LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
Faculty of Technology
Degree Programme in Environmental Technology

THE EVALUATION OF HAZARDOUS GAS COMPONENTS CAUSED BY THE THERMAL DEGRADATION OF PLANT OILS AND ANIMAL FATS

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ABSTRACT

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The evaluation of hazardous gas components caused by the thermal degradation of plant oils and animal fats

Master's thesis

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103 pages, 26 figures, 31 tables and 9 appendices

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Keywords: thermal degradation, pyrolysis, triglyceride, plant oil, animal fat, harmful gas, acrolein, pyrolysis product, occupational exposure limit

Neste Oil has introduced plant oils and animal fats for the production of NExBTL renewable diesel, and these raw materials differ from the conventional mineral based oils. One subject of new raw materials study is thermal degradation, or in another name pyrolysis, of these organic oils and fats. The aim of this master's thesis is to increase knowledge on thermal degradation of these new raw materials, and to identify possible gaseous harmful thermal degradation compounds. Another aim is to determine the health and environmental hazards of identified compounds. One objective is also to examine the formation possibilities of hazardous compounds in the production of NExBTL-diesel.

Plant oils and animal fats consist mostly of triglycerides. Pyrolysis of triglycerides is a complex phenomenon, and many degradation products can be formed. Based on the literature studies, 13 hazardous degradation products were identified, one of which was acrolein. This compound is very toxic and dangerous to the environment. Own pyrolysis experiments were carried out with rapeseed and palm oils, and with a mixture of palm oil and animal fat. At least 12 hazardous compounds, including acrolein, were analysed from the gas phase. According to the experiments, the factors which influence on acrolein formation are the time of the experiment, the sphere (air/hydrogen) in which the experiment is carried out, and the characteristics of the used oil. The production of NExBTL-diesel is not based on pyrolysis. This is why thermal degradation is possible only when abnormal process conditions prevail.

TIIVISTELMÄ

Lappeenrannan teknillinen yliopisto
Teknillinen tiedekunta
Ympäristötekniikan koulutusohjelma

Raila Heiskanen

Kasviöljyjen ja eläinrasvojen termisestä hajoamisesta aiheutuvien vaarallisten kaasumaisten komponenttien arviointi

Diplomityö

2009

103 sivua, 26 kuvaa, 31 taulukkoa ja 9 liitettä

Tarkastajat:	Professori Risto Soukka Diplomi-insinööri Helka Turunen

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Keywords: thermal degradation, pyrolysis, triglyceride, plant oil, animal fat, harmful gas, acrolein, pyrolysis product, occupational exposure limit

Neste Oil käyttää kasviöljyjä ja eläinrasvoja NExBTL renewable-dieselin valmistuksessa. Nämä raaka-aineet eroavat konventionaalisesta mineraalipohjaisista öljyistä. Kasviöljyjen ja eläinrasvojen terminen hajoaminen on yksi raaka-aineisiin liittyvä tutkimuksen kohde. Tämän työn tavoitteena on lisätä ymmärrystä termisestä hajoamisesta, sekä tunnistaa orgaanisten rasvojen termisessä hajoamisessa mahdollisesti muodostuvat haitalliset aineet ja määrittää niiden terveys- ja ympäristövaarat. Tarkoituksena on myös pohtia haitallisten aineiden muodostumismahdollisuuksia NExBTL-dieselin valmistuksessa.

Kasviöljyt ja eläinrasvat koostuvat suurimmaksi osaksi triglyserideistä. Niiden terminen hajoaminen on monimutkainen ilmiö, ja hajoamisessa muodostuvia mahdollisia yhdisteitä on hyvin paljon. Tutkitun kirjallisuuden perusteella identifioitiin 13 haitallista hajoamistuotetta, joista yksi oli akroleiini. Akroleiini on erittäin myrkyllinen ja ympäristölle vaarallinen aine. Omissa pyrolyysikokeissa käytettiin raaka-aineena rypsi- ja palmuöljyä sekä palmuöljy-eläinrasvaseosta. Kokeissa vahvistettiin ainakin 12 haitallisen aineen muodostuminen, mukaan lukien akroleiini. Koetulosten perusteella akroleiinin muodostumiseen vaikuttavat tekijät ovat koeaika, sfääri (ilma/vety), jossa koe tehtiin ja kokeessa käytetyn öljyn ominaisuudet. NExBTL-dieselin valmistus ei perustu pyrolyysiin. Tällöin terminen hajoaminen on mahdollista vain normaalista poikkeavissa olosuhteissa.

PREFACE

Environment and nature sciences have always fascinated me, and already a long time ago I knew that my education would have something to do with them.

I want to thank Neste Jacobs and Esa Lindgren, who saw enough potential in me and hired me to carry out this master's thesis. Big thanks also for my examiners professor Risto Soukka, and especially Helka Turunen from Neste Jacobs, who at the same time acted as a close instructor. Thanks also for Jukka Myllyoja from Neste Oil who as another instructor gave his contribution to the chemistry of the thesis. In addition, I want to thank Raija Heikkilä who helped me with the experiments in the laboratory, and thanks also for the staff at the analytical laboratory for analysing my samples.

I have always been determined in my studies, but studying would have not been as fluent without the support of my parents. Therefore I want to thank them for always trusting and supporting me on whatever I do. Moreover, studying in Lappeenranta would not have been as rich without new and old friends. Some of us environmental engineering students have this dream of "saving the world". Though it seems childish, I do hope that in years to come I still have a piece of this dream left wherever my life will take me.

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SYMBOLS AND ABBREVIATIONS

Symbols

m	mass	[g], [kg]
M	molar mass	[g/mol]
n	number of moles of a gas	[mol]
p	absolute pressure of a gas	[Pa]
R	universal gas constant	[J/mol K]
T	absolute temperature	[K]
V	volume of a gas	[m^3]
ρ	density	[kg/m^3]

Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
CFD-models	Computational fluid dynamic models
CPO	crude palm oil
F/F+	Flammable/Extremely flammable substance
GC	Gas chromatography
GPC	Gel permeation chromatography
HTP-value	Concentration known to be hazardous-value (Haitalliseksi tunnettu pitoisuus)
ILO	International Labour Organization
IV	Iodine value
MS	Mass spectrometry
OLP	organic liquid product
ppm	parts per million
RBD palm oil	refined, bleached and deodorised palm oil

t	tonne
T/T+	Toxic/Very toxic substance
TAN	Total acid number
TLV-C	threshold limit value- ceiling
TLV-TWA	threshold limit value- time-weighted average
WHO	World Health Organization
Xi/Xn	Irritating/Harmful substance

Subindexes

flush	refers to the flushing of the sampling pipe in experiments
*H*2	refers to hydrogen
oil	refers to the oil used in the experiments
sample,l	refers to the liquid sample taken from the experimental system
vessel	refers to the reactor vessel
1,2,3,4,5	refer to the different states of the experiment
dev	refers to the development of gas in experiments
sample,g	refers to the gaseous sample taken from the experimental system
dev_1	refers to the development of gas between the states 1 and 2
dev_2	refers to the development of gas between the states 4 and 5
dev_{1+2}	refers to the sum of developed gases in between the states 1 and 2 and between the states 4 and 5

1 INTRODUCTION

In order to slow down the climate change, a good aim is to produce traffic fuels that are environmentally friendly. This happens when the production uses renewable raw materials that are carbon dioxide neutral and do not contribute global warming. The Directive 2003/30/EY of the European Parliament and of the Council of 8 May 2003 on the promotion of the use of biofuels or other renewable fuels for transport obligates the member countries to use renewable fuels in parallel with the conventional mineral based transport fuel. Because of the less polluting fuel production, the need to expand the sources of the raw materials has occurred.

For the production of biodiesel, oils from organic sources have been introduced as raw materials and their composition differs from the traditional mineral oil components. Plant oils and animal fats used among others are rapeseed-, soybean-, and palm oil and lard and tallow. In Europe, rape is grown as a raw material the most, so biofuel or biodiesel is usually made of rapeseed oil, but the oils from soybean grown in the United States and South America and palm oil grown in Asia are also becoming more popular as for the production of biodiesel in Europe (Promar International 2005, 12; Nylund et al. 2008, 55). Figure 1 represents the total production of biodiesel in the member countries of the European Union.

Figure shows that the production of biodiesel in the EU member countries has grown steadily from the beginning of the millennium being approximately 5,7 million tonnes in 2007. Compared to the production statistics the production capacity is even bigger. (European Biodiesel Board 2008) Every year when the production increases, so will naturally the need for raw materials. With a thorough research and analysis of the renewable raw materials we can ensure, that the use of these materials in the production processes is safe and harmless for the people and for the environment.

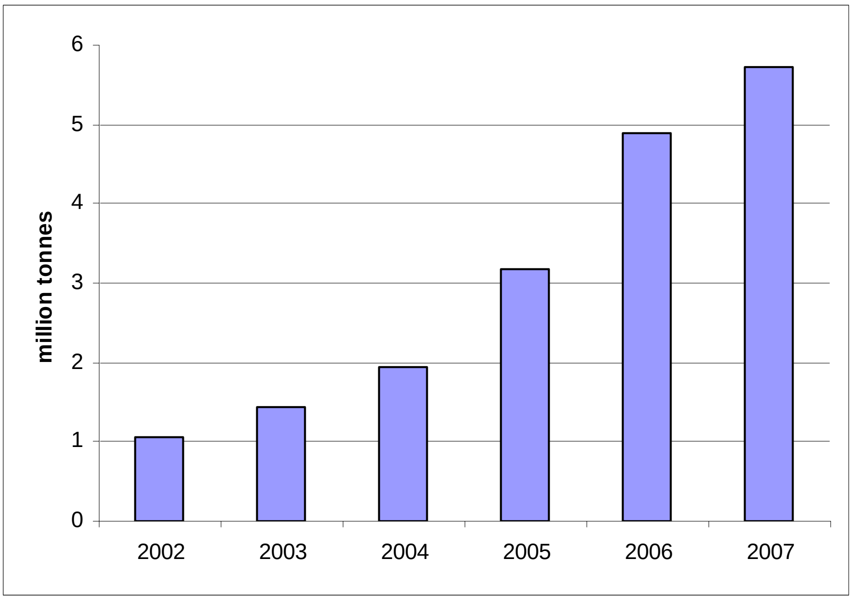


Figure 1. The total production of biodiesel in the EU countries from 2002 to 2007 (European Biodiesel Board 2008).

1.1 Background of the work

The development of the biodiesel technology is one of Neste Oil's ventures. Nest Jacobs as an engineering office mainly owned by Neste Oil takes part of this research and development work. This master's thesis gives its contribution to Neste Oil's NExBTL renewable diesel- research program. Expanding the basis of raw materials gives rise to the fact that the behaviour of these new substances has to be known in normal as well as in abnormal process conditions. In NExBTL-process thermal degradation may take place in a situation, where raw material is at high temperature and hydrogen is not present. These kinds of conditions may exist during hydrogen feed cut or in a leakage of hot raw material. This master's thesis is decided to carry out to study this thermal degradation of the new raw materials. In addition, it is known that one thermal degradation product can be acrolein that is highly flammable, very toxic and dangerous to the environment (Tuotevalvontakeskus 2003). Because of this its behaviour and diffusion in the environment is important to determine. Also other harmful substances can be formed, and it would be good to identify them and understand their behaviour as well.

1.2 Objectives of the work

The objective of this work is to gain more understanding about thermal degradation of plant oils and animal fats and their degradation products and give additional value for the research of thermal degradation in this context. One aim is also to identify the hazardous degradation products which will be the focus substances of this study. More information about them is needed, as their formation is possible in the NExBTL-process if hydrogen is not present or a leakage to the atmosphere occurs. This study also aims to reduce the number of questions related to thermal degradation of the new raw materials, and guide potential further research. Furthermore, this study targets to evaluate the hazards caused by the thermal degradation products of plant oils and animal fats through the hazardousness of the gaseous degradation products. In order to increase the understanding, a comprehensive literature survey is carried out and thermal degradation experiments with three different plant oil and animal fat based oils were carried out.

1.3 Implementation of the work

This study examines plant oils and animal fats and especially their thermal degradation. According to this, chapter 2 presents most common plant oils and animal fats used as raw materials for the production of biofuels, so that the reader is familiar to them before further study in later chapters. In addition, chapter 2 also clarifies the differences between the fossil mineral based oils and plant oils and animal fats.

Chapter 3 is a crucial part of the theory of the study. It focuses on the reaction mechanisms and degradation products of thermal degradation of triglycerides that are the main constituents in the new raw materials. Degradation mechanisms for saturated and unsaturated triglycerides are examined and examples of the pyrolysis of certain triglycerides are presented. Also formation of acrolein and other aliphatic aldehydes in cooking oil heating is examined. At the end of chapter 3 a summary of the degradation products is presented. The information gained in chapter 3 is used to identify the hazardous degradation products that are presented in chapter 4.

Chapters 5 and 6 are the empirical part of this master's thesis. Chapter 5 discusses the thermal degradation experiments carried out with three different oils. The chapter is very thorough giving full information about the experimental conditions and analyses. Also errors and differences in the gas analysis results, calculations and mass balances of the experiments are discussed. Chapter 6 discusses the results of the experiments, the formation of hazardous thermal degradation products and especially acrolein formation. In the end in chapter 6.3 further study subjects are presented. The conclusions made on the basis of this thesis and its contents are presented in chapter 7, and finally chapter 8 presents the summary of this study.

2 PLANT OILS AND ANIMAL FATS USED IN THE PRODUCTION OF NExBTL RENEWABLE DIESEL

Plant oils and animal fats are consisting mostly of triglycerides which are esters of glycerol, where three fatty acids are attached to glycerol molecule. Usually all the fatty acids are not the same ones, but two or even three different kinds of fatty acids are attached to glycerol. Plant oils contain usually also some free fatty acids because of the enzymatic decomposition. The use of triglycerides in both food and biodiesel production is based on modifying carboxyl groups and unsaturated groups which means the double bonds between the carbon atoms. Figure 2 presents the structure of a triglyceride, where the glycerol skeleton on the left is attached by three fatty acids with different lengths of carbon chains. The most common fatty acids are C_{16} and C_{18}, and over 1000 acids are known. Still only about 20 of these are found in commercially exploited plant oils and animal fats, the length of carbon chains in fatty acids ranging between C_{16} and C_{22}. The most common fatty acid in plant oils is C_{18} while animal fats have several common fatty acids. (Scrimgeour 2005, 1, 4 and 5; Wittcoff et al. 2004, 411 and 415)

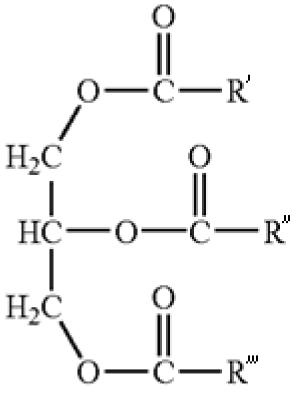


Figure 2. Atomic formula of a triglyceride. R’, R’’ and R’’’ describe different fatty acids (modified from Li 2008, 1).

2.1 Plant oils

Plant oils consist mostly of triglycerides, but they also contain small amounts of free fatty acids. In addition, they contain some monoglycerides, diglycerides and variable amounts of phospholipids, triterpene alcohols, carotenes, esterified sterols, chlorophylls and other colouring matters and even trace amounts of metals, to mention just a few. To get rid of undesirable compounds, plant oils are refined to gain the wanted composition. Some of the unwanted compounds can be very desirable in their own right and they are separated and used elsewhere. (Gunstone 2005, 217)

World's plant oil production is mostly dependent on four major oil sources which are soybean, palm, rapeseed and sunflower (Gunstone 2005, 259). The production of fats and oils in total in 2007 was approximately 154 million tons, of which about 84,3 % was plant oils and the rest was animal fats. This means that in 2007 the total production of plant oils was about 130 million tonnes. Figure 3 presents the distribution of world's total plant oil production. It shows that palm oil and soybean oil were produced the most, the shares being 31 and 29 %, respectively. Rapeseed oil and sunflower oil production became next, their productions being 15 and 8 %, respectively. Others that denote 14 % of the production include such as coconut, cotton seed, olive, sesame, corn and peanut oils. In addition, palm kernel constituted 3 % of the total production. (Oil World 2008)

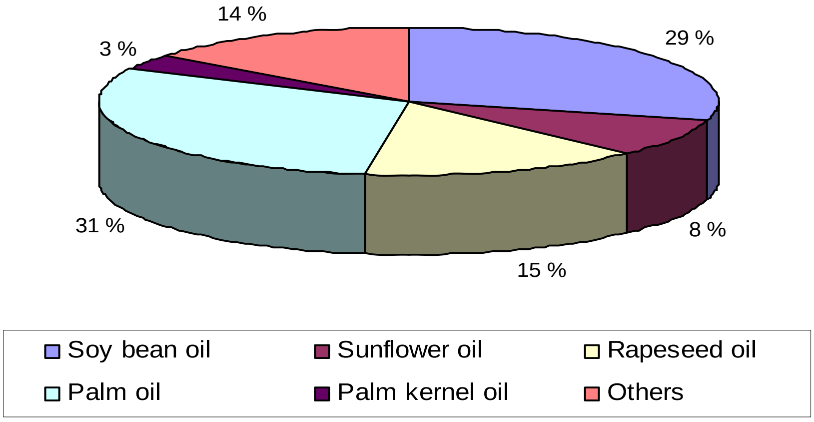


Figure 3. The distribution of world's plant oil production (Oil World 2008).

