation of undecadienes and undecenes having double bonds at varying positions). Other reaction mechanisms are analogous with those of saturated sodium stearate pyrolysis reactions, thus, explaining the presence of a homologous series of alkenes and alkanes.

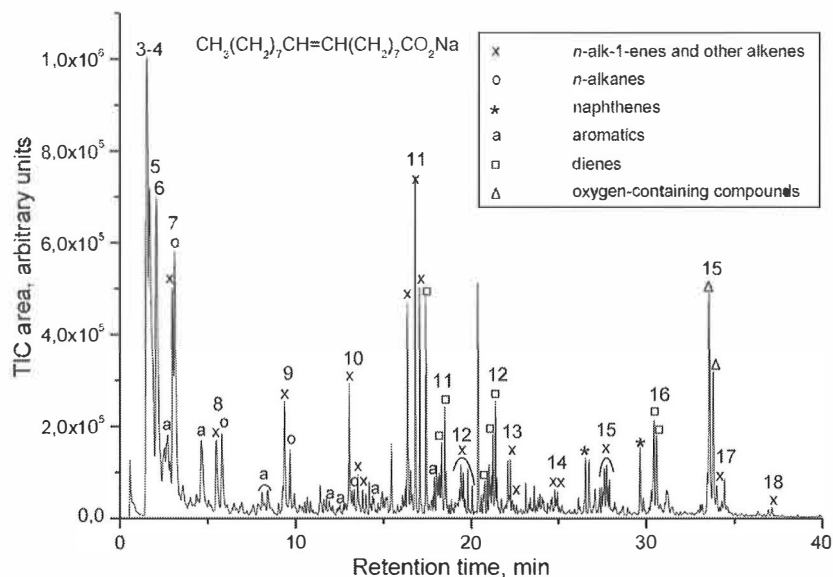


FIGURE 15 Main products formed in the pyrolysis experiments (750 °C and 20 s) with sodium oleate. Numbers indicate the amount of carbon atoms in a molecule (I).

The main products that were formed in pyrolysis experiments with sodium linolate were small compounds (C₃-C₇), aromatics, and oxygen-containing compounds together with alkenes and alkanes (Fig. 16). As in the case of sodium oleate, only traces of high-molecular-mass oxygen-containing compounds were detected. Only sodium linolate pyrolysis detected aromatics that had more than one benzene ring (i.e., mainly naphthalene derivatives). However, the amount of these polyaromatics was also very low (see Appendix IV). As Hartgers et al. (1995) proposed, the additional double bond in the alkyl chain favored cyclization and the subsequent aromatization of the alkyl chain.

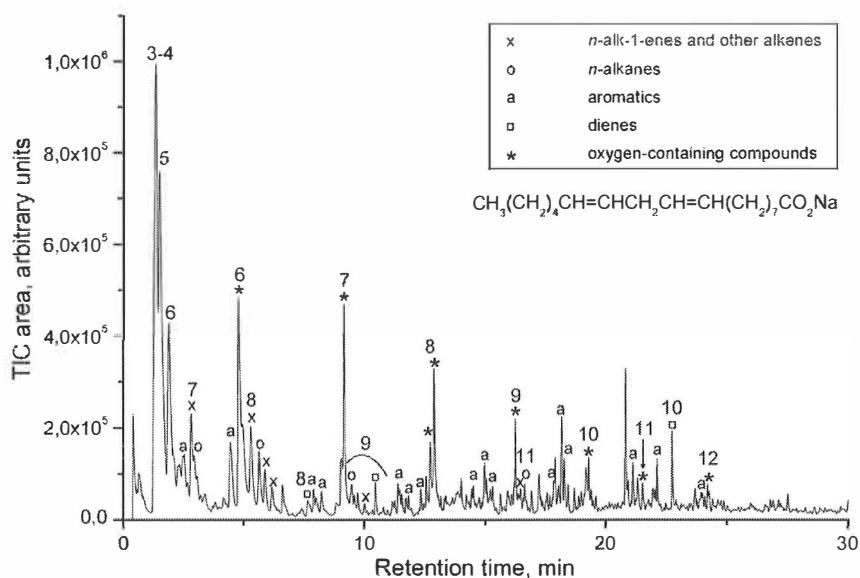


FIGURE 16 Main products formed in pyrolysis experiments (750 °C and 20 s) with sodium linolate. Numbers indicate the amount of carbon atoms in a molecule (I).

The pyrolysis of the FA sodium salts primarily resulted in volatile products similar to those found in diesel fuels, although, some undesired oxygen-containing products were formed as well. The highest relative proportions of various alkenes and alkanes were obtained from saturated sodium stearate. Conversely, the lowest relative proportions of these products, with the highest proportion of aromatics and oxygen-containing compounds, were detected in unsaturated sodium linolate. All these findings indicated that the formation of products clearly depends on the unsaturation of a fatty acid carbon chain and follows the typical reaction pathways generally outlined for pyrolysis.

The effects of pyrolysis when considering temperature and time as well as the thermochemical behavior of sodium salts are summarized in Figure 17. As expected, in most cases, a prolonged pyrolysis time generally favored the formation of the products detected and its influence seemed to be most significant within a temperature range of 550 °C and 600 °C. However, in the case of sodium linolate, the duration of pyrolysis did not seem to have a clear effect on conversion. This was probably due to the enhanced reactivity caused by the two double bonds in the carbon chain. The presence of two double bonds within a sodium linolate carbon chain also explains its different behavior related to pyrolysis temperature compared to two other different model compounds. By contrast, for sodium stearate and sodium oleate, the yield

increased with an increase in temperature (450 °C → 750 °C). In the pyrolysis of sodium linolate, the detected product yield increased until the temperature reached 700 °C and after that, decreased, thus higher pyrolysis temperatures were not tested. The influence that temperature has on product formation is discussed more in detail in Publication I. It was concluded that optimal pyrolytic conditions for future research (II-IV) with similar raw materials and equipment are achieved at 750 °C in 20 seconds.

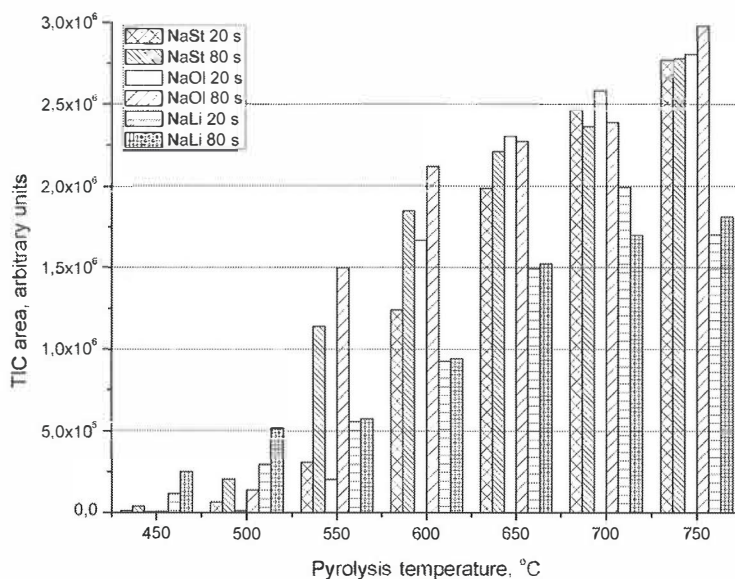


FIGURE 17 Effect of pyrolysis time and temperature on product yield in the pyrolysis experiments with sodium stearate (NaSt), sodium oleate (NaOl), and sodium linolate (NaLi). TIC areas are reported as the total peak areas corresponding to a sample mass of 100 µg (I).

5.2 Vegetable oil soaps – Palm, olive, rapeseed, and castor oils

5.2.1 Chemical composition

As expected, vegetable oil analysis revealed that, with respect to the main fractions, the raw materials (olive and rapeseed oils) had a rather similar chemical composition (Table 5). Palm oil had a slightly higher amount of DGs and slightly lower amount of TGs than other oils as well as a remarkably higher amount of steryl esters. Castor oil had the highest amount of TGs of the selected oils. The saponification values are also presented in Table 5.

TABLE 5 Relative composition of the lipophilic extractives fraction in the vegetable oils studied, (% of total), and saponification values (II)

| | Palm oil | ●live oil | Rapeseed oil | Castor oil |
|-----------------------|----------|-----------|--------------|------------|
| Fatty acids | 1.1 | 1.3 | 1.8 | 0.5 |
| Sitosterol | - | 0.2 | 0.3 | 0.2 |
| Steryl esters | 8.8 | 3.0 | 3.2 | 2.3 |
| Diglycerides | 7.1 | 6.3 | 2.0 | 2.2 |
| Triglycerides | 83.0 | 89.2 | 92.7 | 94.8 |
| Saponification values | 196 | 184 | 186 | 173 |

In olive and rapeseed oils, of FAs oleic acid was clearly the most abundant component (Table 6). The chemical composition of palm oil was characterized as having over 50% of saturated fatty acids (i.e., palmitinic, stearic, and behenic acids) from its total fatty acid fraction. Other notable property on its chemical composition was the high amount of oleic acid (~43%). Castor oil had a distinctive chemical composition with ~86% of ricinoleic acid which has one hydroxyl group attached to its carbon skeleton.

TABLE 6 Relative compositions of the fatty acid fractions (free and esterified) in the vegetable oils studied, % of total (II)

| Fatty acid | Palm oil ^{a)} | Olive oil | Rapeseed oil | Castor oil | Formula |
|--------------------|------------------------|-----------|--------------|------------|--|
| Palmitelaidic acid | - | 0.7 | 0.2 | - | $\text{HO}_2\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_5-\text{CH}_3$ |
| Palmitic acid | 47.0 | 11.9 | 4.8 | 1.1 | $\text{HO}_2\text{C}-(\text{CH}_2)_{14}-\text{CH}_3$ |
| Margaric acid | 0.1 | 0.1 | - | - | $\text{HO}_2\text{C}-(\text{CH}_2)_{15}-\text{CH}_3$ |
| | 0.2 | | | 3.5 | $\text{HO}_2\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$ $(\text{CH}_2)_4\text{CH}_3$ |
| Linoleic acid | | 0.3 | 0.6 | | |
| Oleic acid | 42.9 | 81.3 | 87.6 | 3.5 | $\text{HO}_2\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$ |
| Stearic acid | 4.5 | 2.9 | 1.8 | 1.2 | $\text{HO}_2\text{C}-(\text{CH}_2)_{16}-\text{CH}_3$ |
| Ricinoleic acid | - | - | - | 86.2 | b) |
| Gondoic acid | - | 0.4 | 1.6 | - | $\text{HO}_2\text{C}-(\text{CH}_2)_9-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$ |
| Arachidic acid | 0.4 | 0.4 | 0.6 | - | $\text{HO}_2\text{C}-(\text{CH}_2)_{18}-\text{CH}_3$ |
| Miscellaneous | 3.0 | 2.0 | 2.8 | 4.5 | |

^{a)} In addition, palm oil contained 0.3% of azelaic acid $\text{HO}_2\text{C}-(\text{CH}_2)_7-\text{CO}_2\text{H}$, 0.4% lauric acid $\text{HO}_2\text{C}-(\text{CH}_2)_{10}-\text{CH}_3$ and 1.2% myristic acid $\text{HO}_2\text{C}-(\text{CH}_2)_{12}-\text{CH}_3$,

^{b)} $\text{HO}_2\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}(\text{OH})-(\text{CH}_2)_5-\text{CH}_3$.

5.2.2 Pyrolysis experiments

The main aims were to clarify the pyrolysis chemistry of vegetable oil soaps (i.e., common saturated and unsaturated FAs as their sodium salts in natural vegetable oil matrices) and to verify earlier findings obtained from model substances. Compounds marked as C₃–C₆ hydrocarbons corresponded primarily to both alkenes and alkanes, but also other highly volatile compounds

were present in minor amounts (Figs. 18-21). However, due to the low resolution of these low-molecular-mass compounds, their proper identification was not possible.

The pyrolysate of palm oil soap was mainly characterized by linear alkenes (up to C₁₉) and alkanes (up to C₁₇) (Fig. 18 and Appendix V). Besides alk-1-enes, other alkenes with double bonds at different positions appeared. The main product 1-pentadecene could be considered to represent the typical degradation product of a main fatty acid component, palmitic acid (saturated FA). The fragmentation of sodium palmitate proceeds analogously to sodium stearate fragmentation. Other compounds present in pyrolysate in significant amounts were alkene (having 11 carbon atoms) and alkadienes (having 11, 12, and 17 carbon atoms). These could be considered to represent typical degradation products of oleic acid. Although no sterols were detected in an extractives analysis, a stigmast-4-en-3-one peak was detected in pyrolysis products.

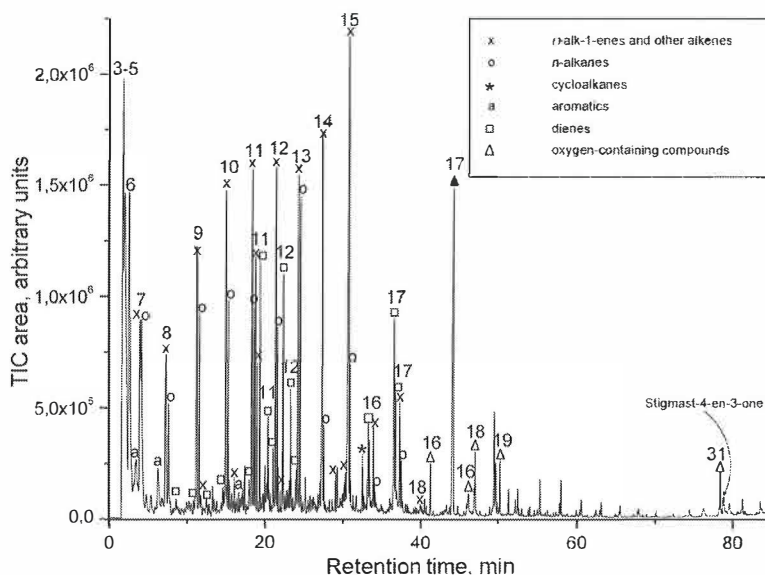


FIGURE 18 Main products formed in pyrolysis experiments (750 °C and 20 s) with saponified palm oil. Numbers indicate the amount of carbon atoms in a molecule (II).

In addition to some aromatics, the pyrolysate of olive oil soap was mainly characterized by linear alkenes (up to C₁₈), alkanes (up to C₁₆), and alkadienes (up to C₁₇) (Fig. 19 and Appendix V). Besides alk-1-enes, other alkenes and alkadienes with double bonds at different positions also appeared. The main volatile products detected in the pyrolysate were an alkene with 11 carbon

atoms and alkadienes with 11, 12 or 17 carbon atoms. They can be considered as representative of the typical amount of degradation that were present in the products that derived from the main fatty acid component, oleic acid. The peak of 10-demethylsqualene indicated the presence of squalene at a high level (150-170 mg/100 mL) in the original oil.

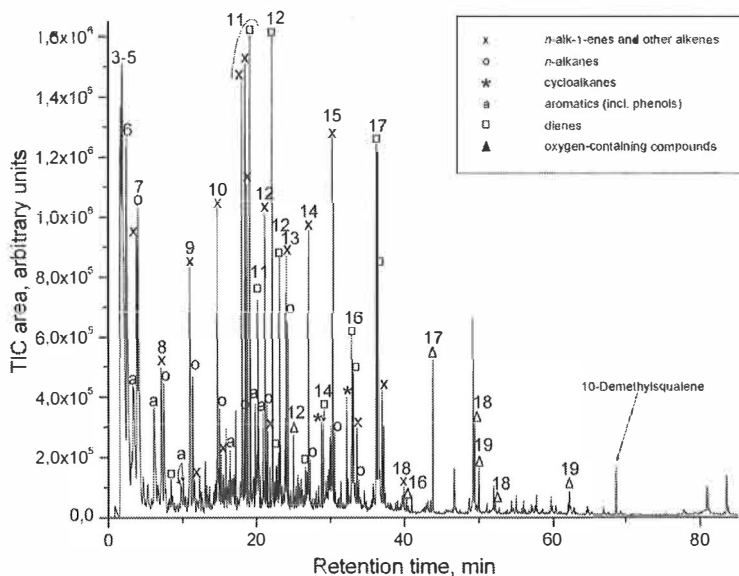


FIGURE 19 Main products formed in pyrolysis experiments at (750 °C and 20 seconds) with saponified olive oil. Numbers indicate the amount of carbon atoms in a molecule (II).

As expected, the relative composition of the volatile pyrolysis products in the rapeseed oil soap was rather similar to that obtained from the olive oil soap (Fig. 20 and Appendix V). In general, the relative amounts of alkadienes, alkenes, and alkanes were somewhat lower than those formed during the pyrolysis of olive oil soap. Although, due to slightly higher amounts of the initial unsaturated fatty acids, higher amounts of aromatics were also obtained. Some characteristic sterols that originated from the rapeseed oil were also detected.