2.1.1 Soy bean oil

Soy bean is mainly grown in the United States, Brazil, Argentina and China (Gunstone 2005, 231). Soy bean is not grown just for the oil, but principally because of its high content of protein that is much lower in other oil crop species. Like other plant oils, soy bean oil contains primarily triglycerides about 94,4 %, but the fatty acid composition changes with maturity and deposition of the oil: palmitic and linolenic acids usually decrease with maturity, while linoleic acid content increases. Efforts are being made to enhance the usefulness of soy bean by modifying the fatty acid composition towards more wanted compositions. (Hammond et al. 2005, 577)

2.1.2 Palm oil

Oil palm produces two kinds of oils: palm oil that is obtained from the fruit flesh, and palm kernel oil that is gained from the kernel of the fruit. They possess different chemical compositions and hence different physical properties and they have different markets accordingly their own supply and demand. Oil palm is grown in tropical regions in Asia, Africa and America. Majority of the oil palms are grown in Malaysia and Indonesia. Most of the countries grow oil palms to satisfy their own oil demand, but Malaysia and somewhat Indonesia are exceptions in this and produce palm oil for export. (Basiron 2005, 334; Gunstone 2005, 228)

Oil palm produces more oil per hectare than any other oil crop: on average, oil palm can produce 4 tonnes of palm oil and palm kernel oil combined per hectare, while even the records of other crops such as soybean and rapeseed have lower oil yields, being 2 tonnes and 3 tonnes per hectare, respectively. Records of sunflower and coconut oil production per hectare are about the same as the average yield of palm oil. (Basiron 2005, 352; Gunstone 2005, 228) Neste Oil’s main raw material to produce NExBTL renewable diesel is palm oil because at the moment it is the cheapest plant oil available.

About 50 % of the fatty acids present in triglycerides of palm oil are unsaturated and another half is saturated. Palm oil contains also minor components such as carotenoids, tocopherols, sterols and phosphatides, some of which increase the nutritional value of palm oil: carotenoids are mainly α- and β-carotenes which are precursors of vitamin A. The properties of palm oil are being developed with lower palm height, higher oil yields, with more unsaturated oil and a higher share of kernel (Gunstone 2005, 228; Basiron 2005, 339-340)

2.1.3 Rapeseed oil

Figure 3 shows that rapeseed oil production is the third biggest in the world. Natural rapeseed oil contains substantial amounts of erucic acid and glucosinolates which are a health concern. Because of this, rapeseed line containing low levels of erucic acid was developed by backcrossing and selection in Canada. This kind of rapeseed is called canola and it can be safely used in food production, though it is more commonly called as rapeseed in Europe. (Przybylski et al. 2005, 61-62) In this study the term ′rapeseed' is used for all kinds of rapeseed lines.

Rapeseed is principally grown in Western Europe, China, Canada and India. It contains the largest share of unsaturated fatty acids than any other oil crop. Fatty acid composition is also modified by genetic modification, though it is unclear whether all these varieties will be of economic value. Rapeseed oil contains triglycerides from 91,8 to 99,0 %. It also contains minor amounts of tocopherols, chlorophylls, unsaponifiables and fatty acids. Additionally, rapeseed contains also minor quantities of sulphur and is thus the only edible oil known to have sulphur-containing fatty acids. (Gunstone 2005, 229; Przybylski et al. 2005, 63 and 65)

2.1.4 Sunflower oil

Sunflower oil production comes after rapeseed oil production according to figure 3, having 8 % of the world’s total plant oil production. Sunflower grows in moderate climates, and is mainly grown in the areas of former Soviet Union, Argentina, Western and Eastern Europe, the United States and China. Especially Argentina has ideal climate conditions for cultivating sunflower because of different influences of the Atlantic Ocean. (Gunstone 2005, 231; Grompone 2005, 658-659)

Sunflower oil contains 98 to 99 % triglycerides. The rest is phospholipids, sterols, tocopherols and waxes. Fatty acids present in triglycerides of regular sunflower oil are mostly unsaturated, and no more than 15 % are saturated. There are two kinds of sunflower types grown: oilseed and non oil type, the latter of which is grown for the purposes of bird meal and confectionary products. Oilseed type has an oil content of 40 % and non oil type contains 30 % of oil, and oil content of seeds gets lower in the areas of extreme heat. Ambient factors, like temperature and light have an influence on the oil consistency and fatty acid composition of sunflower seeds. (Grompone 2005, 658-659 and 662-664)

2.1.5 Jatropha oil

The traditional plant oils used as raw materials for biodiesel are also food products, so their production for fuel competes with the food production. Because of this it is worth finding oil crops that are inedible and can produce oil for the biodiesel production. One of these kinds of crop is jatropha that is a shrub or a tree and is toxic to humans and animals. It is cultivated in Central and South America, South East Asia, India and Africa. Inedible jatropha has another good quality: it resists drought well and grows in arid conditions and places where other crops can not cope. This is why it is also used for erosion control. (Gübitz et al. 1998, 73) Especially from the jatropha species *Jatropha curcas* is very suitable for oil production, because the oil content of its seeds is the highest (Banerji et al. 1985, 278).

2.2 Animal fats

Major animal fats are produced from pigs, cattle, and sheep and from poultry, and they are usually solid at room temperature (24°C). Fats in animals are situated mostly under skin and coating superficial muscles, but also as intermuscular fat between muscles. Fat sites vary to some extent between species, breed and also degree of finish. (Haas 2005, 161-162) In 2007 the world's production of animal fats was about 24 million tonnes (Oil World 2008). Figure 4 shows the distribution of animal fats produced.

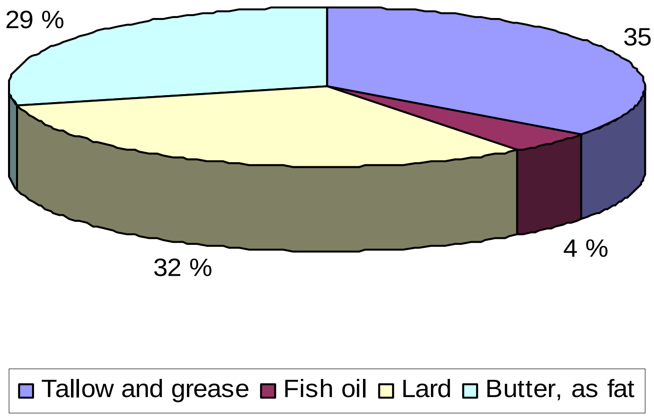


Figure 4. The distribution of animal fats production in the world in 2007 (Oil World 2008).

Animal fats consist mostly of triglycerides, but differ from plant oils in that minor amounts constitute less than 0,05 %. Minor compounds among others include phospholipids, carotenoids and tocopherols. Fatty acid composition of triglycerides depends on the species, but also on the diet, sex of the animal and on genetic background. Diet has more influence than sex or genes, and with a certain diet fatty acid composition can be somewhat modified. Most common fatty acids are those of 16 or 18 carbons and they are fully saturated or contain one or two double bonds. In general, animal fats have more saturated fatty acids than plant oils. (Haas 2005, 162-168)

2.3 Comparison of the characteristics of plant oils and animal fats

Table 1 shows some relevant characteristics of the four major plant oils and tallow for the comparison. The properties seem to be quite close to each other; only the values of kinematic viscosity of plant oils are slightly different. High viscosity is due to large molecular weights: plant oils have a molecular mass from 600 to 900 that are at least three times higher than that of diesel fuels (Srivastava & Prasad 2000, 116).

Table 1. Some characteristics of tallow and the most produced plant oils in the world (Haas 2005, 175; Srivastava & Prasad 2000, 118).

	Soy bean oil	**Palm oil**	**Rapeseed oil**	**Sunflower oil**	**Tallow**
Density [kg/l]	0,9138	0,9180	0,9115	0,9161	0,893-0,904*
Kinematic viscosity at 38°C [mm^2/s]	32,6	39,6	37,0	33,9	Not available
Heating value [MJ/kg]	39,6	Not available	39,7	39,6	40,0
Flash point [°C]	254	267	246	274	201

*) For edible tallow, relative density at 40°C/water at 20°C

Table 1 also shows that the flash point of tallow is considerably lower than those of plant oils. Also density is lower, but it is determined in a different manner so it may not be comparable with plant oil densities. In contrast, the heating value for the tallow is slightly higher than corresponding figures for plant oils.

2.4 The differences between renewable and mineral based oils

Both renewable and mineral oils are raw materials of diesel fuels. Depending on the origin of the raw material another fuel is called biodiesel and another simply diesel. A big distinction between the two raw materials is in their compositions: crude oil is composed of hydrocarbons such as alkanes, cycloparaffins and aromatic compounds, non-hydrocarbons and organometallic and metallic compounds (Matar & Hatch 2001, 12), and as stated already plant oils and animal fats are mainly triglycerides that contain glycerol and different fatty acids. In crude oil alkenes and alkynes are absent, which perhaps indicates that crude oil has originated under reducing conditions (Matar & Hatch 2001, 12), whereas double bonds are present in triglycerides depending on the fatty acids they contain (Scrimgeour 2005, 2). In addition, crude oil contains sulphur compounds, while in plant oils and animal fats the amounts of sulphur are negligible. Thus by using biodiesel, the environmental damages caused by sulphuric acid is decreased. (Crabbe et al. 2001, 66) Furthermore, plant oils and animal fats as raw materials are renewable, and the combustion of generally called biodiesel releases less carbon dioxide emissions (Srivastava & Prasad 2000, 115-116).

3 THERMAL DEGRADATION OF PLANT OILS AND ANIMAL FATS

When talking about thermal degradation of plant oils and animal fats, usually thermal degradation of triglycerides is meant. In this study thermal degradation, also called pyrolysis, is considered as an adverse transaction. Pyrolysis phenomenon produces breakdown components and formation of hazardous substances is also possible. It is important to know pyrolysis mechanisms, products and behaviour of thermal degradation in different conditions. Pyrolysis is also one way to produce biodiesel (Srivastava & Prasad 2000, 119). Neste Oil uses hydro treatment process to produce NExBTL renewable diesel which consists of hydrocarbons. The most common way to produce biodiesel is through transesterification, where the product is methyl ester that contains oxygen (Srivastava & Prasad 2000, 122).

Thermal decomposition of triglycerides is likely very complex, because there are numerous mixed triglycerides (glycerols attached by three different fatty acids) which may react by different reaction paths and form different compounds (Srivastava & Prasad 2000, 120). Also as a result of studies been done, there are many factors that influence on the degradation products and their yields and these are as follows: characteristics of oil, reaction temperature and the nature of catalyst if used (Dandik et al. 1998, 1149 and 1151). Additionally, residence time and by this the pyrolysis column height had an effect on the pyrolysis products formed (Idem et al. 1996, 1158). In the study of Dandik et al. (1998, 1151), increasing reaction temperature and the amount of catalyst increased the conversion of oil in pyrolysis of used sunflower oil into pyrolysis products. Similar results have also reported Idem et al. (1996, 1157). In contrast, when the column height increased, conversion of used sunflower oil into degradation products decreased (Dandik et al. 1998, 1151).

These factors having an effect on pyrolysis suggest that by adjusting the reactor conditions that may cause pyrolysis of triglycerides inside a reactor, have an important effect on what kind of degradation products happen to form and in which ratio. In the case of this study adjusting the conditions could mean abnormal conditions which might enable pyrolysis. Especially the degradation products of following cases are of interest:

- leakage in the hydro treatment reactor
- loss of the hydrogen feed into the reactor.

3.1 Thermal degradation reaction mechanisms of triglycerides

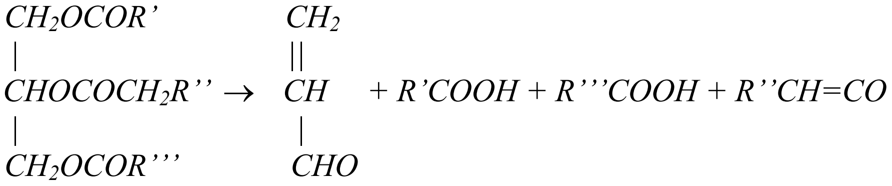
This chapter presents the reaction mechanisms of thermal cracking of plant oils found in the literature. The mechanisms presented first propose only the degradation of saturated or unsaturated triglycerides, and the last one proposes a mechanism for both in the form of thermal cracking of rapeseed oil.

3.1.1 Reaction mechanisms for saturated triglycerides by Chang & Wan

Chang & Wan (1947) are the first researchers to have reported proposed reaction mechanisms for the pyrolysis of saturated triglycerides. They carried out thermal cracking of the soap of tung oil to yield a crude oil that was then refined to produce diesel fuel, gasoline and kerosene; 50 litres of crude oil could be obtained from 68 kilograms of soap (Ma & Hanna 1999, 5). No precise information about the experimental conditions such as temperature or pressure was reported. Also the information about what kind of atmosphere prevailed in the reactor where the experiments were carried out was absent.

Because the information about experiments is not available in the article, there is a reason to believe, that the mechanism Chang & Wan (1947) developed is based on earlier studies and not their own experiments with tung oil. The suggested reaction scheme includes 16 types of reactions which are shown below. Chang & Wan (1947) stated that majority of the acids, acrolein and ketenes that were formed in the decomposition of a triglyceride (reaction equation (1)), were rapidly degraded according to equations (2)-(7). Moreover, they stated that equations (10), (16) and (17) were probably major reactions responsible for the formation of hydrocarbons that constitute liquid fuels, specially the gasoline fraction. (Maher & Bressler 2007, 2357)

1. Decomposition of the triglyceride



$$\begin{array}{lcl} CH_2OCOR' & & CH_2 \\ | & & \| \\ CHOCOCH_2R'' & \rightarrow & CH \quad + R'COOH + R'''COOH + R''CH{=}CO \\ | & & | \\ CH_2OCOR''' & & CHO \end{array} \tag{1}$$

The R’, R’’ and R’’’ are radicals which are hydrocarbon chains of different fatty acids (Chang & Wan 1947, 1545). The R in the equations below represents a hydrocarbon chain of any length.

2. Decomposition of fatty acids

$$RCOOH \rightarrow CO_2 + RH \tag{2}$$

$$2RCOOH \rightarrow CO_2 + H_2O + RCOR \tag{3}$$

3. Decomposition of ketenes and acrolein

$$2R''CH{=}CO \rightarrow 2CO + RHC{=}CHR \tag{4}$$

$$CH_2{=}CHCHO \rightarrow CO + C_2H_4 \tag{5}$$

$$RCOCH_2R \rightarrow R - R + CH_2CO \tag{6}$$

$$2RCOCH_2R \rightarrow 2R_2 + CO + C_2H_4 \tag{7}$$

4. Decomposition into elements

$$C_nH_{2n+2} \rightarrow nC + (n+1)H_2 \tag{8}$$

5. Dehydrogenation of paraffins

$$C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2 \tag{9}$$

6. Splitting decomposition of paraffins

$$C_nH_{2n+2} \rightarrow C_{n-m}H_{2n-2m+2} + C_mH_{2m} \tag{10}$$

7. Alkylation of paraffins, the reverse of reaction (6)

$$C_{n-m}H_{2n-2m+2} + C_mH_{2m} \rightarrow C_nH_{2n+2} \tag{11}$$

8. Isomerization of paraffins

$$n - C_nH_{2n+2} \rightarrow iso - C_nH_{2n+2} \tag{12}$$

9. Aromatic cyclization of paraffins

$$C_{(2n+6)}H_{(2n+14)} \rightarrow C_nH_{2n+1} + 4H_2 \tag{13}$$

10. Polymerization of olefins

$$2C_nH_{2n} \rightarrow C_{2n}H_{4n} \tag{14}$$

$$C_nH_{2n} + C_mH_{2m} \rightarrow C_{(n+m)}H_{2(n+m)} \tag{15}$$

11. Depolymerization of olefins, reverse of reactions (14) and (15)

$$C_{2n}H_{4n} \rightarrow 2C_nH_{2n} \tag{16}$$

$$C_{(n+m)}H_{2(n+m)} \rightarrow C_nH_{2n} \tag{17}$$

12. Decomposition of olefins to diolefins
13. Decomposition of olefins to acetylenic hydrocarbons
14. Aromatization or cyclization of olefins

15. Hydrogenation of olefins

$$C_nH_{2n} + H_2 \rightarrow C_nH_{2n+2} \tag{18}$$

16. Isomerization of olefins

$$n - C_nH_{2n} \rightarrow iso - C_nH_{2n} \tag{19}$$

The equation (1) being the basis of the mechanism proposed by Chang & Wan (1947) is in itself very concise and does not tell anything about the mechanism how a triglyceride degrades in to two carboxylic acids, acrolein and a ketene. This degradation can be explained by pyrolytic elimination of esters that are formed when fatty acids attach to the glycerol to form a triglyceride. Pyrolytic elimination is believed to take place in a temperature range of 300-500°C by a mechanism that involves a six-centre transition state (Streitwieser & Heathcock 1981, 564) that is presented in figure 5.