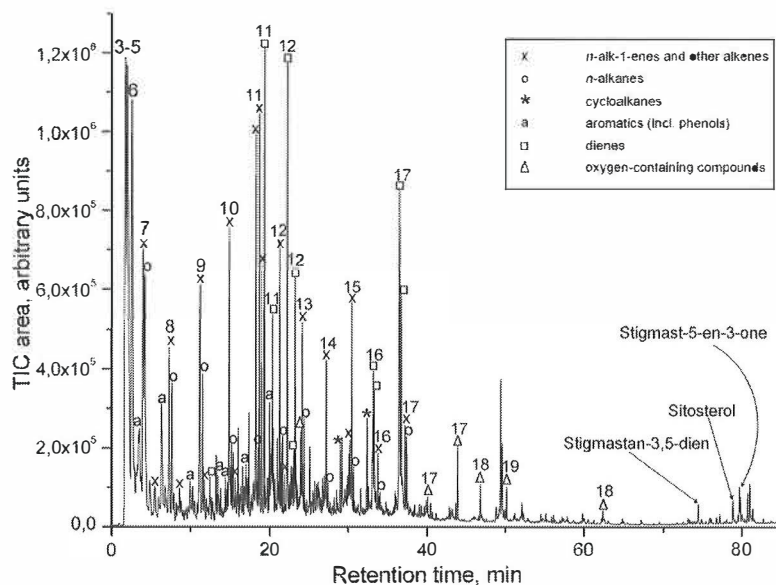


FIGURE 20 Main products formed in the pyrolysis experiments (750 °C and 20 s) with saponified rapeseed oil. Numbers indicate the amount of carbon atoms in a molecule (II).

The pyrolysate of castor oil soap was mainly characterized by ketones and other oxygen containing compounds (i.e., aldehyde and alcohols) (Fig. 21 and Appendix V). The chemistry of castor oil is centered on its high content of ricinoleic acid and the three points of functionality existing in the molecule; (1) carboxyl group, (2) single point of unsaturation, and (3) the hydroxyl group (Ogunniyi 2006). The major fragmentation pathways are mainly controlled by the hydroxyl group in an alkyl chain (Hartgers et al. 1995). Hartgers et al. (1995) have pyrolyzed the sodium salt of ricinoleic acid. Like in castor oil soap pyrolysis, the main products that were produced in the pyrolysis of sodium salt of ricinoleic acid were octan-2-one and heptanal. This was in agreement with the reaction of those mechanisms. Hartgers et al. (1995) postulated this for sodium ricinoleate thermal dissociation. The reaction mechanism is first comprised of the formation of an unsaturated keto acid ($\text{NaO}_2\text{C}(\text{CH}_2)_7\text{CH}=\text{CHCH}_2\text{CO}(\text{CH}_2)_5\text{CH}_3$), which then further degrades via different reaction routes for various products as explained in Section 3.4.3. The amount of linear alkadienes, alkenes, and alkanes was notably low in this pyrolysate, whereas the amount of ketones and other oxygen containing compounds was notably high. These results were in agreement with the reaction mechanism postulated by Hartgers et al. (1995).

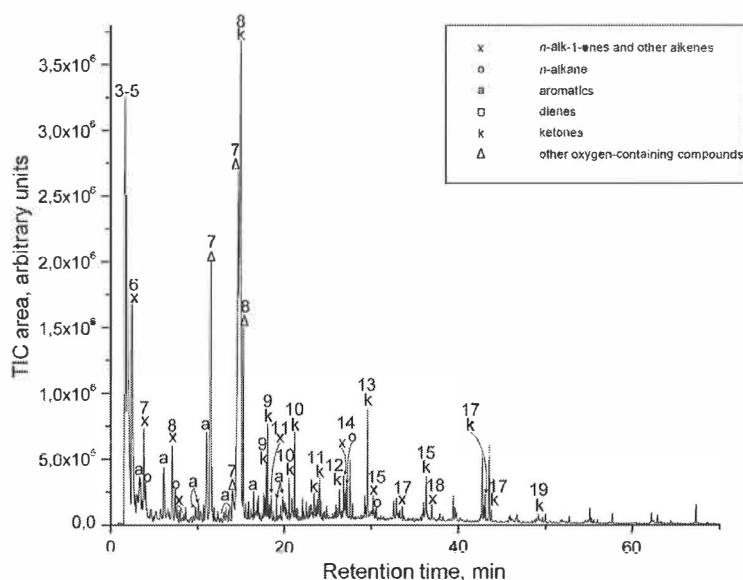


FIGURE 21 Main products formed in pyrolysis experiments (750 °C and 20 s) with saponified castor oil. The numbers indicate the amount of carbon atoms in a molecule (II).

Quantification using pyrolysis could be ascertained following typical procedures in GC/MS analyses after generating a calibration curve between the MS response (peak area count) and a specific amount of analyte (Moldoveanu 2010c). However, with complex pyrolysates, it was very complex and difficult to generate such calibrations for such a large number of compounds. An estimation for the levels of various compounds in the pyrogram could be done by simply comparing the peak area counts of the compound of interest with that peak generated by a compound present in a known amount. It should be pointed out that this method based on an external standard was only semi-quantitative due to the fact that there are unavoidable errors in measurement. An additional error was also caused by the fact that the detector response for each compound was generally different and two compounds showing the same peak area in a chromatogram were not necessarily present in equal quantities (Moldoveanu 2010c). The results of quantification could be presented by reporting the total fraction of their volatiles that are seen in a chromatogram. This simple approach gave only a relative comparison. Thus, it was concluded that the use of an external standard would give more accurate results. However, no response factors were available for the result (i.e., yield) calculation. Otherwise, the quantification of products would have been impossible and external standard approximate values for each compound group yields could be achieved. When the total mass balance is aimed at char and compounds which are not eluted from the chromatographic column must be accounted for.

However, due to the small sample size and limitation of this analysis method, this appeared to be impossible.

The total amount of pyrolysis products that are recovered from laboratory-scale pyrolyzers is normally low. In our experiments, quantitative analyses indicated that the detectable amounts of volatile products were (expressed as a % of their initial dry solids) 1.4% from palm oil, 1.5% from olive oil, 1.6% from rapeseed oil, and 1.5% from castor oil. In one study (Lehtonen 2005) freeze-dried aquatic humic substances were pyrolyzed after thermally assisted TMAH ((tetramethylammonium hydroxide) treatments under inert atmosphere prior to pyrolysis. Also in this study the yield of pyrolysis product was low - the relative product yield was 1.79%. The relative content of alkenes and alkanes was seen to be the highest in palm oil soap pyrolysate of all the detected soap pyrolysates (Fig. 22). The lowest amounts of aromatic compounds were also detected in the palm oil soap pyrolysate. This was probably due its having the highest amount of saturates in palm oil. The amount of alkenes and alkanes was almost as high in the olive oil soap pyrolysate. The highest amount of alkadienes was formed in the olive oil soap pyrolysis. Olive oil, which had the second highest amount of saturated FAs in its extractives fraction, produced a more similar product with the palm oil soap than any other vegetable oil soaps. The resemblance of olive oil soap pyrolysate with the rapeseed oil soap pyrolysate was remarkable. These two pyrolysates had the highest concentration of aromatics and cycloolefins. This was to be expected due the high amount of unsaturates in their composition. The amount of linear alkadienes, alkenes, and alkanes was notably low in the castor oil soap pyrolysate, whereas the amount of ketones and other oxygen-containing compounds were notably high compared to other soap pyrolysates. The distinctive chemical composition of castor oil explains the remarkably different pyrolysate when compared to other vegetable oil soaps pyrolyzed in this research.

The pyrolysis of vegetable oil soaps obtained from the alkaline (aqueous NaOH) hydrolysis of palm, olive, and rapeseed oils mainly resulted in volatile products similar to those found in gasoline and diesel fuel boiling range fractions of petroleum. However, some undesired oxygen-containing products were formed as well. The differences in the chemical compositions of the pyrolysates obtained from these raw materials could be explained through variations in the raw materials. Typical fragmentation patterns of the main product group were detected in both pyrolysates and these results were in accordance with previous data on the pyrolysis of sodium salt model compounds.

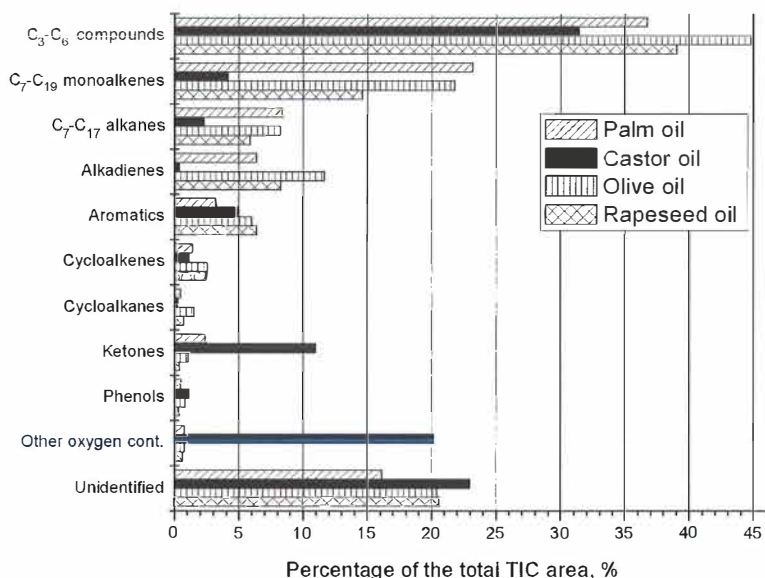


FIGURE 22 Relative amounts of the products formed in the pyrolysis of saponified palm, castor, olive, and rapeseed oils. The number of replicate pyrolysis experiments was 12 (II).

As Fortes and Baugh (1999) have showed, the critical problem with the Py-GC/MSD technique is the reproducibility of the pyrolysis experiments. There are several parameters that should be carefully controlled, such as the quantitative transfer of the pyrolysate material as well as sample size. In our case, due to variations in the size of the samples (as a consequence of small sample sizes and the sample application method used), some unavoidable weighing errors also took place. Additionally, part of the devolatilized 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 also have had some effect on product formation and was not totally avoided by increasing the pyrolysis interface and injector temperatures. For this reason, the pyrolysis apparatus was regularly cleaned after a few runs. Additionally, the pyrolyzed products were prepared in the laboratory and ground up with a mortar. This procedure also likely resulted in some variations for particle size distribution and with the homogeneity of the soap. It was also noticed that the analytical pyrolysis seemed to be sensitive to the position of the sample in the platinum coil filament.

The results (Tables 7 and 8) indicate that the intraday repeatability was rather poor in most cases. This trend was especially pronounced when the product groups that had a low portion were considered. By contrast, the day-to-

day repetition was satisfactory, ranging from 2.3% to 13.0% for (palm oil soap), 1.5% to 6.8% (olive oil soap), 1.1% to 12.1% (rapeseed oil soap), and 1.1% to 11.0% for (castor oil soap).

TABLE 7 Percentage of the TIC peak areas of various pyrolysis product groups (see Table 3) and intraday (n=4), day-to-day (n=3) and intermediate precisions of the results

| Class of compounds | Palm oil | | | | Castor oil | | | |
|--|----------------------------------|------------------|--------------------|----------------------|----------------------------------|------------------|--------------------|----------------------|
| | Average composition ^a | RSD (%) Intraday | RSD (%) Day-to-day | RSD (%) Intermediate | Average composition ^a | RSD (%) Intraday | RSD (%) Day-to-day | RSD (%) Intermediate |
| C ₃ -C ₆ compounds | 36.7 | 9.1 | 4.2 | 10.1 | 31.4 | 3.4 | 4.9 | 6.0 |
| C ₇ -C ₁₉ alkenes | 23.2 | 6.7 | 3.2 | 7.5 | 4.1 | 9.1 | 4.6 | 10.2 |
| C ₇ -C ₁₇ alkanes | 8.4 | 4.7 | 2.3 | 5.2 | 2.3 | 4.7 | 1.9 | 5.1 |
| Aromatics | 3.3 | 6.5 | 2.7 | 7.0 | 4.9 | 4.2 | 6.0 | 7.3 |
| Phenols and other oxygen-cont. arom. | 0.5 | 17.5 | 5.3 | 18.3 | 1.2 | 3.9 | 1.1 | 4.1 |
| Ketones | 2.4 | 26.5 | 13.0 | 29.5 | 11.0 | 7.0 | 3.3 | 7.7 |
| Other oxygen-cont. compounds | 0.8 | 16.2 | 5.9 | 17.3 | 20.2 | 7.4 | 2.9 | 7.9 |
| Cycloalkenes | 1.5 | 8.8 | 4.1 | 9.7 | 1.2 | 7.1 | 2.9 | 7.6 |
| Cycloalkanes | 0.5 | 14.1 | 6.5 | 15.5 | 0.3 | 11.6 | 3.0 | 12.0 |
| Dienes | 6.4 | 11.9 | 5.8 | 13.2 | 0.3 | 17.6 | 11.0 | 20.7 |
| Trienes | - | 25.2 | 8.3 | 26.5 | - | - | - | - |
| Others | 0.2 | 10.9 | 3.9 | 11.6 | 0.2 | 15.1 | 7.3 | 16.8 |
| Unidentified | 16.1 | 5.5 | 3.9 | 6.7 | 22.9 | 6.4 | 5.2 | 8.2 |

^a) Based on the analyses during three days (four determinations in each day).

TABLE 8 Percentage of the TIC peak areas of various pyrolysis product groups (see Table 3) and intraday (n=4), day-to-day (n=3), and intermediate precisions of the results

| Class of compounds | Olive oil | | | | Rapeseed oil | | | |
|--|----------------------------------|------------------|--------------------|----------------------|----------------------------------|------------------|--------------------|----------------------|
| | Average composition ^a | RSD (%) Intraday | RSD (%) Day-to-day | RSD (%) Intermediate | Average composition ^a | RSD (%) Intraday | RSD (%) Day-to-day | RSD (%) Intermediate |
| C ₃ -C ₆ compounds | 44.8 | 7.0 | 2.5 | 7.4 | 39.0 | 7.9 | 4.2 | 9.0 |
| C ₇ -C ₁₉ alkenes | 21.8 | 3.6 | 1.5 | 3.9 | 14.6 | 5.5 | 1.1 | 5.6 |
| C ₇ -C ₁₆ alkanes | 8.3 | 9.2 | 4.4 | 10.2 | 5.9 | 8.6 | 3.2 | 9.2 |
| Aromatics | 6.0 | 8.2 | 3.6 | 9.0 | 6.4 | 11.5 | 3.9 | 12.2 |
| Phenols | 0.9 | 11.8 | 5.0 | 12.8 | 0.4 | 25.4 | 5.6 | 26.0 |
| Ketones | 1.1 | 14.3 | 5.3 | 15.2 | 0.4 | 22.2 | 12.1 | 25.2 |
| Other oxygen-cont. compounds | 0.8 | 18.8 | 4.6 | 19.4 | 0.7 | 12.7 | 7.2 | 14.6 |
| Cycloalkenes | 2.6 | 2.8 | 1.3 | 3.1 | 2.5 | 9.6 | 8.6 | 12.9 |
| Cycloalkanes | 1.6 | 5.3 | 1.5 | 5.6 | 0.8 | 9.2 | 8.8 | 12.8 |
| Dienes | 11.7 | 7.3 | 1.9 | 7.5 | 8.3 | 9.0 | 1.9 | 9.2 |
| Trienes | 0.1 | 17.0 | 6.8 | 18.4 | - | - | - | - |
| Others | 0.4 | 8.2 | 4.1 | 9.2 | 0.5 | 15.9 | 2.1 | 16.1 |
| Unidentified | 20.4 | 9.5 | 4.3 | 10.4 | 20.7 | 10.8 | 4.6 | 11.7 |

^a) Based on analyses over three days (four determinations each day).

5.3 Neutralized tall oil products

5.3.1 Chemical composition

The amount of CTO recovered from the CTOS (DS content 61%) was 54%. The total amount of extractives detected in this, *separated CTO* was 761 g/kg DS. In the case of the, *separated CTO*, this also reflects the composition of the initial CTO soap that was investigated. The content of the FAs and RAs was about 58% and 34%, respectively, of the compounds that were determined (Table 9).

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 FAs as earlier reported by Holmbom and Avela) (1971a). In this case, the content of FAs and RAs was about 53% and 27%, respectively, of the compounds determined (Table 9). The DTO consisted of about 67% of FAs and about 25% of RAs. In addition to FFA, *reference CTO* contained esterified FAs.

The total amount of FAs and RAs detected in TOFAs were about 94% and 3%, respectively. Values were slightly different from those given by the manufacturer (97% and 1.7%, respectively) which was probably due to inaccuracies in compound quantification (i.e., in all cases, the response factors used between the GC peak areas were derived from internal standards and compounds were equal to 1). In fact, not all peaks (the amount of unidentified peaks was about 3%, Table 9) could be identified. The total amounts of RAs and FAs detected in TORs were about 86% and 3%, respectively. These values also differed from the values given by the manufacturer (92% and 3.5%), probably due the above-mentioned limitation of the analysis method.

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 2009). 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 1971a). In practice, this could be seen through the formation of four isomers of conjugated C_{18:2} acids and two conjugated C_{18:3} acid isomers (Table 9). The composition of RAs in TORs differed significantly from that in CTO indicating various decomposition and isomerisation reactions during distillation. For this reason, the amount of unidentified peaks (mainly various RA derivatives) was also relatively high in our case (about 10% of the total peak areas).

TABLE 9 Composition of the extractives in the samples studied (as a % 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", DTO distilled tall oil, TOFA tall oil fatty acid mixture and TOR tall oil resin acid mixture (for details, see the text) (III-IV)

| Compound | | CTO soap | CTO | DTO | TOFA | TOR |
|--------------------------------|-------------------|----------|------|------|------|------|
| FATTY ACIDS | | 57.8 | 53.2 | 66.8 | 94.0 | 3.1 |
| Myristic acid | C _{14:0} | + | 0.1 | - | - | - |
| Pentadecanoic acid | C _{15:0} | - | 0.2 | - | - | - |
| Palmitic acid | C _{16:0} | 0.9 | 2.0 | 0.8 | 0.1 | - |
| Palmitelaidic acid | C _{16:1} | 0.2 | 0.2 | + | - | - |
| Margaric acid | C _{17:0} | 0.7 | 0.5 | 0.8 | 0.1 | - |
| 17:0 anteiso | - | - | - | 0.1 | 0.1 | - |
| Stearic acid | C _{18:0} | 3.5 | 2.4 | 2.1 | 3.5 | + |
| Oleic acid | C _{18:1} | 15.0 | 11.3 | 17.6 | 24.6 | - |
| Linoleic acid | C _{18:2} | 20.3 | 23.5 | 33.3 | 48.1 | - |
| C _{18:2} (conjugated) | | 2.3 | 1.4 | 0.6 | 0.8 | - |
| C _{18:2} (conjugated) | | 2.3 | 1.7 | 1.8 | 1.8 | - |
| C _{18:2} (conjugated) | | - | - | 1.6 | 2.4 | - |
| Linolenic acid | C _{18:3} | 5.9 | 4.5 | 6.5 | 8.5 | - |
| C _{18:3} (conjugated) | | - | - | - | 0.9 | - |
| Nonadecanoic acid | C _{19:0} | - | + | - | 0.2 | - |
| 10-Nonadecenoic acid | C _{19:1} | 0.8 | 0.6 | 0.6 | 1.1 | - |
| Arachidic acid | C _{20:0} | 0.4 | 0.7 | 0.2 | 0.2 | 0.4 |
| Eicosenoic acid | C _{20:1} | - | - | - | 0.2 | - |
| Eicosadienoic acid | C _{20:2} | 0.7 | 0.5 | 0.2 | 0.2 | - |
| Eicosatrienoic acid | C _{20:3} | 4.3 | 2.5 | + | 1.2 | - |
| Behenic acid | C _{22:0} | 0.5 | 0.7 | 0.6 | - | 2.2 |
| Tricosanoic acid | C _{23:0} | - | 0.1 | - | - | - |
| Lignoceric acid | C _{24:0} | + | 0.3 | - | - | 0.5 |
| RESIN ACIDS | | 33.7 | 27.6 | 25.4 | 3.0 | 86.2 |
| Abietic acid | | 8.9 | 10.2 | 9.9 | | 36.2 |
| Neoabietic acid | | 5.3 | 3.9 | 1.0 | | 1.7 |
| Levopimaric acid | | 2.7 | + | 0.9 | | 0.3 |
| Palustric acid | | 5.7 | 4.3 | 3.3 | | 10.6 |
| Secodehydroabietic acid | | - | + | + | + | + |
| Isodehydroabietic acid | | + | + | - | | + |
| Dehydroabietic acid | | 4.6 | 3.9 | 6.1 | | 21.4 |
| Abietatetraenoic acid | | 0.2 | 0.2 | - | | |
| Hydroxydehydroabietic acid | | - | 0.2 | - | | 1.2 |
| 7-Oxodehydroabietic acid | | 0.2 | - | - | | |
| Pimaric acid | | 3.1 | 2.5 | 1.0 | 1.0 | 3.3 |
| Isopimaric acid | | 2.2 | 1.8 | 1.1 | 0.1 | 4.3 |
| Sandaracopimaric acid | | 0.8 | 0.6 | 0.3 | 0.1 | 1.2 |
| 8,15-Isopimaridien-18-oic acid | | | | | + | 1.3 |
| 8,15-Pimaradien-18-oic acid | | | | | 1.8 | 1.1 |
| Dihydroabietic acid | | | | | | 0.5 |
| Abietatetraenoic acid | | | | | | 1.0 |

TABLE 9 Continued

| Compound | CTO soap | CTO | DTO | TOFA | TOR |
|--|----------|------|-----|------|------|
| Dihydroxydehydroabiatic acid | | | | | 0.3 |
| Hydroxy-7-oxodehydroabiatic acid | | | | | |
| Unidentified acids | + | + | 1.8 | | 1.4 |
| RESIN ALCOHOLS AND ALDEHYDES | | | | | |
| Thunbergol | 0.8 | 0.3 | - | | |
| Neobienol | 0.2 | - | - | | |
| Neobienol | 0.4 | 0.2 | - | | |
| Isopimarol | + | - | - | | |
| Abietol | + | - | - | | |
| Neobietol | + | - | - | | |
| Pimaral | 0.2 | 0.1 | - | | |
| STEROLS | | | | | |
| Sitosterol | 4.7 | 5.9 | - | | |
| Sitostanol | 3.2 | 2.9 | - | | |
| Sitostanol | 0.7 | 0.7 | - | | |
| Campesterol | 0.5 | 0.4 | - | | |
| Cycloartenol | 0.3 | 0.6 | - | | |
| Methylene cycloartenol | - | 0.6 | - | | |
| Citrostadienol | - | 0.7 | - | | |
| MISCELLANEOUS (e.g. , stilbenes and fatty alcohols) | | | | | |
| | 3.0 | 13.0 | 7.8 | 3.0 | 10.7 |

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

5.3.2 Pyrolysis experiments

The characteristic feature for all of the pyrolysates was a prominent amount of volatile products, "C₃-C₅ compounds" primarily containing both alkenes and alkanes, but also other highly volatile compounds were 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, III-IV).

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. 23 and Appendix VI). Most of the aliphatic compounds were unsaturated alkenes (C₆-C₂₂) or alkadienes (C₆-C₂₂) and a major part of the detected aromatics contained one benzene ring. In this case, only a very low amount of sulfur-containing pyrolysis product was present. This finding suggests that a small amount of black liquor impurities in the CTO soap did not have a substantial effect on the quality of the product.

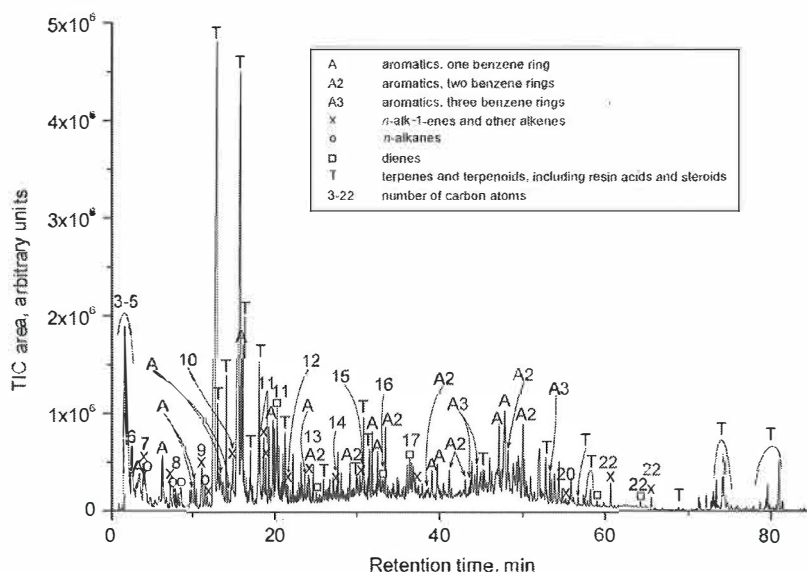


FIGURE 23 Main products formed in pyrolysis experiments of (750 °C and 20 seconds) with crude tall oil soap (III).

While the chemical composition of the neutralized, *reference CTO* was rather similar to that of the CTO soap, the total amount of the initial extractive-type of pyrolysis product was clearly lower (Fig. 24 and Appendix VI). Pyrolysate is comprised mostly of aliphatic hydrocarbons and aromatics. Also in this case, aliphatic hydrocarbons consisted mostly of alkenes (C₆-C₂₀) and alkadienes (C₈-C₁₆). Additionally, no significant differences caused by black liquor impurities (i.e., the pyrolysis of CTO soap vs. neutralized *reference CTO*) could be found.

The difference in the amount of initial extractives-based compounds in different pyrolysates is due to the initial moisture content of the raw material. The CTO soap received from the pulp mill was pyrolyzed without drying prior to pyrolysis. The wet feedstock decomposition is primarily composed of reaction mechanisms similar to those in dry pyrolysis and include: hydrolysis, dehydration, decarboxylation, aromatization and recondensation (Minkova et al. 2001). Water, during pyrolysis, primarily enters into hydrolysis (Moldoveanu 2010a). Hydrolysis exhibits a lower activation energy than most of the pyrolytic decomposition reactions (Libra et al. 2011). This has been shown by calorimetric measurements. Therefore, the principle biomass components are less stable under hydrothermal conditions, which lead to lower decomposition temperatures. Water vapour has the ability to penetrate solid material and to help with the desorption, distillation and efficient removal of volatile products (Minkova et al. 2001). Water vapour is also a reactive agent and reacts with the

pyrolysis products. It may also stabilise the radicals obtained in the thermal decomposition of the fuel, and thereby, increase the yield of volatiles.

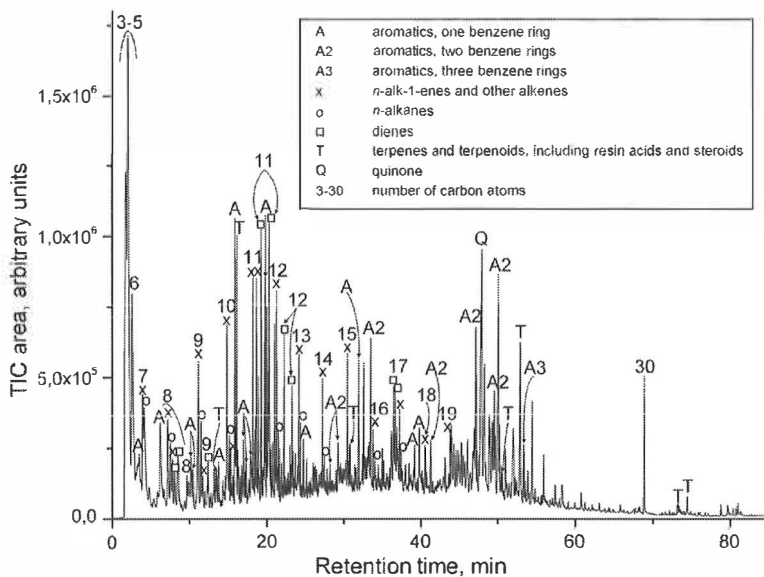


FIGURE 24 Main products formed in pyrolysis experiments (750 °C and 20 s) with neutralized, "reference crude tall oil" (III).

The pyrolysis products of DTO, after neutralization, also primarily contain aliphatic hydrocarbons and aromatics rather than an extractive type of compound (Fig. 25). As in previous cases, the amount of phenolics was very low and the aliphatic hydrocarbons were primarily unsaturated alkenes (C₆-C₂₃) and alkadienes (C₆-C₁₇).

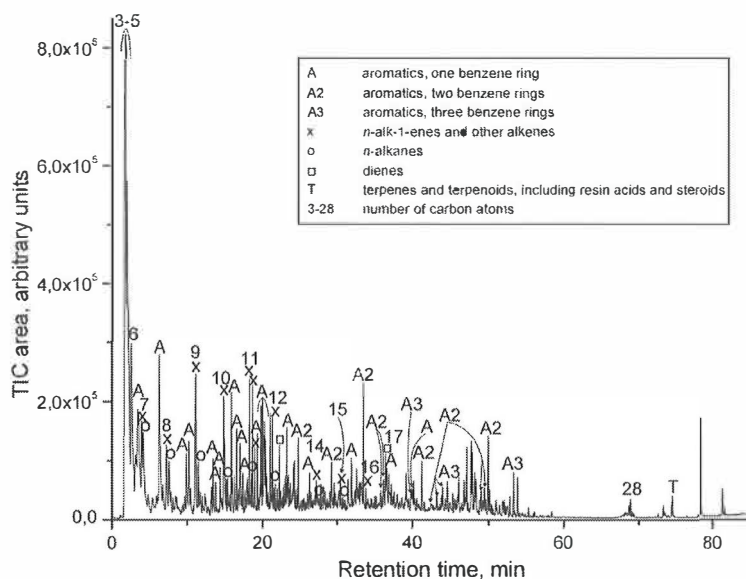


FIGURE 25 Main products formed in pyrolysis experiments of (750 °C and 20 seconds) with neutralized distilled tall oil (III).

The pyrolysis of neutralized TOFAs resulted in a high amount of unsaturated aliphatic hydrocarbons, although some aromatics with one benzene ring were also formed (Fig. 26). The most prominent fractions were alkenes (C_6 - C_{12}) and alkadienes (C_{11} , C_{12} , and C_{17}) together with benzene and methylbenzene. The alkadienes can be considered to be representative of a typical reaction of products that are derived from it as in oleic acid ($C_{18:1}$). The additional double bonds in the alkyl chain (cf., linoleic ($C_{18:2}$) and linolenic ($C_{18:3}$) acids) favored cyclization and aromatization explaining a considerable amount (about 13% of the total compounds) of aromatics detected in the TOFAs pyrolysate. No significant amount of phenolics was formed.

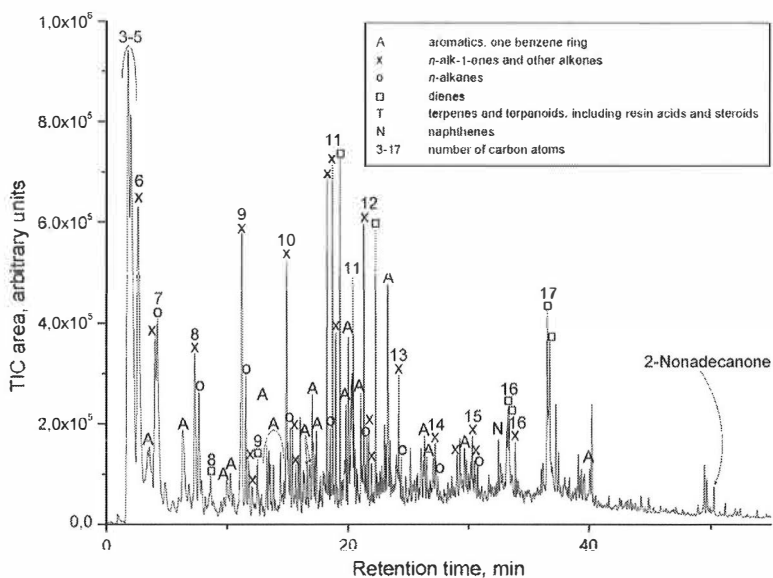


FIGURE 26 The primary products that were formed in pyrolysis experiments of (750 °C and 20 seconds) with neutralized tall oil fatty acid mixture (IV).

The main compounds in the pyrolysate from the neutralized TORs were mostly comprised of various aromatics having one to three benzene rings. Significantly low amounts of aliphatic hydrocarbons could be detected (Fig. 27). In this case, a portion of these unknown pyrolysis products were very high (about 44%). However, it could be assumed (based also on MS spectra) that a large portion of these unidentified compounds consisted of a wide range of polyaromatic hydrocarbon derivatives. In the pyrolysis of the neutralized TORs, no significant amounts of phenolics were formed.

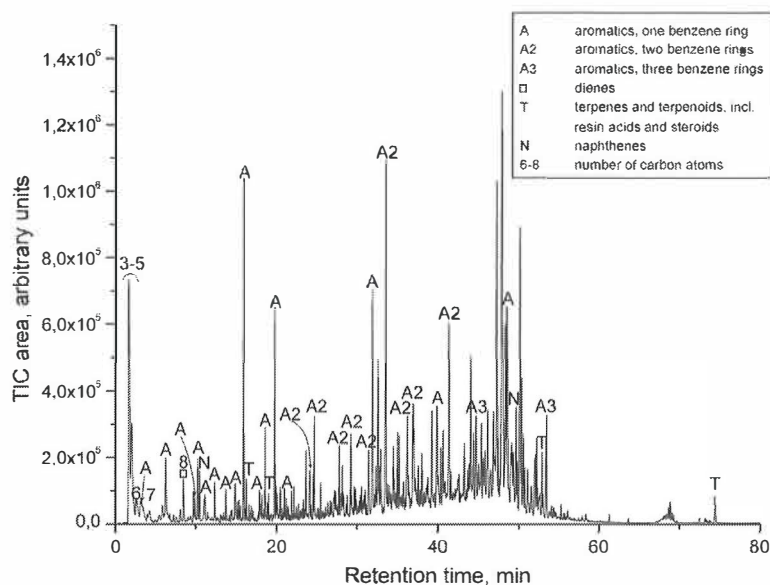


FIGURE 27 The primary products that were formed in pyrolysis experiments of (750 °C and 20 seconds) with a neutralized tall oil resin acid mixture (IV).