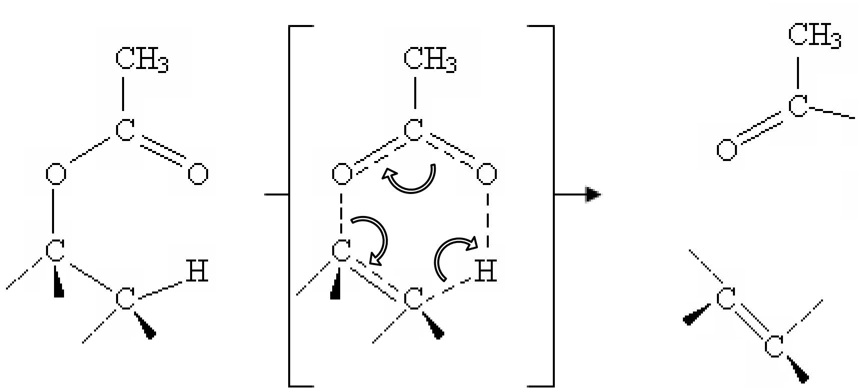


Figure 5. Pyrolytic elimination of carboxylic ester into carboxylic acid and an alkene (Streitwieser & Heathcock 1981, 564).

With the help of the six-centre transition, new bonds are formed, and carboxylic ester degrades into a carboxylic acid and an alkene (Streitwieser & Heathcock 1981, 564). The mechanism is applicable to triglycerides that have three carboxylic esters, the two of which form carboxylic acids in the pyrolysis, and one ester is degraded in to a ketene. The glycerol skeleton forms the alkene which in the case of a triglyceride is acrolein.

3.1.2 Reaction mechanism for saturated triglycerides by Alencar et al.

Alencar et al. (1983) proposed a reaction mechanism based on their experiment of pyrolysis with tropical plant oils. They performed pyrolysis of piqui (*Caryocar coriaceum*), babassu (*Orbignya martiana*) and palm (*Elaeis guineensis*) oils at 300-500°C in an atmospheric pressure in a Pyrex apparatus. No information about the atmosphere, where the experiments were conducted, was reported. Thermal cracking was carried out without a catalyst, because former studies have shown that pyrolysis products are very dependent on the catalyst and in this way the impact of catalytic action could be excluded. (Alencar et al. 1983, 1268)

Major products formed were *n*-alkanes and 1-alkenes. Differences occurred if plant oil contained unsaturated fatty acids: when a triglyceride contained an unsaturated fatty acid, principally oleic acid, this was likely to produce more volatile molecules than a triglyceride with saturated fatty acids. In addition to *n*-alkanes and 1-alkenes, triglyceride having oleic acid as the major fatty acid, formed small amounts of cycloparaffins and cyclo-olefins. Alencar et al. (1983) concluded this to be related to the double bond between the carbon atoms 9 and 10 in oleic acid. There was also an association between the prevailing saturated fatty acid present in the original oil and the major saturated hydrocarbon produced in the pyrolysis, as the hydrocarbon was generated by decarboxylation of the major saturated fatty acid. (Alencar et al. 1983, 1269)

Because there were no oxygenated compounds in the volatiles detected, this indicated that the elimination of carbon dioxide (CO_2) and ketene (CH_2=CO) were prevailing steps in thermal cracking reactions of triglycerides and their fatty acids. This seemed to be the case at least when no catalyst was used. On the basis of gained results, Alencar et al. (1983) composed a scheme that shows some likely paths of decomposition of saturated triglycerides. The scheme is founded on the mechanisms of pyrolysis originally suggested by Chang & Wan (1947) and Greensfelder et al. (1949). (Alencar et al. 1983, 1269) The scheme is presented in figure 6.

According to the scheme, the cracking of a triglyceride generates free radicals (A) and (B) (Maher & Bressler 2007, 2357). Pathway (A) happens when one of the ester bonds in a triglyceride is thermally cracked so that both oxygen atoms come along with the fatty acid chain R’ to form a radical as shown in figure 7. Pathway (B) happens when one of the ester bonds is cracked so that only the oxygen atom next to R’ comes along with fatty acid chain to form a radical that reacts further. This radical formation can happen to all three fatty acid esters in the glycerol skeleton.

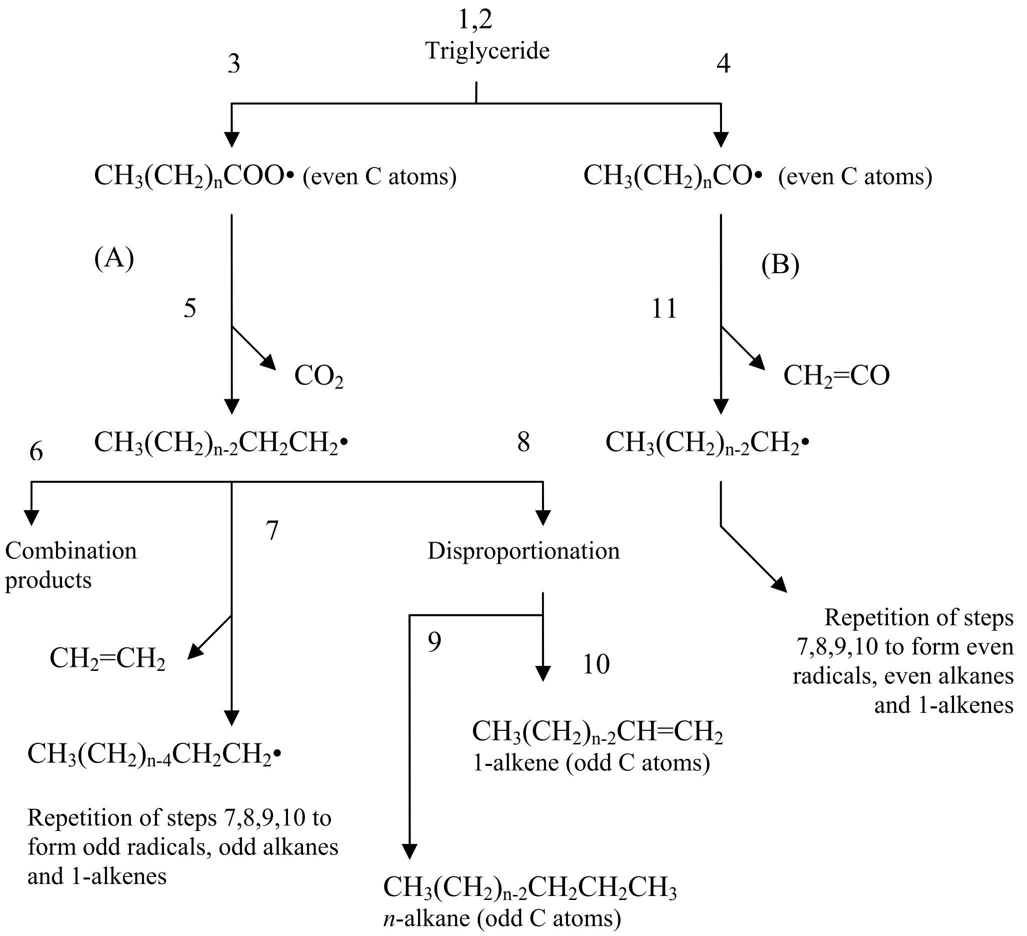


Figure 6. Probable reaction mechanism for the thermal cracking of saturated triglycerides (Alencar et al. 1983, 1269).

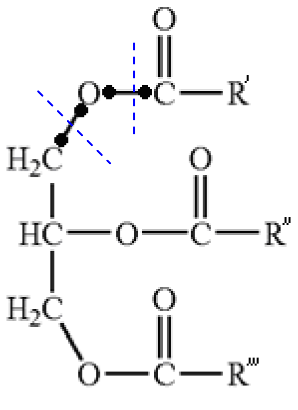


Figure 7. The cracking of an ester into radicals (A) and (B).

The odd *n*-alkanes and 1-alkenes are generated by decarboxylation of radical (A), followed by disproportionation and ethylene elimination. The even *n*-alkanes and 1-alkenes are formed by the loss of a ketene from radical (B), again followed by disproportionation and ethylene elimination. (Maher & Bressler 2007, 2357) In the scheme Alencar et al. (1983) presents the thermal degradation mechanism for the fatty acid chains but does not discuss the decomposition mechanism of the glycerol skeleton.

3.1.3 Reaction mechanisms for unsaturated triglycerides

The next researchers to report about the reaction mechanisms for the pyrolysis of triglycerides were Schwab et al. (1988). The pyrolysis of soybean and safflower (high in oleic acid) oil by subsequent distillation were conducted in air and also in a nitrogen spray. Interestingly, no information about the pyrolysis temperature or pressure was mentioned. Compounds from classes of alkanes, alkenes, alkadienes, aromatic compounds and carboxylic acids were detected as pyrolysis products. Schwab et al. (1988) reported that only small distinctions in composition were noted for the pyrolysis in air and in nitrogen, and larger differences were noted between soy bean and safflower oil. (Schwab et al. 1988, 1781) Table 2 shows the distribution of thermal degradation product oils of safflower and soy bean oils.

Table 2. Product distribution of pyrolysis oils of safflower and soy bean oils (Schwab et al. 1988, 1784).

	[% by weight]			
	High oleic safflower		**Soy bean**	
Product	**N_2 spray**	**Air**	**N_2 spray**	**Air**
Alkanes	37,5	40,9	31,3	29,9
Alkenes	22,2	22	28,3	24,9
Alkadienes	8,1	13	9,4	10,9
Aromatics	2,3	2,2	2,3	1,9
Unresolved unsaturates	9,7	10,1	5,5	5,1
Carboxylic acids	11,5	16,1	12,2	9,6
Unidentified	8,7	12,7	10,9	12,6

In order to explain the classes of compounds found, Schwab et al. (1988) presented a scheme of reaction mechanisms for the pyrolysis of unsaturated triglycerides which is showed in figure 8. It is based on the mechanisms proposed by Alencar et al. (1983) which was originally suggested by Chang & Wan (1947).

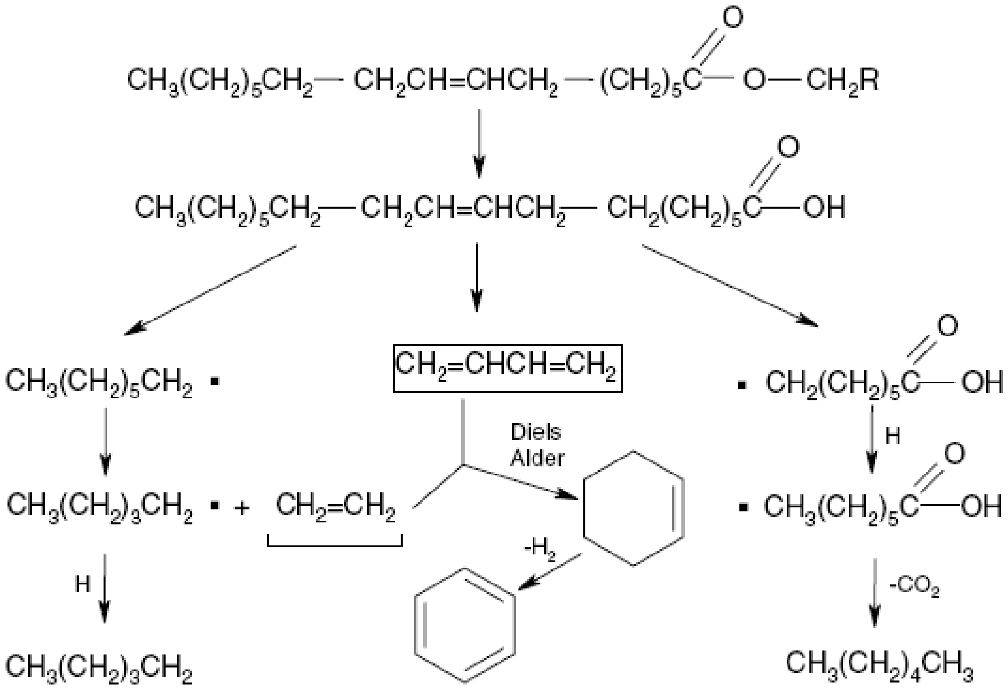


Figure 8. Reaction mechanisms for the thermal decomposition of triglycerides. The source material to be decomposed in the picture is one fatty acid ester and the R may represent for example a diglyceride (Schwab et al. 1988, 1784).

According to the mechanism it is generally believed, that thermal degradation of structures of triglycerides proceeds by either carbonium or a free radical mechanism. The formation of aromatic compounds is supported by Diels-Alder addition where ethylene unites with a conjugated diene formed in the thermal cracking reaction. (Schwab et al. 1988, 1784-1785) Carboxylic acids formed in the pyrolysis, in stead, are probably formed through cleavage of the glyceride moiety (Nawar 1969, 20). While Alencar et al. (1983) concentrated on the degradation mechanism of ester bonds the mechanism of Schwab et al. (1988) focuses on the cracking of double bonds in the fatty acid chains.

3.1.4 Reaction mechanisms for saturated and unsaturated triglycerides

The reaction mechanisms presented above have been concerning only the pyrolysis of either saturated or unsaturated triglycerides. Idem et al. (1996) examined the thermal cracking of triglycerides of rapeseed oil in an atmospheric pressure in a presence and absence of steam in temperatures between 300-500°C. No information about the atmosphere where the experiments were carried out was reported. On the basis of products formed, they suggested a reaction scheme for the pyrolysis of rapeseed oil which contains both saturated and unsaturated triglycerides. In addition, the experiments were carried out in a continuous flow reactor unlike the previous pyrolysis experiments of other researchers, which had been carried out in batch reactors. (Idem et al. 1996, 1150-1151)

Rapeseed oil conversion to pyrolysis products turned out to be high, from 54 to 100 %, and conversion was very dependent on the operating variables such as reaction temperature and residence time. In the thermal cracking, five different fractions were detected: gas, organic liquid product, coke, residual oil and unaccounted fraction. (Idem et al. 1996, 1150-1152) Table 3 shows the formed fractions and their portions in the products as a function of cracking temperature.

Table 3. Product fractions as a function of cracking temperature*. The figures correspond overall mass balance as weight % of rapeseed oil fed. (Idem et al. 1996, 1153)

	Temperature [°C]				
Product fraction [wt % of rapeseed oil fed]	**500**	**450**	**400**	**370**	**300**
gas	75	71	55,8	38	15
organic liquid product, OLP	14,8	17,2	34,4	45,9	38,1
coke	3,9	3,9	3,9	3,9	0
residual oil	0	1,2	1,6	6,1	41,9
unaccounted fraction	6,3	6	4,3	6,1	5
total	100	100	100	100	100
rapeseed oil conversion [%]	100	98,8	98,4	93,9	58,1

*) runs conducted at gas hourly space velocity of 3,3 h^{-1}

The chemical groups found in the fractions were as follows: hydrocarbon gases, olefins, alcohols, ketones, aldehydes, aliphatic hydrocarbons containing six or more carbon atoms, benzene, toluene, xylenes, ethylbenzene, aromatic hydrocarbons containing nine or more carbon atoms, total aromatic hydrocarbons and residual oil. There were also some compounds that could not be identified. (Idem et al. 1996, 1152) Tables 4 and 5 show the compositions of gas and organic liquid product fractions as a function of pyrolysis temperature.

Table 4. Composition of gas fraction as a function of temperature as weight % of gas* (Idem et al. 1996, 1154).

	Temperature [°C]				
Product [wt-% of gas]	**500**	**450**	**400**	**370**	**300**
methane	14,2	13,9	12,7	10,7	9,6
ethylene	31,4	31,1	30,5	28,3	27
ethane	9,3	9,4	9,7	10,7	11,5
propylene	18	18,2	18,5	18,4	18,3
propane	1,4	1,5	1,7	2,7	3,6
isobutane	0,02	0,02	0,02	0,02	0,03
n-butane	8,7	8,9	9,8	10,7	10,8
isobutylene	1,3	1,4	1,4	1,6	1,8
1-butene	0,7	0,8	0,7	0,6	0,7
C_xH_y gases, $x>5$	0,7	0,8	0,7	0,6	0,7
dimethyl ether	0,1	0,1	0,1	0,1	0,1
$CO+CO_2$	5	5,2	5,2	5,3	5,3
hydrogen	2,1	1,8	1,6	1,2	0,6
total	100	100	100	100	100

*) runs conducted at gas hourly space velocity of 3,3 h^{-1}

Table 5. Composition of organic liquid product fraction as a function of temperature as weight % of OLP* (Idem et al. 1996, 1154).

	Temperature [°C]				
Product [wt-% of OLP]	**500**	**450**	**400**	**370**	**300**
alcohols	5,9	5,6	3,5	4,2	5
acetone	0,5	0,2	0	0,4	3,8
ketones	0	0	0	0,3	0,1
benzene	27	23,3	14,7	10	6,5
toluene	18,6	16,2	11,3	7,6	4,3
xylenes	4,1	3,8	3,4	2,7	1,4
ethylbenzene	2,8	2,7	2,2	2	1,1
C_9^+ aromatics	8	8	7,9	7,4	7,1
aliphatics	4,2	4,8	4,3	4,2	2,6
unidentified	29,1	34,4	52,7	61,2	67,8
total	100	100	100	100	100
total aromatics	60,5	54,7	36,5	29,7	20,4

*) runs conducted at gas hourly space velocity of 3,3 h^{-1}

The reaction scheme for the thermal cracking of rapeseed oil suggested by Idem et al. (1996) is presented in figure 9. It is more complex than the mechanisms proposed previously, but is still based on them (Maher & Bressler 2007, 2358), which are presented in chapters 3.1.1 and 3.1.2.

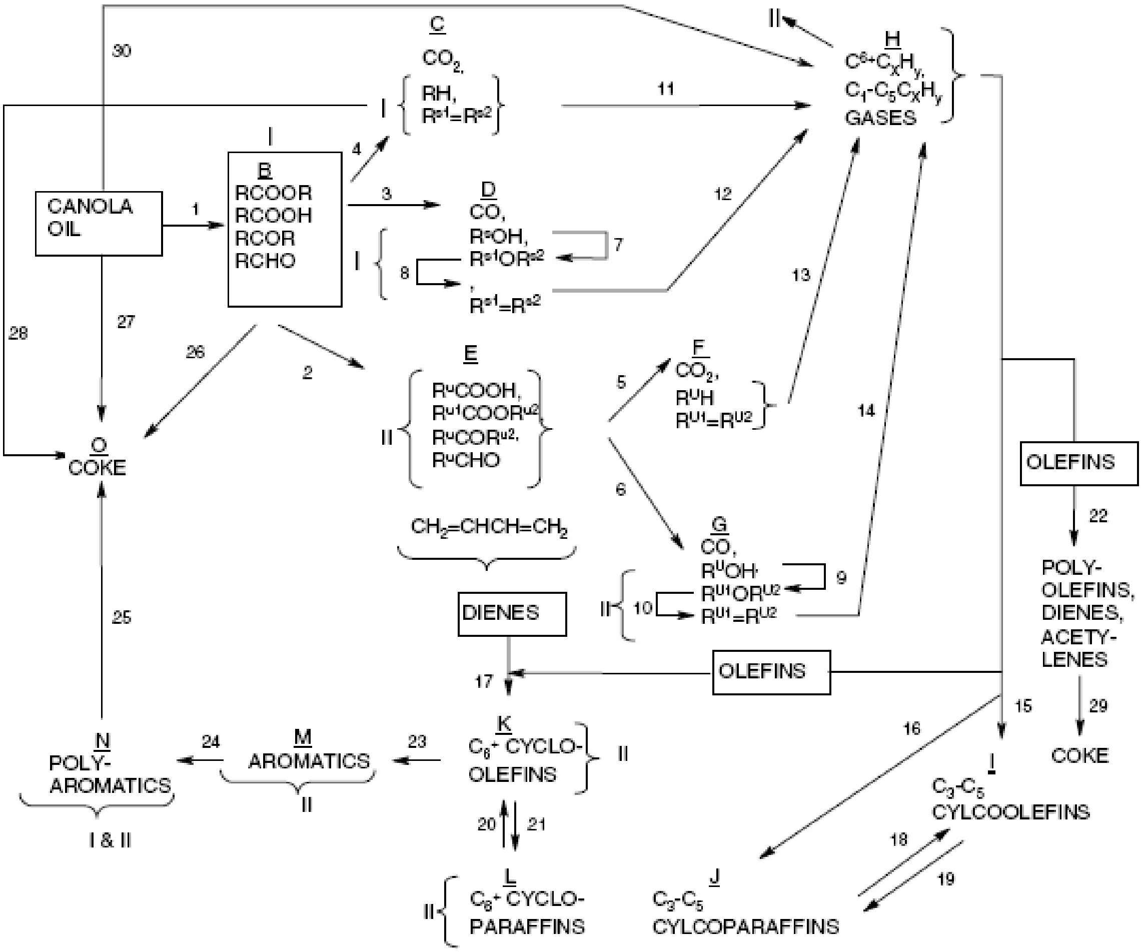
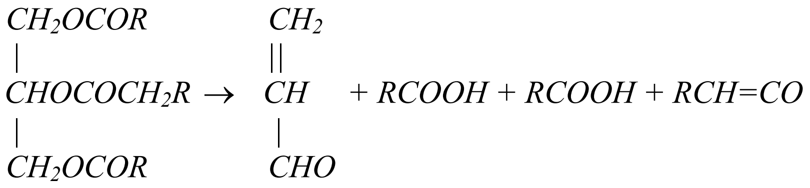


Figure 9. Reaction scheme for the pyrolysis of rapeseed oil containing saturated and unsaturated triglycerides (Idem et al. 1996, 1155).

Idem et al. (1996) refer long-chain fatty acids, ketones, aldehydes and esters as heavy oxygenated compounds. These products are the result of initial decomposition of a triglyceride molecule of rapeseed oil, and the reactions related to it are as follows (Idem et al. 1996, 1154):



$$\begin{array}{lll} CH_2OCOR & CH_2 & \\ | & \| & \\ CHOCOCH_2R \rightarrow & CH & + RCOOH + RCOOH + RCH{=}CO \\ | & | & \\ CH_2OCOR & CHO & \end{array} \qquad (20)$$

Rapeseed oil

$$2RCOOH \rightarrow CO_2 + H_2O + RCOR' \qquad (21)$$

$$RCOOH \rightarrow CO + RCHO \qquad (22)$$

$$RCOOH \rightarrow CO_2 + RH \qquad (2)$$

$$2RCOOH \rightarrow CO_2 + H_2O + RCOR \qquad (3)$$

The R is a hydrocarbon chain of any fatty acid present in rapeseed oil, and R’ is a different hydrocarbon chain. The most common fatty acids in rapeseed oil are oleic acid, linoleic acid and linolenic acid, which are all carboxylic acids with chain length of 18 carbon atoms (Srivastava & Prasad 2000, 117). Reaction (21) is the same as reaction (3), but reactions (22) and (2) differ from each other in that carboxylic acid degrades into carbon monoxide and aldehyde in reaction (22), when in reaction (2) carboxylic acid degrades into carbon dioxide and hydrocarbon. However, the equations that Idem et al. (1996) have suggested are based on the reactions presented earlier by Chang & Wan (1947).

According to Crossley et al. (1962, 10 and 12), the initial degradation of oils into heavy oxygenated hydrocarbons of equations (1) to (3) starts at temperature range of 240-300°C. The R and R’ in ketone and ester denote that each molecule can contain nonidentical unsaturated and/or saturated hydrocarbon radicals (Idem et al. 1996, 1154).

Also carbon monoxide and carbon dioxide was detected to form in the thermal cracking of rapeseed oil, and they were the most abundant compounds to contain oxygen in the gas phase. Idem et al. (1996) refer to Chang & Wan (1947, 1545), according to whom carbon monoxide is composed by decarbonylation of oxygenated hydrocarbons of equations (1)-(3), which is presented in steps 3 and 6 in figure 9. Carbon dioxide is formed by decarboxylation of saturated fatty acids like stearic and palmitic acids (step 4 in figure 9) and unsaturated acids in step 5 in figure 9. The fact that gas phase does not contain significant amounts of other oxygenated compounds indicates that decarbonylation, decarboxylation and elimination of ketene are predominant steps in the decomposition of a triglyceride when a catalyst is not used. (Idem et al. 1996, 1154)

In addition, methanol (CH_3OH) and dimethyl ether (CH_3OCH_3) were formed as products, but only in small amounts. The presence of methanol can be explained according to step 6 of figure 9, which indicates possible decarbonylation of acetic acid (CH_3COOH) or methyl formate ester ($HCOOCH_3$) into methanol. Dimethyl ether formation can be explained mainly by bimolecular dehydration of methanol showed in step 9 of figure 9. (Idem et al. 1996, 1156)

Also aromatic hydrocarbons were formed in the pyrolysis of rapeseed oil. The emergence of aromatics can be explained by hydrogen elimination from cyclo-olefins containing more than six carbon atoms at high temperatures as presented in step 23 of figure 9. Aromatics can be formed also from linolenic acid after it has gone through decarboxylation, because linolenic acid contains three double bonds. (Idem et al. 1996, 1156)

Among others hydrogen was formed in the thermal cracking of rapeseed oil. Figure 9 shows that hydrogen is formed by proton extraction from processes like the formation of cyclo-olefins in step 17 and aromatic hydrocarbons in step 23. It can also be produced by polycondensation of rapeseed oil, splitting hydrocarbons into its elements and by polymerization of olefins and aromatic compounds in coke formation. Dehydrogenation of olefins to form diolefins and acetylenic hydrocarbons produces also hydrogen. A part of the formed hydrogen is needed to stabilize the hydrocarbon radicals, R^s and R^u, in different stages of cracking, so not all hydrogen formed ends up in the pyrolysis products. (Idem et al. 1996, 1157)

3.2 Thermal degradation - some literature examples of certain triglycerides and process conditions

As mentioned above, several degradation products can be formed from the pyrolysis of triglycerides. One reason to this is that there are so many different triglycerides that can degrade into different compounds. In this chapter, the decomposition of exact known triglycerides and their degradation compounds are examined, which narrows the amount of possible degradation products formed.

3.2.1 Pyrolysis of tricaprin and 2-oleo-dipalmitin by Crossley et al.

Crossley et al. (1962) studied the effect of heat on two triglycerides, tricaprin and 2-oleo-dipalmitin when oxygen was present and when it was absent. They noted that the breakdown of triglycerides is different whether there is oxygen present or not, and that the gross pyrolysis of fats starts approximately at 300°C when fatty acids and acrolein are formed. (Crossley et al. 1962, 9-10)

Tricaprin and 2-oleo-dipalmitin were chosen as triglycerides partly because tricaprin is a saturated triglyceride and 2-oleo-dipalmitin has oleic acid which is unsaturated, so the decomposition of these two triglycerides might be expected to be different at least to some extent. (Crossley et al. 1962, 10) Tricaprin has three capric acids attached to glycerol, and 2-oleo-dipalmitin has one oleic acid and two palmitic acids attached to glycerol. Capric acid is found only in very small amounts (0,2 % or less) in animal fats. From plant oils, coconut and palm kernel oils contain capric acid 7 and 4 %, respectively. In stead, many animal fats such as beef and mutton tallow and chicken fat contain oleic acid. Also practically all plant oils contain considerable amounts of oleic acid. A considerable amount of palmitic acid is found among others from beef and mutton tallow, lard, and palm, soybean and olive oils. (Haas 2005, 163; Gunstone 2005, 221)

When tricaprin was heated at 240-260°C in an atmosphere of nitrogen for 4,5 hours, the oil was rather stable and the only significant degradation product was capric acid. When temperature was raised to 300°C and conditions kept otherwise similar except that the residence time was one hour, larger amounts of capric acid, which was the only fatty acid produced, was formed. Other products formed were ketones and acrolein. Next tricaprin was heated to 190°C with slow stream of dry air. Heating was continued for 30 hours, and during this time water was formed. Acids such as capric acid, nonanoic and caprylic acids were produced in addition to lower acids. Also ketones and traces of n-decanal, which is an aldehyde, were found. (Crossley et al. 1962, 10-11)

Next Crossley et al. (1962) studied the degradation of 2-oleo-dipalmitin. The experimental conditions were somewhat different from those of tricaprin. 2-oleo-dipalmitin was heated at 190°C up to 20 hours in an atmosphere of nitrogen, which resulted in oleic and palmitic acids in the same ratio (1:2) as they are in the triglyceride. When the triglyceride in question was heated in vacuum at 250°C for ten hours, acids and acrolein were formed, but the temperature was too low to the formation of long-chain ketones. Last experiment included heating of the triglyceride also up to 20 hours at 190°C under slow stream of air. The presence of oxygen proved to be more complex: a part of oleic acid had been oxidized so that the fatty acid ratio was 1:4, the formation of volatile fatty acids consisting of mono- and dicarboxylic acids, occurred, and ketones and aldehydes as neutral compounds were formed. (Crossley et al. 1962, 11-12)

The temperatures that Crossley et al. (1962) used in their experiments are quite low compared to the temperature of 300-350°C that in normal process conditions prevails in hydro treatment reactor of Neste Oil’s NExBTL renewable diesel production. This is why the information about the heating of tricaprin and 2-oleo-dipalmitin may not be readily applicable to the process conditions of NExBTL renewable diesel, but they may give directional information.

3.2.2 Pyrolysis of trilaurin and tripalmitin by Kitamura

Kitamura (1971, 1606) examined the pyrolysis of two triglycerides, trilaurin (three lauric acids attached to glycerol) and tripalmitin (three palmitic acids attached to glycerol), in an atmosphere of nitrogen and at a temperature of 300-700°C. Residence time was not mentioned in the study. Lauric acid of trilaurin is found in large amounts in coconut and palm kernel oil, which are referred as lauric oils (Gunstone 2005, 221).

Degradation products of pyrolysis were analyzed and identified and also the mechanism for the series of pyrolysis reactions was presented. According to Kitamura (1971), the pyrolysis was the most effective when the temperature was between 450°C and 550ºC, so the pyrolysis results were reported for these temperatures. Fatty acids, ketones, acrolein and olefins were identified as pyrolysis products, and unsaturated glycol difatty acid esters and acid anhydrides were detected as intermediates (Kitamura 1971, 1606). Table 6 shows the results of pyrolysis of trilaurin and tripalmitin as a summary.

Table 6. Pyrolysis products of trilaurin and tripalmitin (Kitamura 1971, 1609).

Pyrolysis product	Intermediate product	Unchanged sample	Yield [wt-%]
Fatty acids			45,0-55,0
Acrolein			3,5-4,0
α-olefins			small amount
Ketones			small amount
	Unsaturated glycol difatty acid esters		small amount
	Acid anhydrides		2,5-6,5
		Triglycerides	10,0

Important to notice is the acrolein formation, because this particular compound is much of interest in this study. Table 7 presents the acrolein formation from single trilaurin and tripalmitin experiments more closely. It shows that in this particular experiment the acrolein yields for trilaurin and tripalmitin are 3,5 and 3,6 %, respectively, but in theory the yields can be 8,8 % for trilaurin and 6,9 % for tripalmitin.

Table 7. Acrolein formation from trilaurin and tripalmitin (Kitamura 1971, 1608).

Triglyceride	Sample [g]	Acrolein [g]	Yield [wt-%], Found	Yield [wt-%], Theoretical
Trilaurin	0,490	0,017	3,5	8,8
Tripalmitin	0,500	0,018	3,6	6,9

Kitamura (1971, 1609) suggested a reaction mechanism for the pyrolysis of trilaurin and tripalmitin in atmospheric nitrogen on the basis of experimental results and discussion. The mechanism is presented in figure 10 where the R is either the hydrocarbon chain of lauric or palmitic acid.

Kitamura's (1971) experiments were made under inert atmosphere of nitrogen. According to Kitamura (1971, 1606), the pyrolysis of glycerides can be expected to be different when there is air present or when the air is absent, which means that different pyrolysis products may form when experimental conditions such as the sphere are different.