In RA pyrolysis, what was mostly found were molecules showing less fragmentation of the decahydrophenanthrene ring system (i.e., the formation of phenanthrenes). However, in the pyrolysates, traces of various substituted cyclopentanes, cyclopentenes, cyclohexanes, cyclohexenes, cyclohexadienes, benzenes, and naphthalenes were also detected. High amounts of aromatics (also polyaromatics) were formed when the amount of RAs in the raw material was seen as remarkable. This further proved the stability of the aforementioned ring structures in pyrolytic conditions leading to the pronounced formation of aromatic pyrolysis based products.

The pyrolysis experiments of abietic acid at 900 °C suggest that a relatively high amount (about 43%) of abietic acid did not decompose (Moldoveanu 2010d). However, when the salt of an RA mixture was pyrolyzed, no residue acids were detected. The same phenomena have been detected earlier in the analytical pyrolysis of FAs. When FAs were pyrolyzed with a laboratory scale pyrolyzer, high amounts of residue acids were detected in the pyrolysate (Jansson et al. 2007), whereas in FA salt pyrolysis, no residue acids were detected (I).

RAs contained in soaps mostly result in the pronounced formation of aromatics during pyrolysis, whereas aliphatic unsaturated and saturated hydrocarbons can principally be obtained from FA contained soaps (Fig. 28). When considering the possible tall oil-based production of biodiesel with

respect to the product quality a low content of aromatics and oxygen-containing compounds are needed. The FA-rich fractions are more suitable feedstocks than RA-rich fractions.

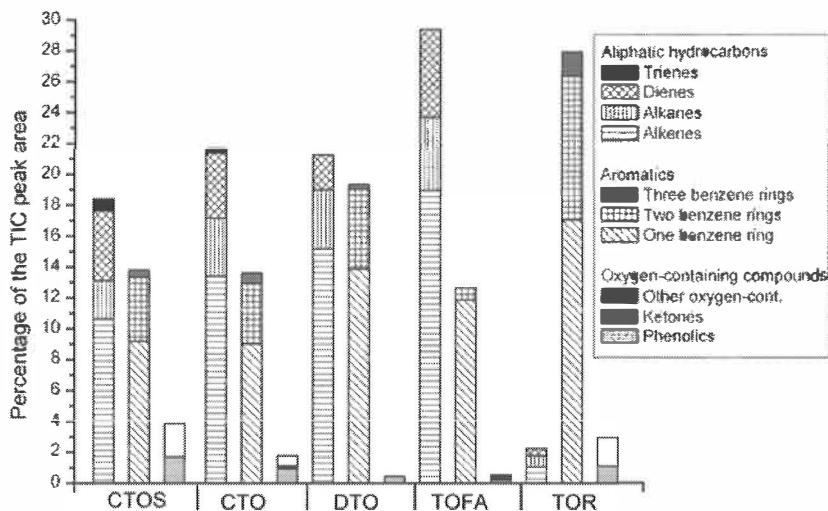


FIGURE 28 Relative amounts of the products formed in the pyrolysis of crude tall oil soap and neutralized products of crude tall oil, distilled tall oil, tall oil fatty acid mixture, and tall oil resin acid mixture. The number of replicate pyrolysis experiments was 12.

The limitations that were observed that relate to quantitative analysis and repeatability have been discussed in Section 5.2.2. Quantitative analysis indicated that detectable amounts of liquefiable products were (expressed as % of the initial dry solids) 1.1% (for CTO soap and the neutralized, *reference CTO*), 0.9% (for the neutralized DTO), 1.4% (for the neutralized TOFAs), and 1.1% (for the neutralized TORs).

As the results in (III and Table 10) suggest, 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 exceptions to this trend were "terpenes and terpenoids" in the CTO soap pyrolysate and the "C₃-C₅ compounds" in the neutralized TORs pyrolysate, which despite a high relative amount, had a very poor intraday repeatability. Intraday repeatability ranged from: 7.6% to 44.4% for (CTO soap), 2.6% to 14.6% (neutralized "reference CTO"), 2.0% to 35.0% (neutralized DTO), 1.6% to 29.5% (neutralized TOFAs), and from 2.7% to 24.6% (neutralized TORs). The day-to-day repeatability was satisfactory, ranging from: 1.2% to 18.6% (CTO soap) 0.7% to 10.2% (neutralized "reference CTO"), 0.9% to 15.2% (neutralized DTO), 0.5% to 12.6% (neutralized TOFAs), and from 0.6% to 11.6% (neutralized TORs).

TABLE 10 Percentage of the TIC peak areas of various pyrolysis product groups and the standard deviation and intraday (n = 4), day-to-day (n = 3), and intermediate precisions of the results. For compounds, see Appendix VI

| Class of compounds | Neutralised TOFA | | | | Neutralised TOR | | | |
|--|---------------------|------------------|--------------------|----------------------|---------------------|------------------|--------------------|----------------------|
| | 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 | 26.8 ± 2.1 | 7.5 | 2.6 | 7.9 | 18.21 ± 3.87 | 23.5 | 11.6 | 26.2 |
| ∑ Aliphatic hydrocarbons | 29.4 ± 0.6 | 1.9 | 0.6 | 2.0 | 2.23 ± 0.41 | 20.3 | 9.9 | 22.6 |
| <i>n</i> -alk-1-enes and other alkenes | 18.9 ± 0.3 | 1.6 | 0.5 | 1.7 | 1.07 ± 0.24 | 24.6 | 11.5 | 27.1 |
| <i>n</i> -alkanes | 4.75 ± 0.24 | 5.1 | 0.8 | 5.1 | 0.70 ± 0.12 | 18.7 | 9.2 | 20.9 |
| dienes | 5.71 ± 0.43 | 7.1 | 3.0 | 7.7 | 0.46 ± 0.07 | 16.8 | 8.0 | 18.6 |
| ∑ Aromatics | 12.84 ± 0.54 | 3.5 | 2.7 | 4.4 | 29.03 ± 0.81 | 2.8 | 0.6 | 2.8 |
| one benzene ring | 11.86 ± 0.54 | 3.9 | 2.8 | 4.8 | 17.02 ± 0.86 | 5.5 | 2.6 | 6.1 |
| two benzene rings | 0.77 ± 0.06 | 8.4 | 3.6 | 9.2 | 9.35 ± 1.19 | 13.3 | 4.7 | 14.1 |
| three benzene rings | - | - | - | - | 1.54 ± 0.23 | 15.5 | 5.7 | 16.5 |
| phenolics and other oxygen-cont. aromatics | 0.21 ± 0.01 | 5.0 | 2.3 | 5.5 | 1.12 ± 0.11 | 11.1 | 5.4 | 12.4 |
| Cycloalkenes | 0.75 ± 0.07 | 8.0 | 6.0 | 10.0 | 2.28 ± 0.37 | 17.8 | 8.8 | 19.8 |
| Cycloalkanes | 0.46 ± 0.04 | 7.6 | 1.3 | 7.7 | - | - | - | - |
| Ketones | 0.24 ± 0.02 | 9.2 | 1.1 | 9.2 | - | - | - | - |
| Other oxygen-containing compounds | 0.10 ± 0.03 | 29.5 | 12.6 | 32.0 | - | - | - | - |
| ∑ Terpenes and terpenoids | - | - | - | - | 2.34 ± 0.17 | 5.7 | 5.4 | 7.8 |
| terpenes containing oxygen | - | - | - | - | 0.49 ± 0.08 | 18.4 | 7.9 | 20.0 |
| terpenes, no oxygen present | - | - | - | - | 1.84 ± 0.21 | 11.1 | 3.4 | 11.6 |
| Other identified | 0.42 ± 0.08 | 17.6 | 5.9 | 18.6 | 2.19 ± 0.19 | 9.5 | 4.5 | 10.6 |

5.4 General considerations

When analyzing pyrolysis results it should be kept in mind that there is a difference between the set pyrolysis temperature and the actual temperature of the sample during pyrolysis (Moldoveanu 2010b). The temperature of the sample is always less than the adjusted pyrolysis temperature. The “real pyrolysis temperature” could be found with the model compound isoprene/styrene (tradename Kraton 1107), which decomposes into smaller molecules. This means that the ratio of the isoprene to dipentene is directly proportional to the pyrolysis temperature that exists between 500 °C and 850 °C with a good correlation coefficient. The most uniform pyrolysis temperature is in the middle of the quartz tube (Ji 2009). In practice, it was noticed that the yield of pyrolysis products is highly dependent on the sample position in relation to the middle of the platinum coil filament.

It is common that some compounds are present at trace levels in pyrolysates and can be below the limit of detection of the analytical instrument (Moldoveanu 2010c). The whole set of constituents of the pyrolysate is not always amenable for gas chromatographic analysis. This is the case when a pyrolysate contains char, water, carbon dioxide, and non-volatile components. Also, as it was found in experiments (I-IV), compounds having a very small molecular mass and a very high volatility were impossible to identify due to their poor chromatographic resolution. Highly volatile compounds would demand the possibility of lowering the GC oven temperature more than was possible with the current system. The choice of a specific type of a chromatographic column is important for pyrolysate separation. For this reason, columns with different stationary phases (and dimensions) were tested for their suitability for product analysis before the selection of columns HP-5MS and ZB-5HT for pyrolysates analysis began.

In order to have reliable quantitative results by Py-GC, an important requirement is the repeatability of the analysis. Any variation of the parameters of the Py-GC analysis may influence the outcome. For this reason, achieving a quantifiable result using Py-GC is more difficult than when using typical chromatography. The variability of the results was due to the fact that certain steps in the pyrolytic process may not be perfectly reproducible. Reproducibility could be improved through the use of an internal standard. However, in this study, due to the multiplicity of products, it was not possible to add any internal standard without having a problem of overlapping peaks in pyrograms. Despite the limitations inherent in analytical pyrolysis, it was concluded that a general trend could be drawn from these results.

6 CONCLUDING REMARKS

6.1 Summary of the results

It was observed that Py-GC/MSD is a useful technique for qualifying pyrolysis products and offers the potential for studying their formation mechanisms. The products that were distributed through pyrolysis for the same sample were found to be the same from one experiment to the other. There was also a problem of repeatability in our quantitative analysis. However, despite these limitations, it was concluded that some general trends could clearly be seen. As expected, in most cases, the prolonged pyrolysis time and increasing pyrolysis temperature generally favored the formation of the aforementioned products.

The composition of the extractive-based raw material had a significant effect on pyrolysate composition. Characteristic fragmentation patterns for each feedstock 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 composed of a complex mixture of various extractive-based compounds. This further proved the importance of the experiments with regards to different model compounds when the aim was to figure out the various pyrolysis mechanisms of complex materials. The presence of the unsaturation and the degree of it, the existence of the hydroxyl groups (in addition to carboxyl groups) or the content of the RAs in the raw material, had a clear effect on the products that were formed through pyrolysis. This, in turn, affected the raw material suitability. For example, this could be seen in the case where biodiesel was produced. Both RAs and unsaturated FAs resulted in the formation of aromatic compounds, whereas hydroxyl groups lead to the formation of oxygen-containing compounds (e.g., ketones). The best product quality (i.e., lesser amounts of aromatics and oxygen-containing compounds) was achieved with the raw material containing mostly salts of the saturated FAs.

Pyrolysis experiments that were done with different tall oil products suggested that small amounts of black liquor had no significant effect on product quality. The most important factor affecting the composition of this bioliquid was the amount of RAs in the feedstock. Crude tall oil soap could be considered as suitable feedstock when it comes to developing economically feasible processes for producing diesel fuel additives.

Pyrolysis experiments with vegetable oil soaps, especially with palm oil soap, indicated that it would be possible to produce hydrocarbons similar to those found in a gasoline and diesel fuel boiling range fraction for petroleum. The pyrolysis of the FA sodium salts of palm oil, olive oil, and rapeseed oil, mostly resulted in the formation of volatile products similar to those found in gasoline and diesel fuel boiling range fractions of petroleum. Castor oil appeared to be an unsuitable raw material for the pyrolytic production of biofuels due its high content of ricinoleic acid. Due to a higher content of saturated FAs, palm oil seemed to be most promising raw material for this kind of biofuel production. The quality of the pyrolysate was better in experiments performed with vegetable oil soaps (excluding castor oil) than in those performed with the tall oil products.

The results of this study were in accordance with the reaction mechanisms postulated for the pyrolytical behavior of the selected raw materials. It should be pointed out that the pyrolysis behavior of saponified RA-based raw materials is a less studied research area. The pyrolysis behavior of RA-contained materials in the saponified form, however, did seem to follow the reaction schemes that were postulated for the RAs with the exception that no original RAs were detected in the pyrolysate. If the aim was to develop new reaction schemes for the pyrolysis of a certain compound, not only laboratory experiments would be required, but additionally, kinetic and thermodynamic studies would be necessary in order to test the validity of the postulated reaction scheme. However, it seems that the pyrolysis reactions of most of the organic compounds with different functionalities are rather well studied, and thus, the results obtained in this study further prove and clarify existing theories.

6.2 Suggestions for future research

In forthcoming studies, the pyrolysis of crude hardwood oil soap with a higher relative amount of neutral compounds ((with FAs) and (without RAs)) would be a good topic of interest. Research has already been continued with two other closely related topics, which will be published later. These studies include the pyrolysis of black liquor and black liquor model compounds (i.e., hydroxy mono- and dicarboxylic acid salts) and the pyrolysis of native wood

extractives in a neutralized form. Black liquor and its components were pyrolyzed to illustrate the possible effect black liquor impurities might have on pyrolysis product distribution with crude tall oil soap and to further understand the matrix effect they might have on pyrolysis reactions when the unpurified mixture is pyrolyzed.

The native wood extractives, including extractives fractions of pine, spruce, aspen, birch, and eucalypt, were pyrolyzed to further clarify the effect of extractives fraction composition to the pyrolysis behavior of extractive-based raw materials. One main aim was to illustrate the differences between softwood and hardwood extractives and to compare the product qualities in different cases. Wood extractives, on one hand, are causing problems in pulping and papermaking as they do not contain useful paper components. Thus, it might be an option to remove extractives from wood chips prior to pulping if they could be used economically in order to produce valuable byproducts. Another approach is to separate them as a crude tall oil soap after pulping. Also, studies made with an extractives fraction of different species give useful data concerning the further refining of soaps originating from different species. The data gained in this research would help to evaluate the best raw material for this kind of biofuel production.

In this research, sodium was selected for saponification in order for it to systemically compare with the thermochemical behavior of different extractive-based materials under pyrolytical conditions. The affect that alkali has on saponification and on pyrolytic behavior would make for an interesting area of research. It could be investigated to see how the pyrolysis product of calcium salt differs from those formed in sodium salt pyrolysis.

In order to gain more accurate information related to the chemical composition, physical properties, and yield of this kind of biofuel production, tests with more technical apparatuses are needed for recovering the liquid product. In the beginning, this can be done on small scale, with a laboratory reactor. The essential kind of information that is needed includes obtaining the: cetane number, distillation range, specific gravity, heat of combustion, flash point, contamination (water/sediment), copper-strip corrosion, cloud point, pour point, cold filter plugging point, carbon residue, amount of sulfur, and particulate matter when the aim is to produce biodiesel. Conducting engine run tests are also essential in order to illustrate whether the product would cause problems in use.

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APPENDICES

APPENDIX I: Chemical structures of common vegetable oil extractives.

APPENDIX II: Chemical composition of palm, olive, rapeseed, and castor oils. Chemical and physical properties of selected vegetable oils and No. 2 diesel fuel.

APPENDIX III: Chemical compositions of the extractives in wood and tall oil products from Scots pine.

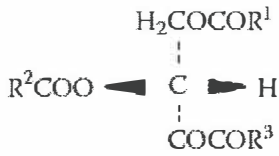
APPENDIX IV: Classification of pyrolysis products (including their formulas and molecular masses) from model compound studies.

APPENDIX V: Classification of pyrolysis products (including their formulas and molecular masses) from vegetable oil studies.

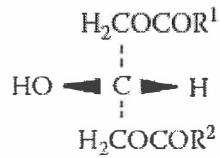
APPENDIX VI: Classification of pyrolysis products (including their formulas and molecular masses) from tall oil studies.