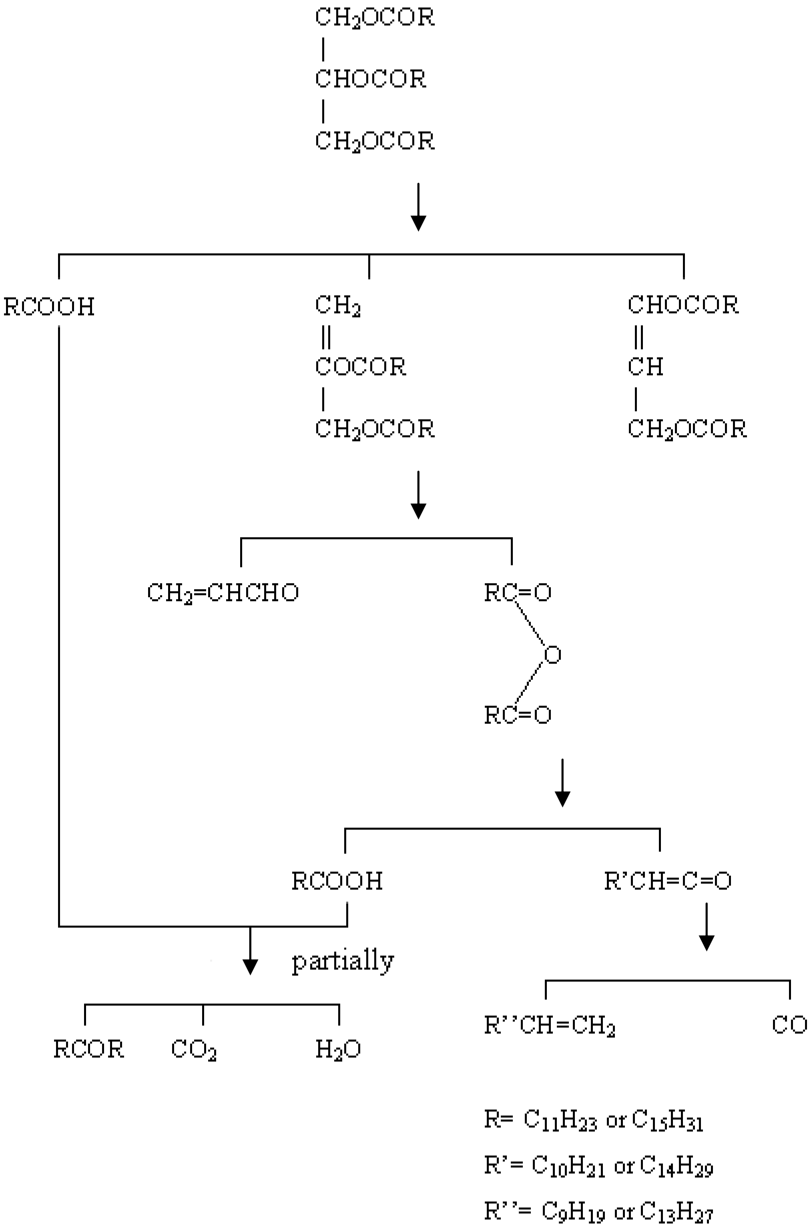


Figure 10. The reaction mechanism for the pyrolysis of trilaurin and tripalmitin in atmospheric nitrogen (Kitamura 1971, 1609).

3.2.3 Pyrolysis of tripalmitin and tristearin by Higman et al.

Higman et al. (1973) studied the pyrolysis of tripalmitin, like Kitamura (1971) presented in chapter 3.3.1, and tristearin (three stearic acids attached to glycerol). A large amount of stearic acid is found mainly from animal fats, but also in cocoa butter (Haas

2005, 163; Gunstone 2005, 221). Pyrolysis temperature was 400°C and it was conducted under nitrogen. The products formed could be divided into two groups: hydrocarbons and carboxylic acids. These pyrolysis products were different in the pyrolysis of tripalmitin compared to Kitamura's (1971) results, probably because the experimental conditions were somewhat different. (Higman et al. 1973, 202) For example, in the Higman et al. (1973) study the pyrolysis time was four hours for tripalmitin and 5,5 hours for tristearin, and there were no mentions about the pyrolysis time in Kitamura's (1971) study.

Hydrocarbons formed in the pyrolysis of both triglycerides were alkanes and alkenes, and acids formed were saturated and monounsaturated carboxylic acids. Also dicarboxylic acids were found in the pyrolysis products of tristearin. Though the products formed from tripalmitin and tristearin were quite the same, there were variations in relative yields in the formation of individual products. The single major acidic products composed were palmitic acid from tripalmitin and stearic acid from tristearin. (Higman et al. 1973, 202-204)

Higman et al. (1973) compared the gained experimental results to Kitamura's (1971) results, and noted that Kitamura (1971) had detected ketones in the pyrolysis products which they did not. Higman et al. (1973) did not suggest a pyrolytic pathway to the studied triglycerides or a general reaction mechanism for triglycerides, because they noted it to be too difficult since the results were different from researchers Crossley et al. (1962) and Kitamura (1971). (Higman et al. 1973, 204)

3.3 Thermal degradation - formation of acrolein and other aliphatic aldehydes from heated cooking oils

There are studies made about the formation of acrolein from heated cooking oils. Umano & Shibamoto (1987) examined the acrolein formation of beef fat and five cooking oils when heated individually at a temperature of 300°C for two hours. In addition, the formation of acrolein from corn oil was examined more thoroughly. Also pathways for the formation of acrolein were suggested.

Acrolein was determined as the morpholine derivative from the headspace volatiles of a 500 ml two neck, round-bottom flask. Each oil or beef fat sample weighed 120 g and the volatiles formed were purged into an aqueous solution of morpholine with nitrogen or air stream. Acrolein and morpholine produced 3-morpholinopropanal that was extracted and analyzed by a gas chromatograph. (Umano & Shibamoto 1987, 909-910) Table 8 presents the results that Umano & Shibamoto (1987) reported from the heating of two hours when the temperature was 300°C, and when headspace samples from the flask were purged with a stream of air and nitrogen of 1 ml/s each.

Table 8. The results from acrolein determination in the headspace of heated beef fat and cooking oils (Umano & Shibamoto 1987, 910).

	Amount of acrolein determined [mg]	
Sample	**N_2**	**Air**
corn oil	54,08	81,05
soy bean oil	29,55	76,11
sunflower oil	36,90	57,61
olive oil	72,01	103,63
sesame oil	58,98	85,51
beef fat	45,45	75,16

Table 8 shows that the acrolein amounts formed are higher when purged with air than when purged with nitrogen. According to Umano & Shibamoto (1987) this suggests that when oxygen is present it promotes common fatty acid degradation. In addition to the experimental results showed in table 8, Umano & Shibamoto (1987) studied the heating of corn oil more closely. The tests were conducted otherwise in the same way as those for other oils and beef fat, but the headspace volatiles were purged only with purified nitrogen stream. In one group of tests corn oil was heated at various temperatures for 2 hours. Another group of tests was conducted at 300°C with different heating times. (Umano & Shibamoto 1987, 910) Tables 9 and 10 show the results of these experiments.

Table 9. The results from acrolein determination in the headspace of corn oil after heating for two hours (Umano & Shibamoto 1987, 910).

Temperature [°C]	**Amount of acrolein determined [mg]**
180	0,00
240	0,42
280	5,36
300	54,08
320	141,56

Table 10. The results from acrolein determination in the headspace of corn oil heated at 300°C with various heating times (Umano & Shibamoto 1987, 910).

Time [h]	**Amount of acrolein determined [mg]**
1	24,16
2	54,08
3	86,82
5	140,52
6	165,01

Table 9 shows that the formation of acrolein increased rapidly when the temperature was 300°C or above. Table 10 shows that the longer corn oil was heated, the more acrolein was formed. Umano & Shibamoto (1987) proposed three pathways from a triglyceride for the acrolein formation when cooking oils or fat were heated. These pathways are presented in figure 11.

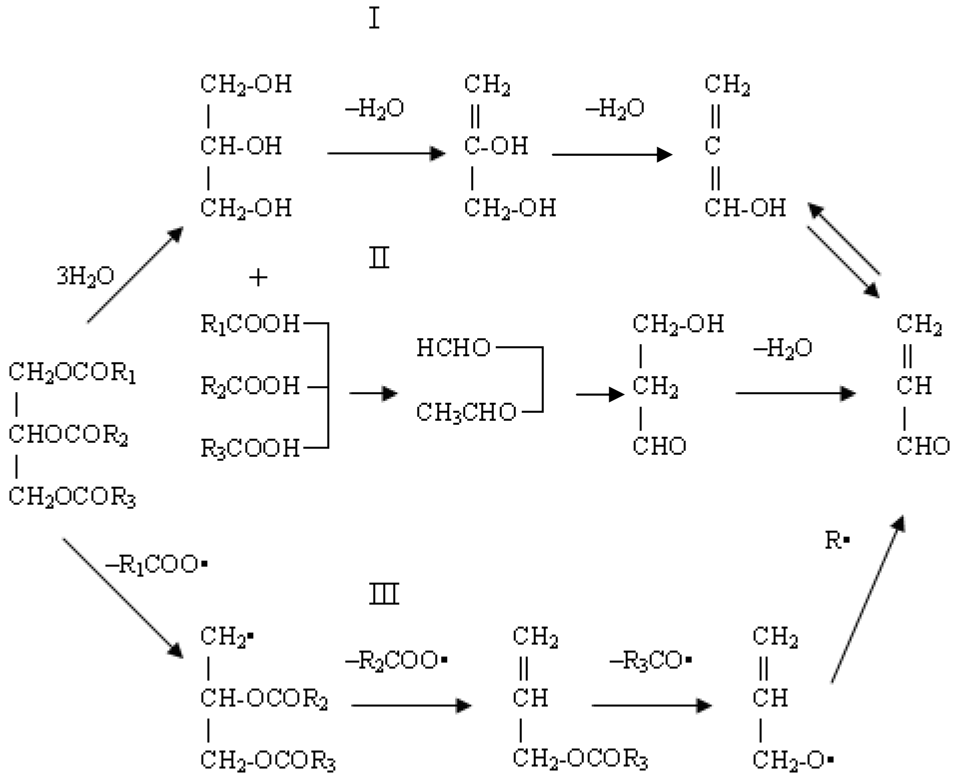


Figure 11. The suggested formation pathway of acrolein for a triglyceride in beef fat and cooking oils (Umano & Shibamoto 1987, 911).

The main pathway to produce acrolein is the dehydration of glycerol which is pathway I in figure 11. The second pathway suggests that acrolein is also formed from formaldehyde and acetaldehyde. The third pathway is a free radical mechanism that involves homolytic fission of R-O bonds and is suggested because formation of acrolein in the tests happened also under nitrogen stream. (Umano & Shibamoto 1987, 911)

Lin & Liou (2000) studied the formation of volatile aliphatic aldehydes when soy bean oil, peanut oil and pork lard were heated in chosen temperatures resembling the conditions of pan frying. The temperatures selected were in between 150ºC and 400°C. Each pyrolysis experiment for each oil sample was conducted in triplicate at each chosen temperature. The samples were heated for 30 minutes at temperatures of 150 ± 2°C, 200 ± 2°C, 250 ± 2°C and 300 ± 2°C, for 5,5 minutes at 350 ± 2°C and for three minutes at 400 ± 2°C. The heating times were chosen so that the charring of the samples could be avoided. Lin & Liou (2000) stated that the formation of aldehydes is dependent on the cooking oil and the temperature used. In the tests the formation of formaldehyde, acetaldehyde, acrolein and propionaldehyde were detected. It also seemed that when temperature was raised to 350°C and 400°C, the yields of aldehydes were higher. (Lin & Liou 2000, 817-819) Table 11 presents the average yields of aliphatic aldehydes at temperatures of 300°C, 350°C and 400°C. The lower temperatures are left out from examination because they are not high enough to be relevant to this study.

Table 11. The average yields of aliphatic aldehydes at 300°C, 350°C and 400°C (Lin & Liou 2000, 822).

		Yield [ppm/mg-min], Mean ± Standard deviation				
Temperature	**Source**	**Formaldehyde**	**Acetaldehyde**	**Acrolein**	**Propionaldehyde**	**Total aldehyde**
300	Soy bean oil	0,03±0,01	0,02±0,01	0,04±0,01	0,01±0,01	0,10
300	Peanut oil	0,04±0,02	0,04±0,01	0,06±0,03	0,02±0,01	0,16
300	Lard	0,06±0,02	0,04±0,01	0,02±0,01	0,02±0,01	0,14
350	Soy bean oil	0,49±0,20	0,46±0,21	0,73±0,39	0,14±0,07	1,82
350	Peanut oil	0,36±0,16	0,29±0,03	0,57±0,17	0,10±0,01	1,32
350	Lard	1,35±0,45	0,59±0,11	0,39±0,01	0,17±0,04	2,50
400	Soy bean oil	2,43±0,35	1,55±0,56	2,61±0,91	0,47±0,08	7,05
400	Peanut oil	1,65±0,34	1,36±0,22	1,85±0,34	0,45±0,07	5,30
400	Lard	10,93±1,29	1,04±0,13	0,66±0,11	0,33±0,03	12,96

Table 11 shows that in general, acrolein and formaldehyde were produced the most in the experiments. It also shows that in most tests conducted with soy bean and peanut oil acrolein was formed the most, and that especially high amount of formaldehyde was formed when pork lard was heated at 400°C.

3.4 Summary of the thermal degradation of plant oils and animal fats

Several researchers have done experiments on the pyrolysis of triglycerides and plant oils and these are presented in chapters 3.1, 3.2 and 3.3. The formation of aliphatic aldehydes has also been studied with animal fats in chapter 3.3. This chapter summarizes the experiments presented in the mentioned chapters. Depending on the experimental conditions, equipment and the feed, several degradation products from the pyrolysis of pure triglycerides, plant oils and animal fats (in chapter 3.3) were detected by different researchers. A summary about the key information in the studies is presented in table 12.

Table 12. Summary of the presented experimental conditions and degradation products (Chang & Wan 1947, 1545; Alencar et al. 1983, 1268-1269; Schwab et al 1988, 1781 and 1784; Idem et al. 1996, 1150-1152; Crossley et al. 1962, 10-12; Kitamura 1971, 1606 and 1609; Higman et al. 1973, 202-204; Umano & Shibamoto 1987, 909-911; Lin & Liou 2000, 817-819 and 822) .

Author(s)	The feed(s) used	Experimental conditions	Found degradation products
Chang & Wan (1947)	Tung oil	Not available, possibly based on the theoretical mechanism study only	acrolein, ketenes and fatty acids as initial products, which are degraded into other compounds according to 16 types of reaction shown in chapter 3.1.1
Alencar et al. (1983)	Piqui, babassu and palm oils	Temperature range 300-500°C, atmospheric pressure, information about atmosphere not available	*n*-alkanes, 1-alkenes, cycloparaffins and cyclo-olefins when oleic acid major fatty acid
Schwab et al. (1988)	Soy bean and safflower (high in oleic acid) oils*	Experiments in air and nitrogen**, temperature and pressure not available	alkanes, alkenes, alkadienes, aromatic hydrocarbons, carboxylic acids
Idem et al. (1996)	Rapeseed oil	Temperature range 300-500°C, atmospheric pressure, in the presence and absence of steam, information about atmosphere not available	Hydrocarbon gases, olefins, alcohols, ketones, aldehydes, aliphatic hydrocarbons, aromatics, toluene, xylenes, ethylbenzene, CO, CO$_2$, H$_2$, residual oil and non-identified compounds
Crossley et al. (1962)	Triglycerides tricaprin and 2-oleo-dipalmitin		
	I Tricaprin	Temperature 240-260°C, residence time 4,5 hours, in a nitrogen atmosphere	capric acid
	II Tricaprin	Temperature 300°C, residence time 1 hour, in a nitrogen atmosphere	capric acid, ketones and acrolein
	III Tricaprin	Temperature 190°C, residence time 30 hours, in a slow stream of air	capric, nonanoic and caprylic acids, lower acids, ketones, traces of *n*-decanal
	IV 2-oleo-dipalmitin	Temperature 190°C, residence time 20 hours,	oleic and palmitic acids in the same ratio as in

		in a nitrogen atmosphere	the parent triglyceride (1:2)
	V 2-oleo-dipalmitin	Temperature 250°C, residence time 10 hours, in vacuum	oleic and palmitic acids, acrolein
	VI 2-oleo-dipalmitin	Temperature 190°C, residence time 20 hours, in a slow stream of air	oleic and palmitic acids in the ratio of 1:4, volatile fatty acids, ketones, aldehydes
Kitamura (1971)	Trilaurin and tripalmitin	Temperature range 450-550°C, in a nitrogen atmosphere, residence time not available	fatty acids, ketones, acrolein and olefins
Higman et al. (1973)	Tripalmitin and tristearin		
	I Tripalmitin	Temperature 400°C, in a nitrogen atmosphere, residence time 4 hours	alkanes, alkenes, saturated and monounsaturated carboxylic acids, palmitic as a major acid
	II Tristearin	Temperature 400°C, in a nitrogen atmosphere, residence time 5,5 hours	alkanes, alkenes, saturated, monounsaturated and dicarboxylic acids, stearic acid as a major acid
Umano & Shibamoto (1987)	Beef fat, corn oil, soy bean oil, sunflower oil, olive oil, sesame oil	Temperature range 180-320ºC, in a nitrogen atmosphere and air for various residence times	only acrolein determination, no other compounds reported
Lin & Liou (2000)	Soy bean oil, peanut oil, pork lard	Temperature range 150-400ºC with various residence times, conditions resembling of pan frying	only aliphatic aldehydes determination, no other compounds reported

*) some differences in the degradation products depending on the oil

**) only small distinctions in the degradation products depending on the atmosphere

Table 12 shows that based on the studies presented in chapters 3.1 and 3.2, the main thermal degradation products of pure triglycerides or plant oils are fatty acids, ketones, acrolein, alkanes and alkenes, fatty acids being the most abundant group of compounds. This seems reasonable because fatty acids are the building blocks of triglycerides and when they degrade, it is very likely that one share of the pyrolysis products is fatty acids. Acrolein was detected in four of the studies presented in chapters 3.1 and 3.2, as were also ketones, alkanes and alkenes. Acrolein and other aldehydes were also found in two other studies of chapter 3.3, where only these compounds and their amounts were reported and not all the degradation products. According to table 12 also aromatic compounds were detected in two of the studies, and ketenes and alcohols were found in one study each.

It can be seen from table 12, that the studies have similarities, but one has to be careful when comparing them to each other as they are not identical. Some of the studies are not necessary applicable to the situation of NExBTL renewable diesel production, firstly because the temperature is too low like some of the experiments from Crossley et al. (1962), and secondly because in most of the studies no information about the pressure is mentioned or the experiments are carried out in atmospheric pressure, while in the hydro cracking reactor of NExBTL the pressure is 5 000 kPa (50 bar). Additionally, none of the experiments examined in this thesis use hydrogen as the sphere of an experiment, while hydrogen is an essential part of the hydro treatment process.

The examined studies have their own conclusions which may be somewhat similar to each other, but they are not necessarily unanimous: Schwab et al. (1988) reported that the distinctions in the pyrolysis products were small when they were conducted in air or nitrogen and larger differences were discovered when experiments were done with different oils, whereas Crossley et al. (1962) stated that the breakdown of triglycerides is different when oxygen is present and when it is absent. Crossley et al. (1962) seem to believe that the differences in pyrolysis products are heavily dependent on the atmosphere as Schwab et al. (1988) concluded that the dependence is not so obvious.

4 HAZARDOUS DEGRADATION PRODUCTS

The studied literature presents many kinds of thermal degradation products. Some of them are identified individually and some are mentioned generally as chemical groups. One aim of this study is to identify thermal degradation products that are hazardous. This aim is carried out with the help of danger symbols that are used in the European Union, the European Economic Area and some other countries (International Labour Organization 2004a). The symbols used in this study are presented in Appendix I. All the degradation products that are labelled as toxic (T) or very toxic (T+), irritating (Xi) or harmful (Xn), environmentally dangerous (N), flammable (F) or extremely flammable (F+) are considered hazardous. Table 13 presents all the thermal degradation products of the studied literature that are considered hazardous at least with one danger symbol. Table 13 presents also the boiling points of these substances. Boiling temperature is related to substance evaporation.

Table 13. Hazardous thermal degradation products identified by danger symbols (International Labour Organization 2004b).

Substance	**Toxic (T)/very toxic (T+)**	**Irritating (Xi)/harmful (Xn)**	**Environmentally dangerous (N)**	**Flammable (F)/extremely flammable (F+)**	**Boiling point [°C]**
Aldehydes					
Acrolein	+	-	+	+	53
Propanal	-	+	-	+	49
Aromatics					
Benzene	+	-	-	+	80
Ethylbenzene	-	+	-	+	136
Toluene	-	+	-	+	111
m-xylene	-	+	-	-	139
o-xylene	-	+	-	-	144
p-xylene	-	+	-	-	138
Carbon monoxide	+	-	-	+	-191
Hydrogen	-	-	-	+	-253
Ketones					
Acetone	-	+	-	+	56
2-heptanone	-	+	-	-	151
Olefins					
Dienes					
1,3-butadiene	+	-	-	+	-4

Benzene, acetone, 2-heptanone and 1,3-butadiene in table 13 were not literally mentioned as degradation products. However, they represent their groups of compounds which are aromatics, ketones and dienes. These chemical groups were mentioned as degradation products.

In addition, the literature reports alcohols as degradation products, but since they are not defined more precisely and there are so many alcohols existing, they are not present in table 13. Some of the compounds are gases and others are liquids in ambient conditions. This study focuses on the gaseous emissions, but at high temperatures liquid compounds can be in a vaporous form and therefore it is justified to take them into consideration in the table. Many studies in the literature mentioned fatty acids as degradation products, but since their boiling points are very high, for example 376°C for stearic acid and 351-352°C for palmitic acid (International Labour Organization 2004b), the boiling points are higher than the temperature in hydro cracking reactor of NExBTL, fatty acids are considered to stay liquid.

The boiling points showed in table 13 are present with good reason. They help to understand what could happen to these substances if a leak occurs. The temperature in the hydro treatment reactor is above 300°C and all the boiling points are well below this temperature. This means that hazardous degradation products in the reactor are superheated under a high pressure. If they are released to a space with atmospheric pressure, they will flash to vapour and can form aerosols with atmospheric gases (Crowl 1999, 57). The following chapters present the hazardous degradation products of table 13 more closely.

4.1 Toxic or very toxic thermal degradation products

The table shows that acrolein is toxic, environmentally dangerous and flammable and is the most hazardous of all compounds presented. Other compounds that are labelled as toxic or very toxic are benzene, carbon monoxide and 1,3-butadiene. These four compounds are the most important when considering the hazardous nature of thermal degradation products. In this chapter the given information about acrolein is more comprehensive because it is not such a familiar substance and more knowledge about hazardous compounds is wanted by Neste Oil.

4.1.1 Acrolein

Acrolein, also called as acrylic aldehyde, is a highly reactive, flammable and toxic aldehyde which contains a double bond and its chemical formula is C_3H_4O. In room temperature it is a yellow or colourless liquid with a pungent odour. It is also corrosive and dangerous to the environment, especially to aquatic organisms. (Tuotevalvontakeskus 2003; International Labour Organization 2004b) Table 14 presents some of the chemical and physical properties of acrolein.

Table 14. Some physical and chemical properties of acrolein (International Labour Organization 2004b; Tuotevalvontakeskus 2003).

Physical or chemical property	
Molecular mass [g/mol]	56,06
Boiling point [°C]	53
Melting point [°C]	-88
Relative density (water = 1)	0,8
Solubility in water (at 20°C) [mg/l]	206-270
Vapour pressure (at 20°C) [Pa]	29 300
Relative vapour density [air = 1)	1,9
Flash point [°C]	-26
Auto-ignition temperature [°C]	234
Explosive limits [Vol-% in air]	2,8-31

Chemical Safety Card for acrolein has comprehensive information about the health and safety issues of the compound. According to the International Chemical Safety Card of International Labour Organization (2004b), the occupational exposure limit for acrolein is 0,1 ppm as a ceiling threshold limit value (TLV-C). This means that acrolein exposure of 0,1 ppm should not be exceeded at any part of the working exposure (ACGIH 2008). The Ministry of Social Affairs and Health has set the same occupational exposure limit value of 0,1 ppm as the ceiling value, when a person can be exposed to the substance for maximum of 15 minutes a day. The value of 0,1 ppm corresponds the concentration of 0,23 mg/m^3 (Sosiaali- ja terveysministeriö 2007, 17).

Usually human exposure to acrolein happens at a work place through skin or respiratory track, but exposure to eyes and through ingestion is also possible. When exposed to acrolein by inhalation, acute symptoms include burning sensation, cough, laboured breathing, sore throat, shortness of breath and nausea. The symptoms can also be delayed, and after a few hours lung oedema can develop, which is worsened by physical effort. Skin exposure causes redness, pain, blisters and skin burns. If eyes are exposed to acrolein, it causes redness, pain and possibly severe deep burns. Ingestion exposure causes a burning sensation in throat and chest, convulsions and nausea. Because eyes are very sensitive to acrolein, tear drawing can be the first symptom that indicates acrolein exposure. If exposure continues and acrolein is inhaled at high levels, developing a lung oedema is likely. (Tuotevalvontakeskus 2003; International Labour Organization 2004b)

In order to prevent acrolein exposure via inhalation, a breathing protection, a good ventilation or local exhaust is needed. Skin can be protected by using proper protective gloves and clothing. The best protection of eyes is achieved when a face shield or eye protection with breathing protection is used. Exposure via ingestion is prevented when eating, drinking and smoking are avoided during work that possibly exposes to acrolein. Also hand washing before eating prevents ingestion exposure. During spillage disposal a chemical protection suit with self-contained breathing apparatus should be used. (International Labour Organization 2004b)

In addition to danger symbols used in labelling, chemicals are also given risk and safety phrases if necessary. (International Labour Organization 2004b) Risk and safety phrases of acrolein are presented in table 15.

Table 15. Risk and safety phrases of acrolein (International Labour Organization 2002).

Risk phrase	
R11	Highly flammable.
R24/25	Toxic in contact with skin and if swallowed
R26	Very toxic by inhalation
R34	Causes burns
R50	Very toxic to aquatic organisms
Safety phrase	
S23	Do not breathe gas/fumes/vapour/spray *(appropriate wording to be specified by the manufacturer)*.
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S28	After contact with skin, wash immediately with plenty of ... *(to be specified by the manufacturer)*.
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
S45	In case of accident or if you feel unwell, seek medical advice immediately *(show the label where possible)*.
S61	Avoid release to the environment. Refer to special instructions/safety data sheets.

From natural sources, acrolein can be formed as a fermentation product and in ripening processes. It can also be released in forest fires when incomplete combustion of organic matter occurs, and by photochemical oxidation of atmospheric hydrocarbons. The quantities of released acrolein from natural sources have not yet been identified. Acrolein is also released to the environment by anthropogenic sources. According to World Health Organization’s sample country Canada, the main anthropogenic source of acrolein is activities that involve the combustion of organic material, when incomplete combustion in waste incinerators, fireplaces, furnaces and power plants releases acrolein. Also combustion of polyethylene plastics and cooking of food can release acrolein due to incomplete combustion. The principal combustion source is found to be petrol and diesel motor vehicle emissions. Generally, in WHO’s sample country Canada, indoor air had acrolein concentrations of 2-20-fold compared to outdoor air. This is possibly due to cooking or processing of fatty foods and cigarette smoke. (Gomes et al. 2002, 7-8 and 10) Studies about the acrolein formation from heated cooking oils have been made and two of them by Umano & Shibamoto (1987) and Lin & Liou (2000) are presented in chapter 3.3 of this study. Acrolein is also manufactured and used in industrial processes, and more about the production of the substance is presented in Appendix II.

As acrolein is of particular interest in this study, the reactions of the compound with other substances should also be examined. Acrolein is known to be reactive, and it may not persist very long time in the environment (Gomes et al. 2002, 9). This is why it may react with other compounds, such as with oxygen that is obtained from air and hydrogen that is present in the hydration reactor of NExBTL renewable diesel. Also reactions with carbon monoxide and a reaction with itself are of interest.

Acrolein formed in the thermal degradation of triglycerides may react with oxygen if a leak happens in the hydro cracking reactor and the fluid gets in contact with air. Oxidation of acrolein produces acrylic acid as follows (Wittcoff et al. 2004, 177):

$$CH_2 = CH - CHO + \frac{1}{2}O_2 \rightarrow CH = CH - COOH \tag{23}$$

It can happen in either vapour or liquid phase, but in liquid phase acrolein tends to polymerize. Vapour phase oxidation is the basis reaction for the manufacture of acrylic acid; when alumina is used as a catalyst and the temperature is 220°C, a molar yield of 98 % can be obtained. (Wittcoff et al. 2004, 177)

When reacting with itself acrolein forms an insoluble, cross linked solid polymer that varies depending on which groups are linked to each other. Figure 12 shows possible polymers of acrolein. When aldehyde groups are linked with each other by 1,2-linkage, a 1,2-polymer is formed. If vinyl groups are linked with each other, a 3,4-polymer is formed. Also aldehyde groups can link with vinyl groups to form another polymer, but 1,4-polymerization is rare. (Hess et al. 1978, 284)

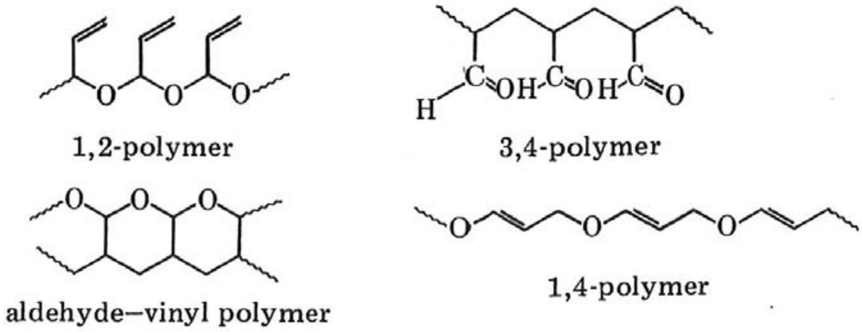


Figure 12. Different acrolein polymers (Hess et al. 1978, 284).

Several factors such as ultra violet and gamma radiation, alkaline materials, metal derivatives and redox and anionic catalysts promote the polymerization of acrolein. Usually polymerization occurs in solvent in a presence of a catalyst (Hess et al. 1978, 285). Therefore it is hard to say whether polymerization could happen in the conditions relevant to this study.

When acrolein reacts with hydrogen, possible reaction pathways presented include the hydrogenation of the C=O bond present in acrolein, leading to the formation of unsaturated alcohol 2-propenol. Hydrogenation of the C=C double bond of acrolein leads to the formation of saturated aldehyde propanal. Further hydrogenation can occur to both products to form the saturated alcohol 1-propanol. (Murillo & Chen 2008, 919) The reaction scheme from hydrogenation of acrolein is presented in figure 13.

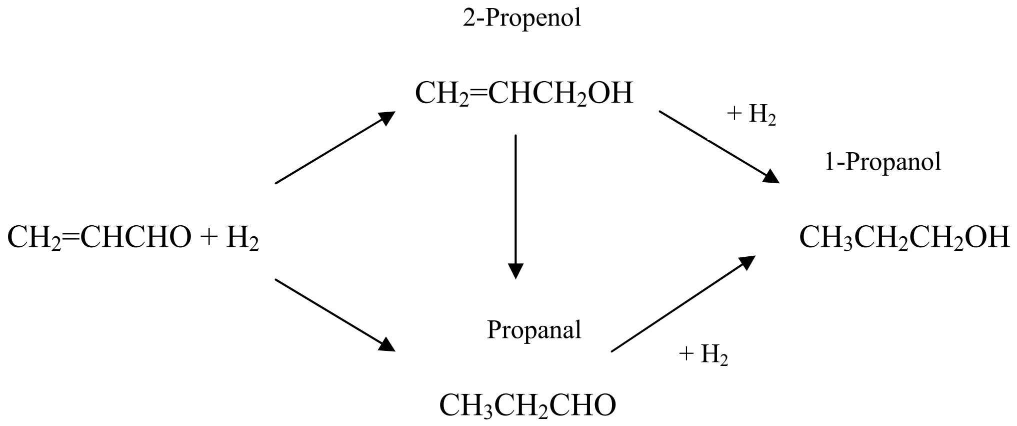


Figure 13. Two hydrogenation pathways of acrolein (Murillo & Chen 2008, 919).

4.1.2 Benzene

In the literature benzene was not mentioned as a thermal degradation product but aromatics were, and since benzene is the simplest aromatic compound, it was selected to represent the group of aromatics in table 13. Benzene is a colourless liquid and it has a characteristic aromatic odour. Its chemical formula is C_6H_6 and molecular mass is 78,1 g/mol. It is nearly insoluble in water and can be fully mixed with many organic liquids. Its vapour-air mixtures are explosive and heavier than air so they can travel along the ground to enable distant ignition. (International Labour Organization 2004b; Speight 2002, 2.75)

Benzene is a toxic (T) and flammable (F) compound that has acute and chronic effects. It is toxic to humans and highly toxic to aquatic organisms. Benzene exposure can occur via inhalation, skin, eyes or ingestion. According to the International Chemical Safety Card the occupational exposure limit of benzene is 0,5 ppm as a time-weighted average of threshold limit value (TLV-TWA). This means that the exposure limit is determined for a work day of 8 hours and workweek of 40 hours. In another source according to Ministry of Social Affairs and Health the corresponding binding limit value for benzene is 1 ppm (3,25 mg/m^3). A short term exposure limit as a threshold limit value (TLV-STEL) for benzene is 2,5 ppm (International Labour Organization 2004b). This limit value allows a worker to be exposed to a substance for 15 minutes during a workday and the limit should not be exceeded (ACGIH 2008). Though the odour of benzene is strong it is insufficient to warn about exceeded exposure limit values. (Purcell 1978, 764-765; International Labour Organization 2004b; Sosiaali- ja terveysministeriö 2007, 37) Table 16 lists acute and chronic symptoms of benzene exposure in humans.