Chemical structures of the common vegetable oil extractives

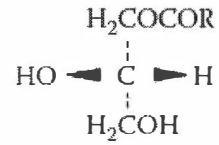
| Chemical structure | Systematic name | Trivial name/ Abbreviation | Shorthand name |
|---|---------------------------|-------------------------------|-------------------|
| $\text{HO}_2\text{C}-(\text{CH}_2)_7-\text{CO}_2\text{H}$ | Nonanedioic | Azelic | |
| $\text{HO}_2\text{C}-(\text{CH}_2)_{10}-\text{CH}_3$ | Dodecanoic | Lauric | 12:0 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_{12}-\text{CH}_3$ | Tetradecanoic | Myristic | 14:0 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_{15}-\text{CH}_3$ | Pentadecanoic | | 15:0 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_{16}-\text{CH}_3$ | Hexadecanoic | Palmitic | 16:0 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_{17}-\text{CH}_3$ | Heptadecanoic | Margaric | 17:0 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_{12}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_3$ | 14-Methylhexadecanoic | Anteismargaric | 17:0 ai |
| $\text{HO}_2\text{C}-(\text{CH}_2)_{16}-\text{CH}_3$ | Octadecanoic | Stearic | 18:0 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_{17}-\text{CH}_3$ | Nonadecanoic | | 19:0 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_{18}-\text{CH}_3$ | Eicosanoic | Arachidic | 20:0 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_{20}-\text{CH}_3$ | Docosanoic | Behenic | 22:0 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_{21}-\text{CH}_3$ | Tricosanoic | | 23:0 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_{22}-\text{CH}_3$ | Tetracosanoic | Lignoceric | 24:0 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_5-\text{CH}_3$ | 9-Hexadecenoic | Palmitelaidic | 16:1 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$ | 9-Octadecenoic | Oleic | 18:1 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_8-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$ | 10-Nonadecenoic | | 19:1 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_9-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$ | 11-Eicosenoic | Gondoic | 20:1 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_6-\text{CH}_3$ | 9,12-Octadecadienoic | Linoleic | 18:2 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_6-\text{CH}_3$ | 11,14-Eicosadienoic | | 20:2 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$ | 9,12,15-Octadecatrienoic | Linolenic | 18:3 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_5-\text{CH}=\text{CH}-(\text{CH}_2)_4-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_4-\text{CH}_3$ | 5,11,14-Eicosatrienoic | | 20:3 |
| $\text{HO}_2\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}(\text{OH})-(\text{CH}_2)_5-\text{CH}_3$ | 12-Hydroxy-9-octadecenoic | Ricinoleic | 12-OH 18:1 |



Triglyceride

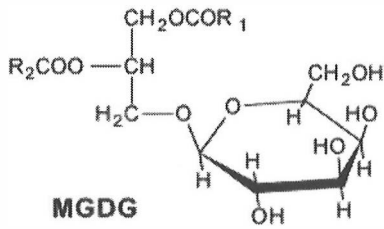


Diglyceride

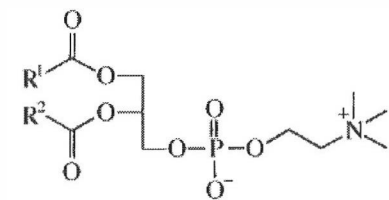
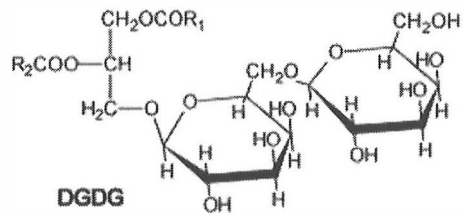


Monoglyceride

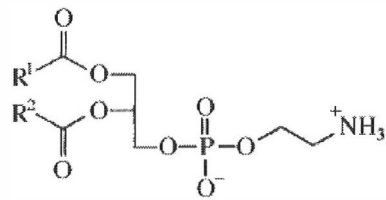
where R is a fatty acid moiety



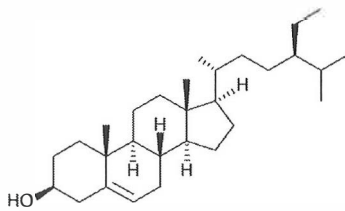
Mono- and digalactosyldiacylglycerol



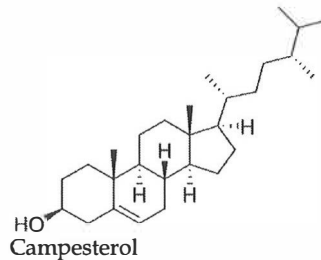
Phosphatidylcholine



Phosphatidylethanolamine

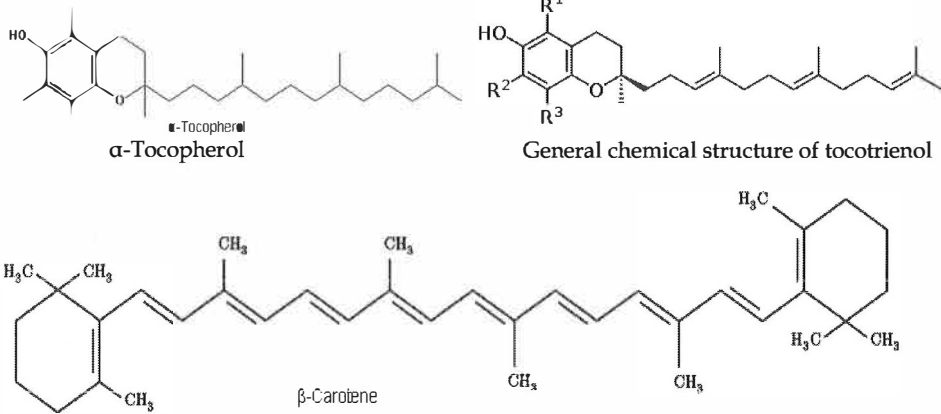


Sitosterol



Campesterol

Compounds not related chemically to fatty acids:



(Gunstone 2004, Yao et al. 2006, Scrimgeour & Harwood 2007, Anon 2010, Christie 2010, Anon 2011)

APPENDIX II

Chemical^a composition of palm, olive, rapeseed, and castor oils [%]

| Fatty acid | Palm oil | Olive oil, | Rapeseed oil | Castor oil |
|-------------------|---|---|---|--|
| C _{12:0} | 0.3 ¹ , 0-1 ² , <0.2 ³ , 0.3 ^{*4} , 0.2 ⁵ , 0-1 ³⁸ | ND ¹⁷ | - | - |
| C _{14:0} | 1.2 ¹ , 0.9-1.5 ² , 1-2 ³ , 1.0 ⁵ , 0.5-2.0 ⁶ , 0.6-2.4 ⁷ , 1.1 ⁸ , 1.5 ⁹ , 0.9-1.5 ³⁸ | 0.1-1.2 ⁶ , 1.3 ⁷ , 0-0.05 ⁹ , 0.0-0.1 ¹⁷ , 0.2 ¹⁸ | 1.5 ⁷ , 0.06 ²⁵ , ND-0.2 ²⁶ | - |
| C _{16:0} | 44.3 ¹ , 39.2-45.8 ² , 43-46 ³ , 45.5 ^{*4} , 42.9 ⁵ , 32.0-45.0 ⁶ , 32-46.3 ⁷ , 43.7 ⁸ , 45.1 ⁹ , 42.6 ¹⁰ , 40.93 ¹¹ , 45 ¹² , 39.2- 45.8 ³⁸ | 7.0-16.0 ⁶ , 7-18.3 ⁷ , 9.3-12 ⁹ , 7.5-20.0 ¹⁷ , 8.9 ¹⁸ , 6.99- 10.01 ¹⁹ , 14.36- 15.33 ²⁰ , 13.15- 14.77 ²¹ , 14.6 ⁴¹ , 6.99-11.05 ²² | 4.9 ^{6,29} , 1-4.7 ⁷ , 3.8 ¹⁰ , 4.72 ²⁵ , 1.5-6.0 ²⁶ , 1-5 ²⁷ , 5.7 ²⁸ , 3.5 ³⁰ , 4 ³¹ , 3.5 ⁴¹ , 4.44 ⁴² | 2.0 ⁶ , 1.1 ¹⁰ , 1.0 ^{33,34,35} , 1.64 ⁴³ , 0.9 ⁴⁴ , 0.7 ⁴⁵ , 0.8-1.1 ⁴⁷ (()) |
| C _{16:1} | 0-0.4 ² , 0.2 ⁸ , 0.3 ¹⁰ , 0-0.4 ³⁸ | 0.3-3.5 ⁹ , 0.3-3.5 ¹⁷ , 4.7 ¹⁸ , 0.49-0.87 ¹⁹ , 1.30-2.08 ²⁰ , 0.96-1.35 ²¹ , 0.49-1.11 ²² , | 0.24 ²⁵ , ND-3.0 ²⁶ , 0.1 ⁴¹ | 0 ¹⁰ , 0.2 ⁴⁴ |
| C _{17:0} | - | 0.0-0.5 ¹⁸ , 0.05-0.07 ¹⁹ , 0.03-0.06 ²¹ , 0.04-0.07 ²² | ND-0.1 ²⁶ | - |
| C _{17:1} | - | 0.0-0.6 ¹⁷ , 0.08-0.11 ¹⁹ , 0.06- 0.09 ²¹ , 0.08-0.11 ²² | ND-0.1 ²⁶ | - |
| C _{18:0} | 4.3 ¹ , 3.7-5.1 ² , 4-6 ³ , 2.0 ^{*4} , 4.4 ⁵ , 2.0-7.0 ⁶ , 4-6.3 ⁷ , 4.5 ⁸ , 4.8 ⁹ , 4.4 ¹⁰ , 4.18 ¹¹ , 5 ¹² , 3.7-5.1 ³⁸ | 1.0-3.0 ⁶ , 1.4-3.3 ⁷ , 0.5-3.5 ⁹ , 0.5-5.0 ¹⁷ , 2.86-4.14 ¹⁹ , 1.46-1.71 ²⁰ , 2.35-3.90 ²¹ , 2.61-4.43 ²² | 1.6 ⁶ , 1-3.5 ⁷ , 2.0 ¹⁰ , 2.49 ²⁵ , 3.1 ²⁶ , 0.5-2.2 ⁷ , 2.2 ²⁸ , 1.8 ²⁹ , 0.9 ³⁰ , 0.5-2 ³¹ , 0.9 ⁴¹ , 2.72 ⁴² | 1.0 ⁶ , 3.1 ¹⁰ , 1.0 ^{33,34,35} , 1.85 ⁴³ , 1.2 ⁴⁴ , 0.9 ⁴⁵ , 0.7-1.0 ⁴⁷ |
| C _{18:1} | 39.3 ¹ , 37.4-44.1 ² , 37-41 ³ , 44.2 ^{*4} , 40.8 ⁵ , 38.0-52.0 ⁶ , 37-53 ⁷ , 40.2 ⁸ , 36.8 ⁹ , 40.5 ¹⁰ , 41.51 ¹¹ , 40 ¹² , 37.4-44.1 ³⁸ | 65.0-80.0 ⁶ , 55.5- 84.5 ⁷ , 68-80.2 ⁹ , 55.0-83.0 ¹⁷ , 66.3 ¹⁸ , 78.12-82.46 ¹⁹ , 64.98-72.45 ²⁰ , 61.96-72.03 ²¹ , 76.5-82.5 ²² , 75.4 ⁴¹ | 33.0 ⁶ , 13-38 ⁷ , 62.2 ¹⁰ , 54.62 ²⁵ , 8.0-60.0 ²⁶ , 50-65 ²⁷ , 58.5 ²⁸ , 57.5 ²⁹ , 64.1 ³⁰ , 62 ³¹ , 54.1 ⁴¹ , 74.15 ⁴² | 7.0 ⁶ , 4.9 ¹⁰ , 3.0 ^{33,34,35} , 5.06 ⁴³ , 3.3 ⁴⁴ , 2.8 ⁴⁵ , 2.2-3.3 ⁴⁷ |
| C _{18:2} | 10.0 ¹ , 8.7-12.5 ² , 12 ³ , 8.0 ^{*4} , 10.2 ⁵ , 5.0- 11.0 ⁶ , 6-12 ⁷ , 9.6 ⁸ , 10.2 ⁹ , 10.1 ¹⁰ , 9-11.64 ¹¹ , 10 ¹² , 8.7- 12.5 ³⁸ | 4.0-10.0 ⁶ , 4-19 ⁷ , 4.6-12 ⁹ , 3.5-21.0 ¹⁷ , 12.3 ¹⁸ , 3.84-6.62 ¹⁹ , 7.90-14.30 ²⁰ , 9.78- 18.18 ²¹ , 10.0 ⁴¹ , 3.07-6.62 ²² , | 20.4 ⁶ , 9.5-22 ⁷ , 22.0 ¹⁰ , 27.20 ²⁵ , 11.0- 23.0 ²⁶ , 15-30 ²⁷ , 24.5 ²⁸ , 20.2 ²⁹ , 22.3 ³⁰ , 22 ³¹ , 22.3 ⁴¹ , 13.23 ⁴² | 5.0 ⁶ , 1.3 ¹⁰ , 4.2 ^{33,34,35} , 6.42 ⁴³ , 3.7 ⁴⁴ , 4.4 ⁴⁵ , 4.1-4.7 ⁴⁷ |

Chemical^a composition of palm, olive, rapeseed, and castor oils [%] (continued)

| Fatty acid | Palm oil | Olive oil, | Rapeseed oil | Castor oil |
|-----------------------|---|--|--|--|
| C _{18:3} | 0-0.6 ^{2,38} , <0.4 ³ , 0.5 ^{8,9} , 0.2 ¹⁰ , | 0-1.5 ⁹ , 0.0-1.5 ¹⁷ , 0.48-0.69 ¹⁹ , 0.74- 0.91 ²⁰ , 0.52-0.82 ²¹ , 0.48-0.95 ²² | 7.4 ⁶ , 1-10 ⁷ , 9.0 ¹⁰ , 7.14 ²⁵ , 13.0 ²⁶ , 5- 13 ²⁷ , 9.1 ²⁸ , 8.4 ²⁹ , 8.2 ³⁰ , 5.0-10 ³¹ | 0 ¹⁰ , 0.3 ^{33,34,35,43} , 0.2 ^{44,45} , 0.5-0.7 ⁴⁷ |
| C _{20:0} | 0-0.4 ^{2,38} | 0.1-1.3 ⁶ , 0.0-0.8 ¹⁷ , 0.3 ¹⁸ , 0.28-0.57 ¹⁹ , 0.35-0.50 ²¹ , 0.28-0.62 ²² , | 0.58 ²⁵ , ND-3.0 ²⁶ | 0.3 ^{34,35,45} |
| C _{20:1} | - | 4.9 ¹⁸ , 0.30-0.37 ¹⁹ , 0.18-0.26 ²¹ , 0.29- 0.39 ²² , | 1.27 ²⁵ , 3.0-15.0 ²⁶ | - |
| C _{20:2} | - | - | ND-1.0 ²⁶ | - |
| C _{22:0} | - | 0.0-0.2 ¹⁷ , 0.12-0.15 ¹⁹ , 0.12-0.21 ²² | 0.42 ²⁵ , ND-2.0 ²⁶ | 0.3 ³³ |
| C _{22:1} | - | - | 23.0 ⁶ , 40-64 ⁷ , 0.58 ²⁵ , >2.0-60.0 ²⁶ | - |
| C _{22:2} | - | - | ND-2.0 ²⁶ | - |
| C _{24:0} | - | 0.0-1.0 ¹⁷ | 0.16 ²⁵ , ND-2.0 ²⁶ | - |
| C _{24:1} | - | - | ND-3.0 ²⁶ | - |
| Ricinoleic acid | - | - | - | 86.0-90.0 ⁶ , 89.6 ¹⁰ , 89.5 ^{33,35} , >89 ³⁴ , 89 ⁴⁴ , 82.88 ⁴³ , 90.2 ⁴⁵ , 87.7-90.4 ⁴⁷ |
| Dihydroxystearic acid | - | - | - | 0.7 ^{33,34,35} , 0.5 ⁴⁵ |
| Triglycerides | ~91 ^{*3} , 92.8 ^{*4} , >95 ³⁸ , >90 ³⁹ | | 91.8-99.0 ³² , 95-99 ⁴⁰ , 96.95 ⁴² | |
| Diglycerides | 8.4 ^{*3} , 4.6 ^{*4} , 5.3-7.7 ³⁷ , 2-7 ³⁹ | 1-2.8 ¹⁷ | 0.5-1.8 ³² , | |
| Monoglycerides | Tr ^{*3} , 1.1 ^{*4} , <0.5 ³⁷ , <1 ³⁹ | <0.25 ¹⁷ | 1.7 ⁴² | |
| Free fatty acids | 0.06 ^{*3} , 0.2 ^{*4} , 3.5 ³⁷ , 3-5 ³⁹ | 0.2-1.8 ¹⁹ | 0.018 ²⁸ , 1.35 ⁴² | |

ND = not determined.

Tr = traces.

^a) Minor compounds are presented in Sections 2.1-2.4.

* = refined oil.