Table 16. Acute and chronic symptoms of benzene exposure (International Labour organization 2004b; Purcell 1978, 765).

Acute symptoms	Chronic symptoms
Dizziness, drowsiness, headache, nausea, convulsions, shortness of breath, unconsciousness. Pain in the skin, dry and red skin (may be absorbed through skin). Redness and pain in the eyes. Abdominal pain, sore throat and vomiting.	Anemia, slow healing, fatigue, chronic headaches, itching, nausea, cutaneous hemorrhage, weight loss and leukemia.

Benzene is carcinogenic, and chronic exposure to the substance has been associated with leukemia. Benzene is not a specialized toxin and this is why it attacks many parts of the body. Most serious benzene exposures in industry occur during maintenance or as a result of equipment malfunction. If the occupational exposure limit is exceeded far above the limit, exposure may result in unconsciousness and even death. Most benzene poisoning deaths occurred in the past have been related to the use of benzene as a solvent. Today benzene is no longer allowed as a solvent except in very special circumstances. (Purcell 1978, 764-765) Risk phrases of benzene give more information about the risks related to the compound and its use and they are presented in table 17.

Table 17. Risk phrases of benzene (International Labour Organization 2002).

Risk phrase	
R11	Highly flammable.
R36/38	Irritating to eyes and skin.
R45	May cause cancer.
R46	May cause heritable genetic damage.
R48/23/24/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
R65	Harmful: may cause lung damage if swallowed.

In order to avoid benzene exposure the same kinds of protective measures as in the acrolein exposure should be taken. To prevent inhalation exposure, a good ventilation or local exhaust is required and workers should wear a breathing protection. Skin should be protected by protective gloves and clothing. Eyes are protected properly when a face shield or eye protection with a breathing protection is used. Eating, drinking and smoking should be avoided during work to avoid the ingestion exposure to benzene. If a spillage occurs, complete protective clothing that includes a self-contained breathing apparatus should be used when disposing the spillage. (International Labour Organization 2004b)

4.1.3 Carbon monoxide

Carbon monoxide is the third thermal degradation product that is labelled as toxic (T) in table 13. It is also extremely flammable (F+). Carbon monoxide is an odourless, colourless and tasteless gas and its molecular mass is 28,0 g/mol. It is produced in incomplete combustion, automobile exhaust gas being maybe the most familiar way to be exposed to carbon monoxide. It is also present in cigarette smoke. It mixes well with air and forms explosive mixtures easily. Carbon monoxide gas also penetrates easily through ceilings and walls. (International Labour Organization 2004b; Bartish & Drissel 1978, 790)

Unlike acrolein and benzene, carbon monoxide exposure is more constricted: the exposure occurs only via inhalation. Symptoms of acute exposure are headache, confusion, dizziness, weakness, nausea and unconsciousness. Carbon monoxide may also have long-term effects on central nervous system and cardiovascular system, and it may be toxic to human development or reproduction. (International Labour Organization 2004b) The risk phrases of carbon monoxide presented in table 18 give the summary of the hazards of the substance.

Table 18. Risk phrases of carbon monoxide (International Labour Organization 2002).

Risk phrase	
R12	Extremely flammable.
R23	Toxic by inhalation.
R48/23	Toxic: danger of serious damage to health by prolonged exposure through inhalation.
R61	May cause harm to the unborn child.

Carbon monoxide is a specialized toxin and its mode of action is based on its reaction with the hemoglobin in blood. Carbon monoxide displaces oxygen in hemoglobin to form carboxyhemoglobin, which leads to asphyxiation. When 10-20 % of the hemoglobin has reacted with carbon monoxide, headaches occur. Further saturation causes other symptoms described above, finally leading to unconsciousness and death. (Bartish & Drissel 1978, 790)

Occupational exposure limits for carbon monoxide are shown from two sources in table 19. TLV-TWA value is from the International Chemical Safety Card of carbon monoxide and other values are concentrations known to be hazardous (HTP-value, haitalliseksi tunnettu pitoisuus-value) set by the Ministry of Social Affairs and Health. In table 19 HTP-value of 8 h corresponds to TLV-TWA value. HTP-value of 15 min is an occupational exposure limit that a person can tolerate for 15 minutes without any symptoms.

Table 19. Occupational exposure limits of carbon monoxide from two different sources (International Labour Organization 2004b; Sosiaali- ja terveysministeriö 2007, 24).

Occupational exposure limit	**[ppm]**	**[mg/m^3]**
TLV-TWA	25	29
HTP-value (8 h)	30	35
HTP-value (15 min)	75	87

In order to avoid carbon monoxide exposure, good ventilation, local exhaust or breathing protection is required. This is important, because carbon monoxide is odourless, so there is no odour warning about hazardous concentrations, and a harmful concentration can be reached in the air quickly. (International Labour Organization 2004b)

4.1.4 1,3-butadiene

1,3-butadiene was not directly mentioned as a degradation product in the literature, but olefins, including dienes were however. Since 1,3-butadiene is a hazardous olefin it was chosen to be presented in table 13. 1,3-butadiene is a colourless gas and it possesses a characteristic odour. Its boiling point is -4°C so the substance is usually stored in the form of compressed liquefied gas. It is a diene which means it has two double bonds between carbon atoms and its molecular mass is 54,1 g/mol. It is toxic and extremely flammable and its main hazards are related to high flammability and chemical reactivity that is based on the double bonds. (International Labour Organization 2004b; Kirshenbaum 1978, 328)

Exposure to 1,3-butadiene can occur via inhalation, skin and eyes and it can be acute, long-term or repeated exposure. As it has impacts on different parts of the body, it is not a specialized toxin like carbon monoxide. The physiological effects of the substance may vary individually. (International Labour Organization 2004b; Kirshenbaum 1978, 328) Acute and chronic symptoms of exposure to 1,3-butadiene are shown in table 20.

Table 20. Acute and long-term symptoms of 1,3-butadiene exposure (International Labour organization 2004b).

Acute symptoms	**Chronic or repeated exposure symptoms**
Cough, sore throat, headache, dizziness, blurred vision, drowsiness, nausea, unconsciousness. Frostbites when in contact with skin in a liquid form and when rapidly evaporated. Redness and pain in the eyes.	May have impacts on the bone marrow, leading to leukemia. Probably carcinogenic and may cause heritable genetic injury in humans. Possible toxic effects on human reproduction.

International Chemical Safety Card sets the occupational exposure limit of 1,3-butadiene to be 2 ppm (4,4 mg/m^3) as TLV-TWA. The corresponding HTP-value for the substance set by the Ministry of Social Affairs and Health is 1 ppm (2,2 mg/m^3) (Sosiaali- ja terveysministeriö 2007, 19). The characteristic odour of the substance does not act as a warning when the exposure limit is exceeded. The hazardous concentration can be reached rapidly when 1,3-butadiene is released to the air. (International Labour Organization 2004b) Like other harmful substances, risk phrases has been established also for 1,3-butadiene and they are presented in table 21.

Table 21. Risk phrases of 1,3-butadiene (International Labour Organization 2002).

Risk phrase	
R12	Extremely flammable.
R45	May cause cancer.
R46	May cause heritable genetic damage.

To prevent 1,3-butadiene exposure via inhalation local exhaust, ventilation or a breathing protection is required. To avoid skin contact with the substance cold-insulating gloves should be used. Safety goggles protect the eyes from the exposure. Eating, drinking and smoking should be avoided during work to avoid the contamination. During spillage disposal a chemical protection suit with self-contained breathing apparatus should be used. (International Labour Organization 2004b)

4.2 Irritating or harmful thermal degradation products

Table 13 shows the compounds labelled as irritating or harmful. These are propanal, ethylbenzene, toluene, xylenes, acetone and 2-heptanone. This chapter briefly presents these substances from the point of view of their harmful nature.

Propanal was mentioned as a degradation product in the aliphatic aldehydes formation in chapter 3.3. Propanal is an irritating (Xi) and a flammable (F) substance and it is a colourless liquid possessing a pungent odour. Exposure to propanal is acute and may occur via many routes; inhalation exposure causes cough and sore throat, skin or eye exposure causes pain and redness in them and if propanal exposure occurs via ingestion it results in burning sensation. Occupational exposure limit of propanal is 20 ppm (48 mg/m^3) which is determined as an average concentration for an 8-hour work week of 40 hours. The limit is the same in International Chemical Safety Card as well as the one set by the Ministry of Social Affairs and Health (International Labour Organization 2004b; Sosiaali- ja terveysministeriö 2007, 31).

Ethylbenzene is a flammable, colourless liquid that is produced from benzene and ethylene (Speight 2002, 2.218). Toluene is alike and is insoluble in water but can be fully mixed with organic liquids. Xylenes are the general name of three isomers where a benzene ring is attached by two methyl groups in ortho, meta and para positions. Like ethylbenzene and toluene, *o*-xylene, *m*-xylene and *p*-xylene are colourless and flammable liquids whose properties are similar to each other. (Speight 2002, 2.523 and 2.557)

All these five compounds are harmful (Xn) and their acute exposure occurs the same way: via skin, eyes, ingestion or inhalation. Acute exposure symptoms include cough, sore throat, drowsiness, dizziness, headache and nausea. In the case of toluene exposure a person may lose consciousness. Skin exposure to these substances makes skin dry and red, and eye exposure causes redness and pain in the eyes. Exposure via ingestion causes burning sensation, also in throat and in the case of ethylbenzene also in chest. Stomach ache is also another symptom of ingestion exposure to ethylbenzene, xylenes and toluene. (International Labour Organization 2004b) Table 22 lists occupational exposure limits for these substances from two different sources.

Table 22. Occupational exposure limits of toluene, xylenes and ethylbenzene from two sources as time-weighted average (TWA) and short-term exposure limit (STEL) threshold limit values (TLV) and concentrations known to be hazardous values (HTP-values). TLV-STEL-value for toluene is not available. (International Labour Organization 2004b; Sosiaali- ja terveysministeriö 2007, 22, 26 and 34)

Compound	**TLV-TWA***		**TLV- STEL***		**HTP-value 8 h****		**HTP-value 15 min****	
	[ppm]	**[mg/m^3]**	**[ppm]**	**[mg/m^3]**	**[ppm]**	**[mg/m^3]**	**[ppm]**	**[mg/m^3]**
Ethylbenzene	100	440	125	550	50	220	200	880
Toluene	50	190	-	-	50	190	100	380
Xylenes	100	440	150	660	50	220	100	440

*) Data from International Labour Organization 2004

**) Data from Sosiaali- ja terveysministeriö 2007

Ethylbenzene, toluene and xylenes can cause symptoms also by long-term or repeated exposure. Toluene and xylenes possibly have impacts on the central nervous system and may cause toxicity to human development or reproduction. Ethylbenzene may have impacts on liver and kidneys causing impaired functioning. Ethylbenzene as the only one of these five compounds is also confirmed as an animal carcinogen and it is possibly carcinogenic also to humans. (International Labour Organization 2004b)

Acetone and 2-heptanone are both colourless liquid ketones with characteristic odours. Acetone is flammable and irritating and 2-heptanone is a harmful compound. Exposure to these substances can occur via inhalation, skin and eyes. In the case of acetone also ingestion exposure is possible. (International Labour Organization 2004b) Table 23 shows acute exposure symptoms of acetone and 2-heptanone.

Table 23. Acute symptoms of acetone and 2-heptanone exposure (International Labour Organization 2004b).

Acute exposure symptoms	
Acetone	**2-heptanone**
Sore throat, cough, headache, confusion, dizziness, drowsiness, unconsciousness. Dry skin. Redness and pain in eyes, blurred vision and possible corneal damage. Nausea and vomiting.	Cough, headache, dizziness, blurred vision, unconsciousness. Dry and red skin. Redness in eyes.

Acetone causes also dermatitis in skin when exposure is long-term or repeated. In addition, acetone may have impacts on bone marrow and the blood. (International Labour Organization 2004b) Table 24 lists the occupational exposure limits for acetone and 2-heptanone from two different sources.

Table 24. Occupational exposure limits of acetone and 2-heptanone from two sources. The TLV-STEL-value is not available for 2-heptanone. (International Labour Organization 2004b; Sosiaali- ja terveysministeriö 2007, 18 and 23)

Compound	**TLV-TWA***		**TLV- STEL***		**HTP-value 8 h****		**HTP-value 15 min****	
	[ppm]	**[mg/m^3]**	**[ppm]**	**[mg/m^3]**	**[ppm]**	**[mg/m^3]**	**[ppm]**	**[mg/m^3]**
Acetone	500	1200	750	1800	500	1200	630	1500
2-heptanone	50	240	-	-	50	240	75	360

*) Data from International Labour Organization 2004

**) Data from Sosiaali- ja terveysministeriö 2007

4.3 Environmentally dangerous thermal degradation products

Acrolein is the only compound in table 13 labelled with environmentally dangerous substance symbol. Its toxicity has been studied with terrestrial and aquatic organisms. The toxicity data from terrestrial organisms are limited to few acute crop plant studies and studies on laboratory mammals. Acrolein toxicity to aquatic organisms has been studied more extensively due to the use as an aquatic herbicide, and it has been discovered that aquatic organisms are more sensitive to single exposures to acrolein than terrestrial organisms. (Gomes et al. 2002, 21)

Because of its high reactivity, acrolein does not usually persist in the environment for a long time, and the intercompartmental movement of the substance is small. Normally, when acrolein is constantly discharged into a certain medium such as air, water, sediment, soil or biota, the main part of it can be expected to stay in that medium, when partitioning from one compartment to another is very small of negligible. (Gomes et al. 2002, 9)

4.4 Flammable or extremely flammable thermal degradation products

Flammable or extremely flammable thermal degradation products are listed in table 13. All except xylenes and 2-heptanone are labelled as flammable. There is one substance in the table that has not been examined earlier; hydrogen is a colourless and odourless gas that is lighter than air and is extremely flammable. It mixes well with air and forms explosive mixtures easily. Heating of the mixture may assist the possible combustion of explosion. High concentrations of hydrogen can cause a deficiency of oxygen and asphyxiation is possible. Caution is needed when dealing with hydrogen, since there is no odour warning when toxic concentrations are present. (International Labour Organization 2004b)

5 PYROLYSIS EXPERIMENTS WITH RAPESEED OIL, PALM OIL AND ANIMAL FAT

In addition to the literature examined in this study, laboratory experiments on thermal degradation of rapeseed oil, palm oil and one mixed animal fat was carried out. In this way more information and an own perspective about the subject and about degradation products could be achieved. The purpose of the experiments was to identify and analyze the gaseous, especially hazardous gaseous substances that were formed in the experimental system. Gas samples were taken to be analyzed and the analysis results are reported and discussed in this study. Also liquid products were analyzed and the results are reported, however not discussed in this study.

Thermal degradation experiments were carried out in a reactor system called autoclave that comprises a vessel of 1 litre and a cover flange both made out of stainless steel. The idea of the experiments was very simple: the chosen raw material was heated in the autoclave up to a set temperature. This temperature was maintained for certain amount of time in a certain pressure, gas and liquid samples were taken during the experiment and in the end heating was stopped and reactor was let to cool down. Gas sample was also taken before stopping the heating and after the reactor was cool enough the liquid product was taken out of the vessel to be analyzed.

The thermal degradation experiments were conducted with three raw materials:

- alkali refined rapeseed oil
- refined, bleached and deodorised palm oil (RBD palm oil)
- mixture of crude palm oil (CPO) and animal fat (AF) in ratio 1:1.

These raw materials were chosen, because they are all used in the process of making NExTBL renewable diesel, but in different amounts and in variable forms of purity and treatment. Literature did not report any experiments with animal fats, where all degradation products would have been identified. This is another reason why crude palm oil and animal fat mixture was chosen as one raw material, so that analysis results from the pyrolysis of such oil would be achieved.

Experiment temperature was chosen to be higher than the average operating temperature of hydro treatment reactor, which is 325°C. Temperature of 340°C is the maximum operating temperature in the autoclave. This temperature was used in eight (8) of the experiments. In addition, one experiment was carried out in 325°C so that also the gaseous compounds formed in this temperature could be examined. Overall nine (9) experiments were carried out.