Chemical and physical properties of selected vegetable oils and No. 2 diesel fuel

| Chemical properties | Palm oil | Olive oil | Rapeseed oil | Castor oil | Diesel fuel, No. 2 |
|--|--|---|--|---|--|
| Iodine value, [centigram I/g oil] | 55 ¹ , 50 ³ , 48-58 ⁶ , 35-61 ⁷ , 54 ¹⁵ | 75-94 ^{7,18} , 77-94 ¹⁵ | 94-120 ⁷ , 108.05 ¹⁰ , 94-102 ¹⁵ , 110-126 ³² | 83-86 ⁶ , 82-88 ⁷ , 88.72 ¹⁰ , 85 ¹⁵ , 82-90 ²⁷ , 80-88 ^{33,34} , 84-88 ³⁵ | - |
| Saponification value, [mg KOH/g oil] | 208.63 ⁶ , 196-205 ¹⁵ , 208.62 ¹⁶ | 185-196 ¹⁵ , 185-203 ¹⁸ | 189.8 ⁶ , 197.07 ¹⁰ , 170-179 ¹⁵ , 189.80 ¹⁶ , 188-192 ³² | 191.08 ⁶ , 202.71 ¹⁰ , 191.08 ¹⁶ , 177-185 ^{33,34} , 176-184 ³⁵ , 181.85 ⁴³ | - |
| Sulfur content, [wt-%] | 0.03 ³ , 0.05 ¹³ | - | 0.01 ^{10,14} | 0.01 ^{10,27} , 0.04 ⁴⁶ | max 0.5 ³⁶ |
| Carbon residue, [wt-%] | - | - | 0.31 ¹⁰ , 0.3 ¹⁴ | 0.21 ¹⁰ , 0.22 ²⁷ | max 0.35 ³⁶ |
| Ash content, [wt-%] | 0.01 ¹³ | - | 0.006 ¹⁰ , 0.05 ⁴ ¹⁴ | 0.01 ¹⁰ , <0.01 ²⁷ , 0.02 ⁴⁶ | max 0.1 ³⁶ |
| Physical properties | Palm oil | Olive oil | Rapeseed oil | Castor oil | D2 |
| Density, [kg/m ³] | 910 ³ , 918.0 ^{6,14} , 915.8 ¹³ | 910-920 ¹⁸ , 915-918 ²³ | 911.5 ^{6,14} , 914 ¹⁰ , 914-917 ³² | 955 ⁶ , 950-974 ²⁷ , 957-961 ^{33,35} | 815 ¹⁰ |
| Viscosity at 300 K, [mm ² /s] | 31(at 50 °C)* ¹³ | 84 mPas at 20 °C ²³ | 39.2 ¹⁰ | - | 4.3 ¹⁰ |
| Heating value, [MJ/kg] | 38 ³ | - | 37.6 ¹⁰ | 39.5 ⁷ , 37.2-39.5 ²⁷ | 43.4 ¹⁰ |
| Higher heating value, [MJ/kg] | - | - | 39.7 ⁶ , 39.709 ⁷ , 39.7 ^{10,14} | 37.4 ^{6,10} | 45.34 ³⁷ |
| Cetane number | 38-40 ³ , 42.0 ^{6,7,14} | 60 ¹⁵ | 37.6 ⁶ , 37.6 ⁷ , 37.5 ¹⁰ | 42.3 ^{6,10} , 42 ²⁷ , 43 ⁴⁵ | 47 ⁷ , min 40 ³⁶ |
| Kinematic viscosity, [mm ² /s] at 311 K | 39.6 ¹⁴ | 39.6 at 40 °C ²⁴ | 37.3 ¹⁰ , 37.0 ^{7,14} | 297 ⁷ , 240-300 at 40 °C ²⁷ | 2.7 ^{7,10} , 1.9-4.1 at 40 °C ³⁶ |
| Cloud point, [°C] | 27-31 ³ , 31.0 ¹⁴ | 10 ¹⁸ | -3.9 ^{7,14} | - | -15.0 ⁷ |
| Pour point, [°C] | - | - | -31.7 ^{7,14} | -31.7 ⁷ | -33.0 ⁷ |
| Flash point, [°C] | 219 ³ , 267 ^{6,14} | - | 246 ^{6,7,14} | 260 ^{7,46} , 229-260 ²⁷ | min 52 ^{7,36} |

Original references: ¹⁾ (Lin 2002), ²⁾ (Sambanthamurthi et al. 2000), ³⁾ (Piocch & Vaitilingom 2005), ⁴⁾ (Khamidov et al. 1994), ⁵⁾ (Noor Lida et al. 2002), ⁶⁾ (Karmakar et al. 2010), ⁷⁾ (Knothe et al. 1997), ⁸⁾ (Tan et al. 2009), ⁹⁾ (Ramirez-Tortosa et al. 2006), ¹⁰⁾ (Demirbas 2008a), ¹¹⁾ (Sang 2003), ¹²⁾ (Sumathi et al. 2008), ¹³⁾ (Haga 2004), ¹⁴⁾ (Srivastava & Prasad 2000), ¹⁵⁾ (Anon. 2011 *Journey to Forever*), ¹⁶⁾ (Sanford et al. 2009), ¹⁷⁾ (Boskou 2002), ¹⁸⁾ (El Bassam 2010), ¹⁹⁾ (Salvador et al. 1998), ²⁰⁾ (Torres et al. 2005), ²¹⁾ (Boggia et al. 2005), ²²⁾ (Salvador et al. 2001), ²³⁾ (Addison et al. 2011), ²⁴⁾ (Dorado et al. 2004), ²⁵⁾ (San José Alonso et al. 2008), ²⁶⁾ (Gunstone & Herslöf 2004), ²⁷⁾ (Scholz & da Silva 2008), ²⁸⁾ (Jeong & Park 2006), ²⁹⁾ (Kirszensztejn 2009), ³⁰⁾ (Demirbas 2003a), ³¹⁾ (Gunstone 2004), ³²⁾ (Przybylski & Mag 2002), ³³⁾ (Naughton 1973), ³⁴⁾ (Ogunniyi 2006), ³⁵⁾ (Naughton 1993), ³⁶⁾ (Bacha et al. 1998), ³⁷⁾ (Gibon et al. 2007), ³⁸⁾ (Sundram), ³⁹⁾ (Choo et al. 2005), ⁴⁰⁾ (Ratnayake & Daun 2004), ⁴¹⁾ (Pinto et al. 2005), ⁴²⁾ (Karaosmanoğlu et al. 1997), ⁴³⁾ (Canoira et al. 2010), ⁴⁴⁾ (Hasenhuettl 1993), ⁴⁵⁾ (Chakrabarti & Ali 2009), ⁴⁶⁾ (Kumar & Sharma 2011), ⁴⁷⁾ (Mutlu & Meier 2010)

APPENDIX III

Chemical compositions of the extractives in wood and tall oil products from Scots pine

| Fatty acid component | Composition of total fatty acids, % by weight | | |
|-----------------------------------|---|-----------|------------------|
| | Wood | Soap | Crude oil |
| 14:0 | | | 0.2 |
| 16:0 ai | 0.2 | + | |
| 16:0 | 1.0 | 1.8-1.9 | 2.6 |
| 17:0 ai | 0.8 | 0.9-1.1 | 0.8 |
| 17:0 | + | ≤0.2 | |
| 18:0 | + | 0.2-0.5 | 0.4 |
| 20:0 | + | 0.2-0.4 | |
| 22:0 | 0.3 | 0.7-1.5 | 0.6 |
| 24:0 | + | 0.4-0.5 | 0.8 |
| ∑ Saturated acids | 2.7 | 5.1-5.5 | 5.5 |
| 16:1 | 0.3 | 0.4-0.5 | 0.4 |
| 9-18:1 | 35.3 | 27.5-27.6 | 32.0 |
| 11-18:1 | 0.5 | 0.7-0.9 | |
| 9-19:1 ai | 0.5 | 0.5 | |
| 11-20:10 | 0.4 | 0.3-0.8 | |
| ∑ Monoenic acids | 37.0 | 29.6-30.1 | 32.5 |
| 5,9-18:2 | 0.7 | 0.9-1.0 | 0.8 |
| 9,12-18:2 | 40.5 | 30.9-31.7 | 39.0 |
| 9c,11t-18:2 | - | 3.6-5.1 | 1.6 ^a |
| 10t,12c-18:2 | - | 3.6-5.2 | 3.8 ^a |
| 9t,11t + 10t,12t-18:2 | - | 1.5-2.7 | |
| 11,14-20:2 | 1.0 | 0.7-1.2 | 0.6 ^a |
| ∑ Dienoic acids | 42.2 | 43.8-44.3 | 46.0 |
| 5,9,12-18:3 | 10.6 | 7.8-8.4 | 9.5 |
| 9,12,15-18:3 | 0.8 | ≤0.2 | 0.2 |
| 5c,9c,11t-18:3 | - | 2.0-2.7 | 1.2 ^a |
| 5c,10t,12c-18:3 | - | 2.8-3.7 | 2.0 ^a |
| 5c,10t,12t-18:3 | - | 0.2-0.9 | |
| 5c,9t,11t-18:3 | - | 0.2-0.7 | |
| 5,11,14-20:3 | 4.6 | 3.8-4.1 | |
| 20:3 | 0.6 | 0.6-0.7 | 4.0 |
| ∑ Trienoic acid | 16.6 | 19.3-19.6 | 17.0 |
| Other minor acids (<0.2% each) | 1.5 | 1.0-1.7 | |
| Fatty acids, % of free acids | 70 | 50-51 | 69 |

^a) Conjugated acids; however, no information about double bond location.

| Resin acid component | Composition of total resin acids, % by weight | | |
|---------------------------------------|---|-------|-----------|
| | Wood | Soap | Crude oil |
| Pimaric | 8-10 | 9-10 | 9-11 |
| Sandaracopimaric | 2-2.5 | 2 | 2 |
| Isopimaric | 4-9 | 5-7 | 5-7 |
| Levopimaric | 30 | 5-9 | 0 |
| Palustric | 15 | 13-16 | 8-13 |
| Abietic | 16-23 | 29-31 | 40-49 |
| Dehydroabietic | 14-21 | 15-21 | 13-16 |
| Neobietic | 11-12 | 10-13 | 10-12 |
| Secodehydroabietic | 0.5 | 1 | 1 |
| <i>Resin acids, % of ee acids</i> | 30 | 49-50 | 31 |

Original references: Holmbom and Avela 1971a, Holmbom 1978a,b, Holmbom and Ekman 1978.

APPENDIX IV

Classification^a of pyrolysis products (including their formulas and molecular masses) from model compound studies

| Alkenes | | | Alkanes | | |
|--|---------------------------------|-----|---|--|-----|
| 1-Heptene ^b and other heptanes ^e | C ₇ H ₁₄ | 98 | Heptane ^b | C ₇ H ₁₆ | 100 |
| 1-Octene ^b and other octenes ^e | C ₈ H ₁₆ | 112 | Octane ^b | C ₈ H ₁₈ | 114 |
| 1-Nonene ^{c,d} and other nonenes ^b | C ₉ H ₁₈ | 126 | Nonane ^b | C ₉ H ₂₀ | 128 |
| 1-Decene ^{c,d} and other decenes ^{c,d} | C ₁₀ H ₂₀ | 140 | Decane ^{c,d} | C ₁₀ H ₂₂ | 142 |
| 1-Undecene ^b and other undecenes ^b | C ₁₁ H ₂₂ | 154 | Undecane ^b | C ₁₁ H ₂₄ | 156 |
| 1-Dodecene ^{c,d} and other dodecenes ^{c,d} | C ₁₂ H ₂₄ | 168 | Dodecane ^{c,d} | C ₁₂ H ₂₆ | 170 |
| 1-Tridecene ^{c,d} and other tridecenes ^{c,d} | C ₁₃ H ₂₆ | 182 | Tridecane ^{c,d} | C ₁₃ H ₂₈ | 184 |
| 1-Tetradecene ^{c,d} and other tetradecenes ^{c,d} | C ₁₄ H ₂₈ | 196 | Tetradecane ^c | C ₁₄ H ₃₀ | 198 |
| 1-Pentadecene ^{c,d} and other pentadecenes ^{c,d} | C ₁₅ H ₃₀ | 210 | Pentadecane ^c | C ₁₅ H ₃₂ | 212 |
| 1-Hexadecene ^{c,d} and other hexadecenes ^c | C ₁₆ H ₃₂ | 224 | Hexadecane ^c | C ₁₆ H ₃₄ | 226 |
| 1-Heptadecene ^c and other heptadecenes ^{c,d} | C ₁₇ H ₃₄ | 238 | Heptadecane ^c | C ₁₇ H ₃₆ | 240 |
| 5-Octadecene ^{c,d} | C ₁₈ H ₃₆ | 252 | | | |
| Ring-containing alkenes | | | Ring-containing alkanes | | |
| 1-Butylcyclopentene ^d | C ₉ H ₁₆ | 124 | Butylcyclopentane ^d | C ₉ H ₁₈ | 126 |
| 1-Cyclohexylheptene ^d | C ₁₃ H ₂₄ | 180 | Nonylcyclopentane ^d | C ₁₄ H ₂₈ | 196 |
| 1-Octylcyclopentene ^d | C ₁₃ H ₂₄ | 180 | Nonylcyclohexane ^d | C ₁₅ H ₃₀ | 210 |
| 1-Octylcyclohexene ^d | C ₁₄ H ₂₆ | 194 | | | |
| 1-Nonylcyclohexene ^d | C ₁₅ H ₂₈ | 208 | | | |
| Aromatics | | | Oxygen-containing compounds | | |
| Benzene ^b | C ₆ H ₆ | 78 | 2,4-Hexadienal ^d | C ₆ H ₈ O | 96 |
| Methylbenzene ^b | C ₇ H ₈ | 92 | Hexanal ^e | C ₆ H ₁₂ O | 100 |
| Ethylbenzene ^b | C ₈ H ₁₀ | 106 | 2-Heptanone ^e | C ₇ H ₁₄ O | 114 |
| <i>o</i> -Xylene ^c and <i>p</i> -xylene ^{d,e} | C ₈ H ₁₀ | 106 | 2-Pentylfuran ^e | C ₉ H ₁₄ O | 138 |
| Styrene ^{d,e} | C ₈ H ₈ | 104 | 2-Octanone ^e | C ₈ H ₁₆ O | 128 |
| 2-Propenylbenzene ^c | C ₉ H ₁₂ | 120 | 2-Nonanone ^e | C ₉ H ₁₈ O | 142 |
| Propylbenzene ^c | C ₉ H ₁₂ | 120 | 2-Decanone ^e | C ₁₀ H ₂₀ O | 156 |
| 1-Ethyl-4-methylbenzene ^e | C ₉ H ₁₂ | 120 | 6-Undecanone ^e | C ₁₁ H ₂₂ O | 170 |
| 1-Ethyl-3-methylbenzene ^d | C ₉ H ₁₂ | 120 | 2,4-Decadienal ^c | C ₁₀ H ₁₆ O | 152 |
| 1-Ethyl-2-methylbenzene ^e | C ₉ H ₁₂ | 120 | 6-Dodecanone ^e | C ₁₂ H ₂₄ O | 184 |
| (1-Methylethyl)benzene ^d | C ₉ H ₁₂ | 120 | 10-Pentadecenol ^d | C ₁₅ H ₃₀ O | 226 |
| 2,3-Dihydro-1 <i>H</i> -indene ^{c,e} | C ₉ H ₁₀ | 118 | 9,12-Octadecadienal ^e | C ₁₈ H ₃₂ O | 264 |
| 2,4-Dihydro-1 <i>H</i> -indene ^d | C ₉ H ₁₀ | 120 | 9,12-Octadecadienoic acid ^c | C ₁₈ H ₃₂ O ₂ | 280 |
| 1 <i>H</i> -Indene ^b | C ₉ H ₈ | 116 | 2-Nonadecanone ^c | C ₁₉ H ₃₈ O | 282 |
| 1-Methyl-1 <i>H</i> -indene ^d | C ₁₀ H ₁₀ | 130 | Octadecanoic acid ^c | C ₁₈ H ₃₆ O ₂ | 284 |
| Butylbenzene ^c | C ₁₀ H ₁₄ | 134 | 3-Eicosanone ^c | C ₂₀ H ₄₀ O | 296 |
| (1-Methylpropyl)benzene ^c | C ₁₀ H ₁₄ | 134 | 18-Pentatriacontanone ^c | C ₃₅ H ₇₀ O | 506 |
| 2,3-Dihydro-4-methyl-1 <i>H</i> -indene ^c | C ₁₀ H ₁₂ | 132 | Dienes | | |
| 2-Butenylbenzene ^c | C ₁₀ H ₁₂ | 132 | 2,4-Octadiene ^e | C ₈ H ₁₄ | 110 |
| Pentylbenzene ^c | C ₁₁ H ₁₆ | 148 | 1,3-Nonadiene ^c | | |
| 1-Methyl-4-(2-methylpropyl)benzene ^e | C ₁₁ H ₁₆ | 148 | 1,9-Decadiene ^c and 1,10-decadiene ^c | C ₁₀ H ₁₈ | 138 |
| 1,1-Dimethyl-1 <i>H</i> -indene ^e | C ₁₁ H ₁₂ | 148 | 1,4-Undecadiene ^d and 2,4-undecadiene ^d | C ₁₁ H ₂₀ | 152 |

Classification^a of pyrolysis products (including their formulas and molecular masses) from model compound studies (continued)

| Aromatics | | Dienes | | | |
|----------------------------------|---------------------------------|---------------|---|--|------------|
| Naphthalene ^e | C ₁₀ H ₈ | 128 | 5,7-Dodecadiene ^d and 2,4-dodecadiene ^d | C ₁₂ H ₂₂ | 166 |
| Hexylbenzene ^e | C ₁₂ H ₁₈ | 162 | 1,12-Tridecadiene ^c 1,13-Tetradecadiene ^c | C ₁₃ H ₂₄ C ₁₄ H ₂₆ | 180 194 |
| 2-Methylnaphthalene ^e | C ₁₁ H ₁₀ | 142 | 1,15-Hexadecadiene ^d and 1,9-hexadecadiene ^d | C ₁₆ H ₃₀ | 222 |

- a) Compounds are listed within each substance group according to their GC retention times.
- b) In all the pyrolysates.
- c) In sodium stearate pyrolysate.
- d) In sodium oleate pyrolysate.
- e) In sodium linolate pyrolysate.

APPENDIX V

Classification^a of pyrolysis products (including their formulas and molecular masses) from vegetable oils studies

| <i>n</i> -Alk-1-enes and other alkenes | | | Alkanes | | |
|--|-----------------------------------|-----|---|--|-----|
| 1-Hexene | C ₆ H ₁₂ | 84 | Heptane | C ₇ H ₁₆ | 100 |
| 1-Heptene | C ₇ H ₁₄ | 98 | Octane | C ₈ H ₁₈ | 114 |
| 1-Octene and other octenes | C ₈ H ₁₆ | 112 | Nonane ^{b,c,d} | C ₉ H ₂₀ | 128 |
| 1-Nonene ^{b,c,d} and other nonenes | C ₉ H ₁₈ | 126 | Decane ^{b,c,d} | C ₁₀ H ₂₂ | 142 |
| 1-Decene ^{b,c,d} and other decenes | C ₁₀ H ₂₀ | 140 | Undecane | C ₁₁ H ₂₄ | 156 |
| 1-Undecene ^{b,c,d} and other undecenes | C ₁₁ H ₂₂ | 154 | Dodecane | C ₁₂ H ₂₆ | 170 |
| 1-Dodecene ^{b,c,d} and other dodecenes ^{b,c,d} | C ₁₂ H ₂₄ | 168 | Tridecane | C ₁₃ H ₂₈ | 184 |
| 1-Tridecene ^{b,c,d} and other tridecenes ^{b,c,d} | C ₁₃ H ₂₆ | 182 | Tetradecane | C ₁₄ H ₃₀ | 198 |
| 1-Tetradecene and other tetradecenes ^{b,c,d} | C ₁₄ H ₂₈ | 196 | Pentadecane | C ₁₅ H ₃₂ | 212 |
| 1-Pentadecene | C ₁₅ H ₃₀ | 210 | Hexadecane ^{b,c,d} | C ₁₆ H ₃₄ | 226 |
| 1-Hexadecene ^{b,c,d} | C ₁₆ H ₃₂ | 224 | Heptadecane ^b | C ₁₇ H ₃₆ | 240 |
| 1-Heptadecene and other heptadecenes ^{b,c,d} | C ₁₇ H ₃₄ | 238 | | | |
| 1-Octadecene and other octadecenes ^{b,c,d} | C ₁₈ H ₃₆ | 252 | | | |
| 1-Nonadecene ^{b,c,d} | C ₁₉ H ₃₈ | 266 | | | |
| Aromatics | | | Phenolics and other oxygen-containing aromatics | | |
| Benzene | C ₆ H ₆ | 78 | Phenol ^{b,c,d} | C ₆ H ₆ O | 94 |
| Methylbenzene | C ₇ H ₈ | 92 | 2-Methylphenol and 4-methylphenol ^{b,c,d} | C ₇ H ₈ O | 108 |
| Ethylbenzene | C ₈ H ₁₀ | 106 | α -Methylbenzenemethanol ^e | C ₈ H ₁₀ O | 122 |
| 1,3-Dimethylbenzene | C ₈ H ₁₀ | 106 | 2,4-Dimethylphenol ^e | C ₈ H ₁₀ O | 122 |
| Styrene ^e | C ₈ H ₈ | 104 | 2,4,6-Trimethylphenol ^e | C ₉ H ₁₂ O | 136 |
| 2-Propenylbenzene ^e | C ₉ H ₁₂ | 120 | 2-Ethyl-6-methylphenol ^e and 4-ethyl-3-methylphenol ^e | C ₉ H ₁₂ O | 136 |
| Propylbenzene | C ₉ H ₁₂ | 120 | Diethylphenol ^e | C ₁₀ H ₁₄ O | 150 |
| 1-Ethyl-2-methylbenzene | C ₉ H ₁₂ | 120 | 4-Pentylphenol ^e and 2-pentylphenol ^b | C ₁₁ H ₁₆ O | 164 |
| 1 <i>H</i> -Indene | C ₉ H ₈ | 116 | <i>o</i> -Pentylanisole ^e | C ₁₂ H ₁₈ O | 178 |
| 2,4-Dimethylstyrene ^e | C ₁₀ H ₁₂ | 132 | | | |
| 1-Phenyl-1-butene | C ₁₀ H ₁₂ | 132 | | | |
| 1-Methyl-1 <i>H</i> -indene | C ₁₀ H ₁₀ | 130 | | | |
| Naphthalene ^{c,d,e} | C ₁₀ H ₈ | 128 | | | |
| 1-Methylnaphthalene | C ₁₁ H ₁₀ | 142 | | | |
| Ketones | | | Other oxygen-containing compounds | | |
| 2-Methylenecycloheptanone ^c | C ₈ H ₁₂ O | 124 | Heptanal ^e | C ₇ H ₁₄ O | 114 |
| 2-Octanone ^e | C ₈ H ₁₆ O | 128 | 1-Heptanol ^e | C ₇ H ₁₆ O | 116 |
| 3-Nonanone and 2-nonanone ^e | C ₉ H ₁₈ O | 142 | 2-Octanol ^e | C ₈ H ₁₈ O | 130 |
| 4-Decanone ^e and 2-decanone ^e | C ₁₀ H ₂₀ O | 156 | 6-Dodecenol ^{b,d} | C ₁₂ H ₂₄ O | 184 |
| 5-Undecanone ^e and 2-undecanone ^e | C ₁₁ H ₂₂ O | 170 | 9,11-Dodecadienal ^c | C ₁₂ H ₂₀ O | 180 |
| 6-Dodecanone and 2-dodecanone ^e | C ₁₂ H ₂₄ O | 184 | 11-Hexadecynal ^{b,d} | C ₁₆ H ₂₈ O | 236 |
| 11-Dodecen-2-one ^e | C ₁₂ H ₂₂ O | 182 | 1-Hexadecanol ^{b,c,d} | C ₁₆ H ₃₄ O | 242 |
| 7-Tridecanone ^e | C ₁₃ H ₂₆ O | 198 | Hexadecanoic acid, methyl ester ^{b,c} | C ₁₇ H ₃₄ O ₂ | 270 |
| 6-Tetradecanone ^e and 2-tetradecanone ^b | C ₁₄ H ₂₈ O | 212 | Hexadecanoic acid ^{b,c} | C ₁₆ H ₃₂ O ₂ | 256 |
| 7-Pentadecanone ^e | C ₁₅ H ₃₀ O | 226 | 9-Octadecenal ^{b,c,d} | C ₁₈ H ₃₄ O | 266 |
| 7-Heptadecanone ^e and 2-heptadecanone | C ₁₇ H ₃₄ O | 254 | 9,12-Octadecadien-1-ol ^c | C ₁₈ H ₃₄ O | 266 |
| 3-Octadecanone ^{b,c} | C ₁₈ H ₃₆ O | 268 | 9-Octadecenal ^c | C ₁₈ H ₃₄ O | 266 |

Classification^a of pyrolysis products (including their formulas and molecular masses) from vegetable oils studies (continued)

| Ketones | | | Other oxygen-containing compounds | | |
|---|-----------------------------------|-----|--|-----------------------------------|-----|
| 2-Nonadecanone | C ₁₉ H ₃₈ O | 282 | Stigmast-5-en-3-ol ^d | C ₂₉ H ₅₀ O | 414 |
| 16-Hentriacontanone ^b | C ₃₁ H ₆₂ O | 450 | | | |
| Stigmast-5-en-3-one ^b | C ₂₉ H ₄₈ O | 402 | | | |
| Stigmast-4-en-3-one ^d | C ₂₉ H ₄₈ O | 412 | | | |
| Cycloalkenes | | | Cycloalkanes | | |
| 1,4-Cyclohexadiene ^{b,c,d} | C ₆ H ₈ | 80 | Ethenylcyclopentane ^c | C ₇ H ₁₂ | 96 |
| Methyl-1,3-cyclopentadiene ^e | C ₆ H ₈ | 80 | Ethylcyclohexane ^e | C ₈ H ₁₆ | 112 |
| Cyclohexene ^{d,e} | C ₆ H ₁₀ | 82 | Propylcyclohexane ^{c,d} | C ₉ H ₁₈ | 126 |
| 3-Methylenecyclohexene | C ₇ H ₁₀ | 94 | Butylcyclopentane ^{b,c,d} | C ₉ H ₁₈ | 126 |
| 1-Butylcyclopentene ^{b,c,d} | C ₉ H ₁₆ | 124 | Butylcyclohexane ^{b,d} | C ₁₀ H ₂₀ | 140 |
| 1-Propylcyclohexene ^{b,c} | C ₉ H ₁₆ | 124 | Nonylcyclopentane ^{b,c,d} | C ₁₄ H ₂₈ | 196 |
| 1-Pentylcyclopentene ^{b,d} | C ₁₀ H ₁₈ | 138 | Nonylcyclohexane ^{b,c,d} | C ₁₅ H ₃₀ | 210 |
| 1-Butylcyclohexene ^b | C ₁₀ H ₁₈ | 138 | | | |
| 1-Octylcyclopentene ^{b,c,d} | C ₁₃ H ₂₄ | 180 | | | |
| 1-Nonylcyclohexene ^{b,c,d} and 3-Nonylcyclohexene ^{c,d} | C ₁₅ H ₂₈ | 208 | | | |
| Dienes | | | Trienes | | |
| 2-Methyl-2,3-hexadiene ^{b,c,d} | C ₇ H ₁₂ | 96 | 1,8,10-Tridecatriene ^c | C ₁₃ H ₂₂ | 178 |
| 1,3-Octadiene ^{b,c,d} | C ₈ H ₁₄ | 110 | 1,11,13-Heptadecatriene ^{b,c} | C ₁₇ H ₃₀ | 234 |
| 1,8-Nonadiene, 1,3-nonadiene ^{b,c,e} and and 2,4-nonadiene ^d | C ₉ H ₁₆ | 124 | | | |
| 1,9-Decadiene ^{b,c} | C ₁₀ H ₁₈ | 138 | | | |
| 1,6-Undecadiene ^b and 1,4-undecadiene ^{b,c,d} and 2,4-undecadiene ^{b,c,d} | C ₁₁ H ₂₀ | 152 | | | |
| 1,11-Dodecadiene ^b and 5,7-dodecadiene ^{b,c,d} and 2,4-dodecadiene ^{b,c,d} | C ₁₂ H ₂₂ | 166 | | | |
| 1,12-Tridecadiene ^{b,c,d} | C ₁₃ H ₂₄ | 180 | | | |
| 1,9-Tetradecadiene ^{b,c,d} and 1,13-tetradecadiene ^b | C ₁₄ H ₂₆ | 194 | | | |
| 1,15-Hexadecadiene ^{b,c,d} and 1,9-hexadecadiene ^b | C ₁₆ H ₃₀ | 222 | | | |
| 6,8-Heptadecadiene ^{b,c,d} | C ₁₇ H ₃₂ | 236 | | | |
| | | | Others | | |
| | | | 5-Decyne ^{b,c} | C ₁₀ H ₁₈ | 138 |
| | | | 1-Heptadecyne ^b | C ₁₇ H ₃₂ | 236 |
| | | | 10-Demethylsqualene ^c | C ₂₉ H ₄₈ | 396 |
| | | | Stigmastan-3,5-dien ^d | | |

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

^b) Only in the pyrolysate of palm oil.

^c) Only in the pyrolysate of olive oil.

^d) Only in the pyrolysate of rapeseed oil.

^e) Only in the pyrolysate of castor oil.

APPENDIX VI

Classification^a of pyrolysis products (including their formulas) from tall oil studies

| n-Alk-1-enes and other alkenes | | Alkanes | |
|---|---------------------------------|--|---------------------------------|
| 1-Hexene | C ₆ H ₁₂ | Heptane | C ₇ H ₁₆ |
| 1-Heptene | C ₇ H ₁₄ | Octane | C ₈ H ₁₈ |
| 1-Octene and other octenes ^{b,c,d,e} | C ₈ H ₁₆ | Nonane ^{b,c,d,e} | C ₉ H ₂₀ |
| 1-Nonene ^{b,c,d,e} and other nonenes ^{b,c,d,e} | C ₉ H ₁₈ | Decane ^{c,d,e} | C ₁₀ H ₂₂ |
| 1-Decene ^{b,c,d,e} and other decenes ^{c,d,e} | C ₁₀ H ₂₀ | Undecane | C ₁₁ H ₂₄ |
| 1-Undecene and other undecenes ^{b,c,d,e} | C ₁₁ H ₂₂ | Dodecane ^{c,d,e} | C ₁₂ H ₂₆ |
| 1-Dodecene and other dodecenes ^{b,c,d,e} | C ₁₂ H ₂₄ | Tridecane ^{b,c,d,e} | C ₁₃ H ₂₈ |
| 1-Tridecene ^{b,c,d,e} and other tridecenes ^{c,e} | C ₁₃ H ₂₆ | Tetradecane ^{b,c,d,e} | C ₁₄ H ₃₀ |
| 1-Tetradecene ^{b,c,d,e} and other tetradecenes ^{b,d,e} | C ₁₄ H ₂₈ | Pentadecane ^{c,d,e} | C ₁₅ H ₃₂ |
| 1-Pentadecene ^{b,c,d,e} | C ₁₅ H ₃₀ | Hexadecane ^c | C ₁₆ H ₃₄ |
| 1-Hexadecene ^{b,c,d,e} | C ₁₆ H ₃₂ | Heptadecane ^{b,c} | C ₁₇ H ₃₆ |
| 1-Heptadecene ^{b,c,d,e} | 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 ₆ H ₁₀ | 1,3,5-Heptatriene ^b | C ₇ H ₁₀ |
| 2-Methyl-2,3-hexadiene ^{e,f} | C ₇ H ₁₂ | 2-Methyl-1,3,5-hexatriene ^b | C ₇ H ₁₀ |
| 2,5-Dimethyl-2,4-hexadiene ^{b,c,d,f} | C ₈ H ₁₄ | 2,4,6-Octatriene ^{b,c} | C ₈ H ₁₂ |
| 1,3-Octadiene ^{b,c,e} and 2,4-octadiene ^c | C ₈ H ₁₄ | Ocimene ^b | C ₁₀ H ₁₆ |
| 1,3-Nonadiene ^{c,d,e} | C ₉ H ₁₆ | | |
| 1,4-Undecadiene ^{c,e} and 2,4-undecadiene ^{b,c,d,e} | C ₁₁ H ₂₀ | | |
| 5,7-Dodecadiene ^{c,d} and 2,4-dodecadiene ^{c,d,e} | C ₁₂ H ₂₂ | | |
| 1,9-Tetradecadiene ^e | C ₁₄ H ₂₆ | | |
| 1,15-Hexadecadiene ^{b,c,e} | C ₁₆ H ₃₀ | | |
| 6,8-Heptadecadiene ^{b,c,d,e} | C ₁₇ H ₃₂ | | |
| 1,21-Docosadiene ^b | C ₂₂ H ₄₂ | | |
| Cycloalkenes | | Cycloalkanes | |
| 1,4-Cyclohexadiene ^d | C ₆ H ₈ | Butylcyclopentane ^e | C ₉ H ₁₈ |
| Methylcyclopentadiene ^f | C ₆ H ₈ | Nonylcyclopentane ^{b,c,d,e} | C ₁₄ H ₂₈ |
| Cyclohexene ^b | C ₆ H ₁₀ | Nonylcyclohexane ^e | C ₁₅ H ₃₀ |
| 1-Methyl-1,4-cyclohexadiene ^{b,e,f} | C ₇ H ₁₀ | | |
| 3-Ethenylcyclopentene ^{b,c,d,e} | C ₇ H ₁₀ | | |
| 1,3-Cyclooctadiene ^b | C ₈ H ₁₂ | | |
| 5,6-Dimethyl-1,3-cyclohexadiene ^f and 1,5-dimethyl-1,4-cyclohexadiene ^f | C ₈ H ₁₂ | | |
| 1,3,8- <i>p</i> -Menthatriene ^{e,f} | C ₁₀ H ₁₄ | | |
| 3-Butyl-4-vinylcyclopentene ^b | C ₁₁ H ₁₈ | | |
| 1,4-Dimethyldihydroazulene ^f | C ₁₂ H ₁₄ | | |
| Cyclododecene ^b | C ₁₂ H ₂₂ | | |

Classification^a of pyrolysis products (including their formulas) from tall oil studies (continued)

| Terpenes and terpenoids | | | |
|--|-----------------------------------|--|--|
| α -Pinene ^b and β -pinene ^b | C ₁₀ H ₁₆ | endo-Borneol ^{b,f} | 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,f} | C ₁₈ H ₂₂ O |
| γ -Terpinene ^{b,c} , α -terpinene ^{b,c,f} | C ₁₀ H ₁₆ | Dehydroabietic acid, methyl ester ^{b,c} | C ₂₁ H ₃₀ O ₂ |
| Δ^3 -Carene ^{b,f} | C ₁₀ H ₁₆ | Methyl abietate ^b | C ₂₁ H ₃₂ O ₂ |
| Limonene ^{b,c,f} | C ₁₀ H ₁₆ | 5-Ethenyl-(5 β)- <i>A</i> -norcholestan-3-one ^c | C ₂₈ H ₄₆ O |
| Chamazulene ^f | C ₁₄ H ₁₆ | 4 β -Methylcholesta-8,24-dien-3 β -ol ^b | C ₂₈ H ₄₆ O |
| α -Longipinene ^b | C ₁₅ H ₂₄ | 5 α -Ergostan-3-one ^b | C ₂₈ H ₄₈ O |
| Ylangene ^b | C ₁₅ H ₂₄ | 4,4-Dimethylcholest-7-en-3-one ^b | C ₂₉ H ₄₈ O |
| α -Copaene ^b | C ₁₅ H ₂₄ | 4-Ergosten-3-one ^b | C ₂₈ H ₄₆ O |
| Epizonarene ^b | C ₁₅ H ₂₄ | 5 α -Stigmastan-3-one ^b | C ₂₉ H ₅₀ O |
| Isolongifolene ^b | C ₁₅ H ₂₄ | Stigmast-4-en-3-one ^{b,c} | C ₂₉ H ₄₈ O |
| Isoledene ^b | C ₁₅ H ₂₄ | | |
| 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 | | |
| Δ -Cadinene ^{b,c} | C ₁₅ H ₂₄ | | |
| 1,4-Dimethyl-7-(1-methylethyl)azulene ^{b,c,d,f} | C ₁₅ H ₁₈ | | |
| Cembrene ^b | C ₂₀ H ₃₂ | | |
| 5 α -Ergost-8(14)-ene ^b | C ₂₈ H ₄₈ | | |
| Stigmastan-3,5-dien ^{b,c,d,f} | C ₂₉ H ₄₈ | | |
| Ketones | | Other oxygen-containing compounds | |
| 2-Dodecanone ^f | C ₁₂ H ₂₄ O | 2,4-Hexadienal ^{b,c,e} | C ₆ H ₈ O |
| 2-Heptadecanone ^c | C ₁₇ H ₃₄ O | 4-Methyl-1-(1-methylethyl)-3-cyclohexen-1-ol ^b | C ₁₀ H ₁₈ O |
| 2-Nonadecanone ^f | C ₁₉ H ₃₈ O | 1-Tetracosanol ^d | C ₂₄ H ₅₀ O |
| | | Hexahydro-7 α -isopropyl-4 $\alpha\beta$,8 $\alpha\beta$ -dimethyl-2(1 <i>H</i>)-naphthalenone ^c | C ₁₅ H ₂₄ O |
| Others | | | |
| Thiobismethane ^{b,c,d} | C ₂ H ₆ S | 9,12,15-Octadecatrien-1-ol ^e | C ₁₈ H ₃₂ O |
| 1,2-Dimethylenecyclohexane ^d | C ₈ H ₁₂ | Retinol ^b | C ₂₀ H ₃₀ O |
| 1,4-Bis(methylene)cyclohexane ^{c,d,f} | C ₈ H ₁₂ | 10-Pentadecen-1-ol ^c | C ₁₅ H ₃₀ O |
| 5-Dodecen-7-yne ^e | C ₁₂ H ₂₀ | 1-Eicosanol ^c | C ₂₀ H ₄₂ O |
| 1-(2'-Methyl-1'-propenyl)-7-[1'-propynyl]tricyclo[3.1.0.0(2,6)]hexane ^{b,c,d,f} | C ₁₄ H ₁₈ | | |
| 1-Hexadecyne ^e | C ₁₆ H ₃₀ | | |
| Hexaethylidenecyclohexane ^f | C ₁₈ H ₂₄ | | |
| 10-Demethylsqualene ^{c,d,f} | C ₁₉ H ₄₈ | | |

^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 neutralized CTO.

^d) Only in the pyrolysate of the neutralized DTO.

^e) Only in the pyrolysate of the neutralized TOFA.

^f) Only in the pyrolysate of the neutralized TOR.

Classification^a of aromatic pyrolysis products (including their formulas) from tall oil studies

| Aromatics, with one benzene ring | | | |
|---|---------------------------------|--|---------------------------------|
| Benzene | C ₆ H ₆ | <i>p</i> -Isobutyltoluene ^{d,e} | C ₁₁ H ₁₆ |
| Toluene | C ₇ H ₈ | 1,1-Dimethylindene, 2,3-dimethylindene ^b , and 1,3-Dimethylindene ^b | C ₁₁ H ₁₂ |
| Ethylbenzene | C ₈ H ₁₀ | Triethylbenzene ^b | C ₁₂ H ₁₈ |
| Styrene | C ₈ H ₈ | Trimethyl(1-methylethyl)benzene ^f | C ₁₂ H ₁₈ |
| <i>o</i> -Xylene ^{d,e,f} , <i>p</i> -xylene ^f , and <i>m</i> -xylene ^{b,c} | C ₈ H ₁₀ | 2,3-Dihydro-1,1,6-trimethylindene ^f | C ₁₂ H ₁₆ |
| Cumene ^{c,d,f} | C ₈ H ₁₂ | 1,4-Dimethyltetralin ^f | C ₁₂ H ₁₆ |
| Propenylbenzene ^{d,e,f} | C ₉ H ₁₂ | 1,3-Dimethylindene ^f and 4,7-Dimethylindene ^f | C ₁₁ H ₁₂ |
| Isocumene ^{c,d,e} | C ₉ H ₁₂ | 1,2-Diethyl-3,4-dimethylbenzene ^f | C ₁₂ H ₁₈ |
| <i>m</i> -Ethyltoluene and <i>o</i> -ethyltoluene | C ₉ H ₁₂ | Hexylbenzene ^{d,e} | C ₁₂ H ₁₈ |
| α -Methylstyrol ^{b,f} | C ₉ H ₁₀ | Tetrahydrocyclopropa[<i>b</i>]naphthalene ^b | C ₁₁ H ₁₂ |
| <i>m</i> -Vinyltoluene ^{d,e} | C ₉ H ₁₀ | 1,2-Dihydro-3-methylnaphthalene ^{d,f} | C ₁₁ H ₁₂ |
| 2-Isopropyltoluene | C ₁₀ H ₁₄ | 1,1,3-Trimethylindene ^{b,c,d,f} | C ₁₂ H ₁₄ |
| Indane ^{d,e} | C ₉ H ₁₀ | β ,2,4,6-Tetramethylstyrene ^f | C ₁₂ H ₁₆ |
| Allylbenzene ^d | C ₉ H ₁₀ | 1,1,6-Trimethyltetralin ^{b,f} | C ₁₃ H ₁₈ |
| Indene | C ₉ H ₈ | 1-Phenyl-1,3-hexadiene ^f | C ₁₂ H ₁₄ |
| 1,2-Diethylbenzene ^f | C ₁₀ H ₁₄ | Heptylbenzene ^{b,c,d,e} | C ₁₃ H ₂₀ |
| <i>m</i> -Propyltoluene ^{d,f} and <i>o</i> -propyltoluene ^{c,d,e} | C ₁₀ H ₁₄ | (2,4,6-Trimethylphenyl)allene ⁵ | C ₁₂ H ₁₄ |
| Butylbenzene ^{c,d,e} | C ₁₀ H ₁₄ | <i>o</i> -Hexyltoluene ^e | C ₁₃ H ₂₀ |
| β -Dimethylstyrene ^{c,e,f} | C ₁₀ H ₁₂ | 1,1-Dimethyl-3-vinylindan ^f | C ₁₃ H ₁₆ |
| 2,5-Dimethylstyrene ^{d,f} | C ₁₀ H ₁₂ | Octylbenzene ^{c,e} | C ₁₄ H ₂₂ |
| <i>p</i> -Methylcumene ^{c,d,f} | C ₁₀ H ₁₄ | 3-Ethyl-1-(1-methylethyl)indene ^f | C ₁₄ H ₁₈ |
| <i>o</i> -Allyltoluene ^f | C ₁₀ H ₁₂ | Octahydro-7-methyl-4-methylene-1-(1- methylethyl)naphthalene ^b | C ₁₅ H ₂₄ |
| 2-Butenylbenzene ^{d,e,f} | C ₁₀ H ₁₂ | [(Tetramethylcyclopropylidene)methyl]- benzene ^{c,d} | C ₁₄ H ₁₈ |
| α , <i>p</i> -Dimethylstyrene ^f | C ₁₀ H ₁₂ | Nonylbenzene ^{d,e} | C ₁₅ H ₂₄ |
| <i>p</i> -Ethylcumene ^{b,c,f} | C ₁₁ H ₁₆ | (4,5,5-Trimethyl-1,3-cyclopentadien-1-yl)- benzene ^b | C ₁₄ H ₁₆ |
| 2,3-Dihydro-2,2-dimethylindene ^b | C ₁₁ H ₁₄ | Decylbenzene ^{d,e} | C ₁₆ H ₂₆ |
| 3-Methyl-3-phenylbutene ^{c,d} | C ₁₁ H ₁₄ | 9-Ethyl-octahydroanthracene ^b | C ₁₆ H ₂₂ |
| 1-Methylindene | C ₁₀ H ₁₀ | 1,7-Dimethyl-5-phenyltricyclo[4.1.0.0]- hept-3-ene ^b | C ₁₅ H ₁₆ |
| 2,4-Dimethylcumene ^f | C ₁₁ H ₁₆ | 4 <i>a</i> -Methyl-1-methyleneoctahydro- phenanthrene ^{b,c,d,f} | C ₁₆ H ₂₀ |
| 1-Methylindene ^e | C ₁₀ H ₁₀ | Undecylbenzene ^{d,e} | C ₁₇ H ₂₈ |
| <i>o</i> -Isopropyl- α -methylstyrene ^f | C ₁₂ H ₁₆ | (1-Methyldecyl)benzene ^c | C ₁₇ H ₂₈ |
| Phenoprene ^f | C ₁₀ H ₁₀ | 4,8-Diethyl-1,5- dimethyldicyclopenta[<i>a,d</i>]benzene ^f | C ₁₈ H ₂₆ |
| 2-Phenyl-2-pentene ^{e,f} and 3-phenyl-2- pentene ^f | C ₁₁ H ₁₄ | 1,4-Dimethyl-7-isopropyl- hexahydrophenanthrene ^{b,c} | C ₁₉ H ₂₆ |
| Pentylbenzene ^{d,e} | C ₁₁ H ₁₆ | Octahydro-4 <i>a</i> -methyl-1-methylene-7-(1- methylethyl)phenanthrene ^b | C ₁₉ H ₂₆ |
| Tetrahydrocycloprop[<i>a</i>]indene ^d | C ₁₀ H ₁₀ | | |
| 1,2-Dihydronaphthalene ^e | C ₁₀ H ₁₀ | | |

Classification^a of aromatic pyrolysis products (including their formulas) from tall oil studies
(continued)

| Aromatics, with two benzene rings | | | |
|---|--|--|--|
| Naphthalene ^{d,e,f} | C ₁₀ H ₈ | 1-Methyl-3-[(4-methylphenyl)methyl]-benzene ^b | C ₁₅ H ₁₆ |
| α-Methylnaphthalene and β-methylnaphthalene | C ₁₁ H ₁₀ | 3-(1-Methylethyl)-1,1'-biphenyl ^d | C ₁₅ H ₁₆ |
| 1,3-Dimethylnaphthalene and 2,6-dimethylnaphthalene ^f | C ₁₂ H ₁₂ | 2,6-Dimethyl-1-(phenylmethyl)benzene ^{b,c} | C ₁₅ H ₁₆ |
| 1-Ethyl-naphthalene ^{b,c,d,f} | C ₁₂ H ₁₂ | 9,10-Dihydro-1-methylphenanthrene ^{b,c,d,f} | C ₁₅ H ₁₆ |
| 2-Ethenylnaphthalene ^{b,d,f} | C ₁₂ H ₁₀ | Tris(1-methylethyl)naphthalene ^d | C ₁₉ H ₂₆ |
| 2-(1-Methylethyl)naphthalene ^{b,c,d,f} | C ₁₃ H ₁₄ | 1,2,3,4-Tetrahydro-9,10-dimethylanthracene ^b | C ₁₆ H ₁₈ |
| 1,4,5-Trimethylnaphthalene ^{b,c,d,f} | C ₁₃ H ₁₄ | 2,6-Bis(1,1-dimethylethyl)naphthalene ^c | C ₁₈ H ₂₄ |
| 1,2,3,4-Tetramethylnaphthalene ^{b,d,f} | C ₁₄ H ₁₆ | 1,1-Diphenyl-1,3-pentadiene ^{d,f} | C ₁₇ H ₁₆ |
| 1-Methyl-7-(1-methylethyl)-naphthalene ^{b,c,d,f} | C ₁₄ H ₁₆ | 9-Butyl-9-methylfluorene ^b | C ₁₈ H ₂₀ |
| 4,4'-Dimethyl-1,1'-biphenyl ^{b,c,d,f} | C ₁₄ H ₁₄ | Bis(1-methylethyl)-1,1'-biphenyl ^{b,c,d,f} | C ₁₈ H ₂₂ |
| 1,6-Dimethyl-4-(1-methylethyl)-naphthalene ^{b,c,d,f} | C ₁₅ H ₁₈ | 9-Butyl-1,2,3,4-tetrahydroanthracene ^f | C ₁₈ H ₂₂ |
| Aromatics, with three benzene rings | | | |
| Phenanthrene ^d | C ₁₄ H ₁₀ | 2,3,5-Trimethylphenanthrene ^{d,f} | C ₁₇ H ₁₆ |
| 4-Methylphenanthrene ^b , 1-Methylphenanthrene ^{b,c,d,f} | C ₁₅ H ₁₂ | 1-Methyl-7-(1-methylethyl)phenanthrene ^{b,c,d,f} | C ₁₈ H ₁₈ |
| 3,6-Dimethylphenanthrene ^c | C ₁₆ H ₁₄ | Methyl- <i>n</i> -propylphenanthrene ^f | C ₁₈ H ₁₈ |
| Phenolics and other oxygen-containing aromatics | | | |
| Phenol ^e | C ₆ H ₆ O | Isomaturin ^{b,f} | C ₁₆ H ₁₄ O ₃ |
| 2-Methylphenol ^{b,c,f} | C ₇ H ₈ O | 5,8-Dihydroxy-3-methyl-1,2-dihydro-9,10-anthraquinone ^c | C ₁₅ H ₁₂ O ₄ |
| 2,5-Dimethylphenol ^f | C ₈ H ₁₀ O | 1,2,9,10-Tetrahydro-2,9-dimethyl-naphtho[2,1- <i>b</i> :7,8- <i>b'</i>]difuran ^c | C ₁₆ H ₁₆ O ₂ |
| 2,3,5-Trimethylphenol ^d | C ₉ H ₁₂ O | | |
| 1-(2,4-Dimethylphenyl)ethanone ^f | C ₁₀ H ₁₂ O | | |
| 4-(1-Methylethyl)benzenemethanol ^f | C ₁₀ H ₁₄ O | 1,2-Dihydro-2-methyl-5-(2-propenyl)-naphtho[2,1- <i>b</i>]furan-4-ol ^d | C ₁₆ H ₁₆ O ₂ |
| Methyleugenol ^b | C ₁₁ H ₁₂ O ₂ | 1-[4-(2- <i>p</i> -Tolulvinyl)phenyl]ethanone ^{b,c} | C ₁₇ H ₁₆ O |
| 1,2-Dimethoxy-4-(1-propenyl)benzene ^b | C ₁₁ H ₁₄ O ₂ | | |
| 2,3-Dihydro-3,3-dimethylinden-1-ol ^f | C ₁₁ H ₁₄ O | Octahydro-1,4 <i>a</i> -dimethyl-7-(1-methylethyl)-1-phenanthrenecarboxaldehyde ^b | C ₂₀ H ₂₈ O |
| [1,1'-Biphenyl]-4-methanol ^b | C ₁₃ H ₁₂ O | Octahydro-1,4 <i>a</i> -dimethyl-7-(1-methylethyl)-1-phenanthrenemethanol ^b | C ₂₀ H ₃₀ O |
| 1-[1,1'-Biphenyl]-4-yl-ethanone ^{d,f} | C ₁₄ H ₁₂ O | | |
| Sulphur-containing aromatics | | | |
| 2-Methyldiphenylsulphone ^b | C ₁₃ H ₁₂ O ₂ S | | |
| 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 neutralized CTO.

^d) Only in the pyrolysate of the neutralized DTO.

^e) Only in the pyrolysate of the neutralized TOFA.

^f) Only in the pyrolysate of the neutralized TOR.

ORIGINAL PAPERS

PAPER I

<https://doi.org/10.1016/j.jaap.2009.07.005>

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