Pressures used in the experiments were 40 bar or slightly below and 1 atm. The higher pressure was chosen, because it is approximately the pressure that prevails in the hydro treatment reactor in the NExBTL process. When experiments were carried out at 40 bar, the autoclave was filled with hydrogen gas (H_2) so that the experiment conditions, in terms of temperature and pressure, would be nearly the same as in the hydro treatment reactor, but in the absence of catalysts. Catalysts were not used in the experiments because the aim was to examine the pyrolysis of the oil in particular. When atmospheric pressure was used in the experiments, they were carried out in air, so that these conditions would be similar to the situation, if a leak occurred in the actual reactor and air would be present.

The first gas sample from the autoclave was taken after the heating period when the wanted temperature was reached. In practice, a few minutes passed by in the reached temperature before the gas and liquid samples were taken. After taking the samples heating was continued for two (2) hours which was chosen according to practical reasons. After longer residence time of two hours another gas sample was taken to examine the components after longer heating time and to be able to compare them with the components of the short residence time, which is the heating period until the wanted temperature was achieved.

5.1 Experimental arrangement

Experimental arrangement is described in figure 14 that shows a schematic figure about the experimental equipment. Though the dimensions are not real (for example the gas bottles are smaller than the reactor vessel of 1 litre), the schematic shows all the instruments that are connected to the system. Only the cooling water circulation is not shown in the figure, but Note 1 informs about its existence.

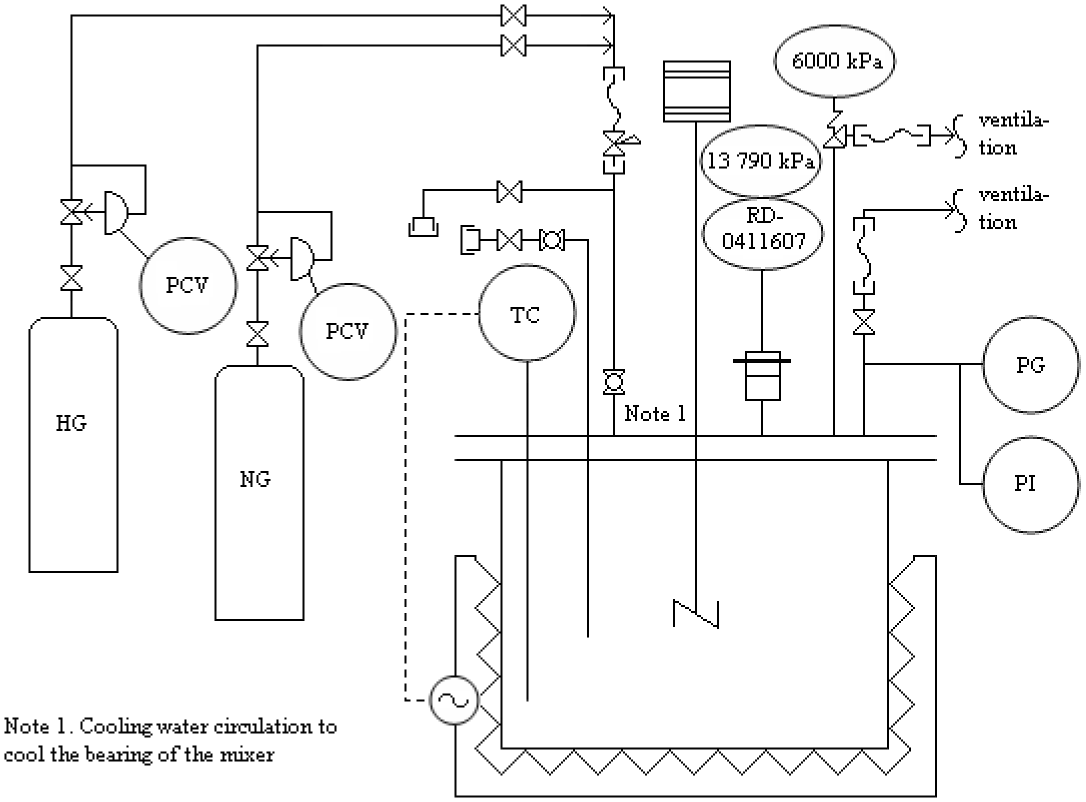


Figure 14. Schematic figure about the experimental equipment used in the thermal degradation experiments.

Figure 15 gives more realistic impression about the equipment and some visible parts of the equipment are pointed in the picture. The gas discharge valve and the rupture disk cannot be seen because they are situated behind the magnetic stirrer. The cooling water flows through the system in white rubber hoses shown in figure 15.

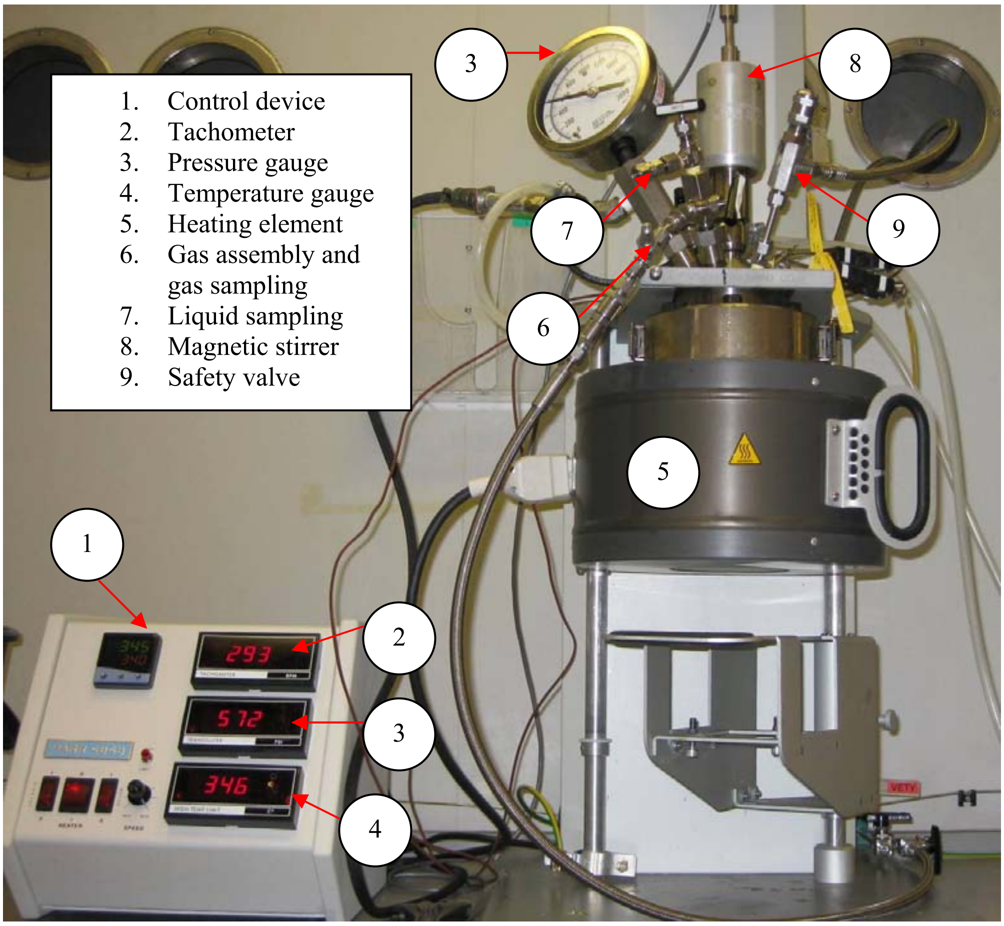


Figure 15. A photograph of the experimental equipment and some of its components.

Number 6 in figure 15 shows the assembly where nitrogen (in the blank experiment) and hydrogen is let to flow inside the autoclave. The air that was used in some of the experiments is not fed from a gas bottle, like nitrogen and hydrogen. The air that stays inside the vessel after putting the test oil in is let to stay there when the cover flange is installed. Comprehensive experimental instructions about carrying out the experiments are shown in Appendix III. In addition, Experiment Matrix about all experiments carried out and their experimental conditions are shown in Appendix IV.

5.2 Analyzing and results

Analysis of gaseous and liquid thermal degradation products were carried out according to figure 16. They were carried out in the analytical laboratory of Neste Oil by laboratory assistants and researchers. All practical experiment work was carried out by the thesis worker. The components of the gaseous phase were analyzed so that hydrocarbons from C_1 to C_9 and inert gases were quantified with gas chromatography and identified with both gas chromatography and mass spectrometry. Four different analyses were carried out for liquid products; gel permeation chromatography, total acid number, iodine value and gas chromatography combined with mass spectrometry.

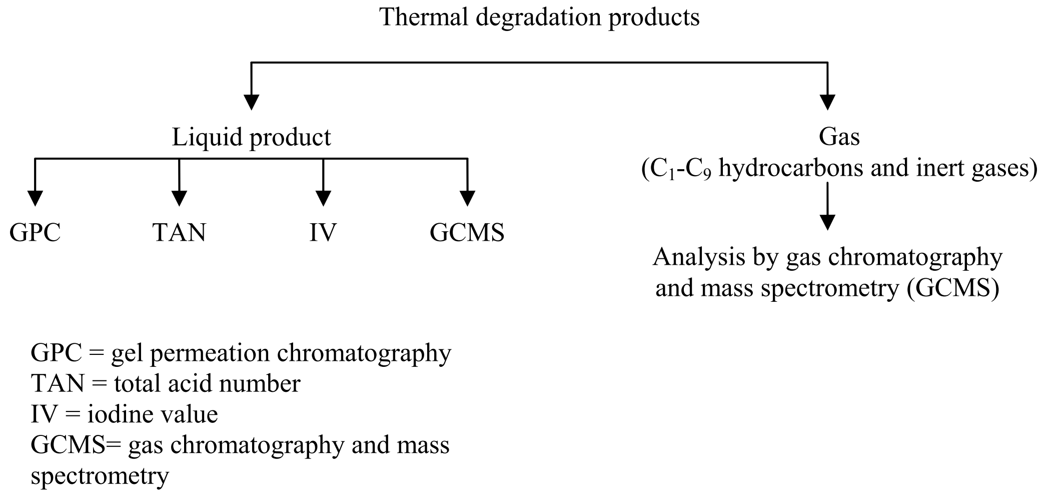


Figure 16. Scheme of the analysis of degradation products of thermal degradation tests.

Gel permeation chromatography (GPC) analysis gives the proportions of triglycerides, diglycerides, monoglycerides, fatty acids, oligomers and cracking products of oil. Total acid number (TAN) determines the amount of acids, in this case the amount of fatty acids, in the sample. Iodine value (IV) determines the amount of unsaturation (double bonds) in fatty acids that are present in the sample. These three analyses were carried out to all oil samples. To determine the fatty acid composition gas chromatography and mass spectrometry (GCMS) were carried out only for the end oil of experiment 5. Because the sample is oil in nature, all of its components are very hard to determine. This is why only one oil sample was analysed with GCMS. The analysis results of TAN, IV and GPC are presented in Appendix V. The research report of fatty acid composition is also presented in Appendix V but in Finnish only. The liquid analysis results are not discussed because they are not the focus of this study.

The gas analysis results of all experiments are presented in Appendix IV, also only in Finnish. Altogether 17 gas samples were analysed and all the compounds of the samples were identified and quantified. Samples were taken and analysed two per experiment with the exception of experiment 2: the analysis of the first sample was failed because the amount of the sample gas was inadequate for complete analysis and only the second sample was analysed. Similarly the first sample of experiment 4 is not totally reliable because the gas run out during analysis and the analysis is not complete.

Table 25 presents the mole percentages of the first gas samples of blank experiment and experiments 1, 3, 5, 7 and 8 that were carried out in hydrogen sphere.

Table 25. The mole percentages of certain categories of compounds in the first samples of blank experiment and experiments 1, 3, 5, 7 and 8.

Group	**Blank ex.**	**Exp. 1**	**Exp. 3**	**Exp.5**	**Exp. 7**	**Exp. 8**
	[mol-%]	[mol-%]	[mol-%]	[mol-%]	[mol-%]	[mol-%]
Paraffins	2,20	3,17	0,57	2,66	3,18	1,25
Olefins	5,36	5,60	0,57	2,44	1,04	1,25
Cyclic compounds	0,62	1,42	0,02	0,15	0,10	0,08
Compounds with oxygen	2,28	2,43	1,36	5,22	4,24	5,01
Hydrogen	0,11	83,68	90,49	86,23	88,25	90,32
Carbon monoxide	1,02	1,75	3,12	0,90	0,00	0,82
Carbon dioxide	0,38	0,48	0,63	0,78	0,25	0,34
Others	88,02	1,46	3,22	1,61	2,94	0,95

Figure 17 elucidates the contents of the table by showing the mole percentages of the groups of compounds in columns. This gives a better understanding about the groups' proportions to each other. As mentioned earlier the first gas samples were taken right after the wanted temperature was reached. As can be seen in the figure the first column consists mostly of nitrogen when other columns consist mostly of hydrogen. In the case of blank experiment the category of ′Others' denote mostly nitrogen. In other experiments it contains all the aromatic hazardous compounds and some other substances. Compounds with oxygen contain acrolein, propanal and acetone, and category of olefins contain 1,3-butadiene of which proportion in all experiments is the lowest of all hazardous compounds.

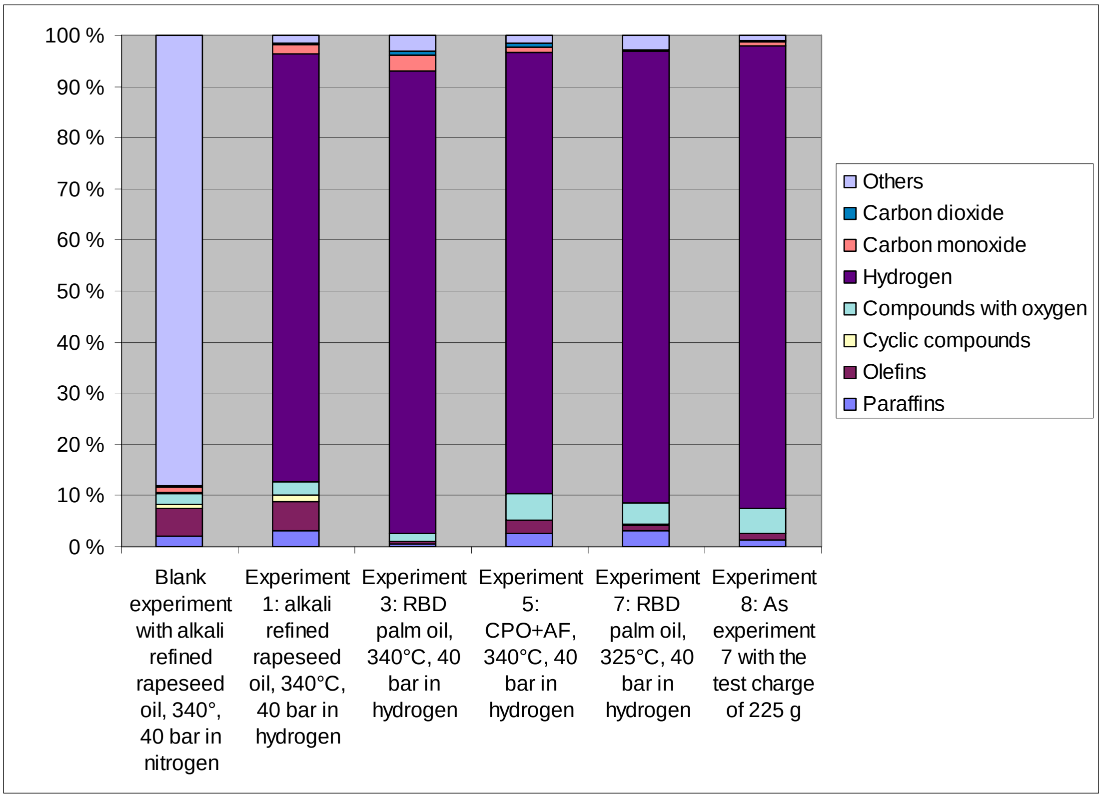


Figure 17. Mole percentages of certain groups of compounds in the first gas samples of blank experiment and experiments 1, 3, 5, 7 and 8.

Table 26 shows the mole percentages of the same categories in the second gas samples of blank experiment and experiments carried out in hydrogen sphere. Second gas samples were taken after two (2) hours counting from the point where the wanted temperature of 340°C or 325°C was reached. Figure 18 elucidates the mole percentages of table 26 with columns.

Table 26. The mole percentages of certain categories of compounds in the second samples of blank experiment and experiments 1, 3, 5, 7 and 8.

Group	**Blank ex.**	**Exp. 1**	**Exp. 3**	**Exp.5**	**Exp. 7**	**Exp. 8**
	[mol-%]	[mol-%]	[mol-%]	[mol-%]	[mol-%]	[mol-%]
Paraffins	6,83	6,18	2,98	5,77	2,04	4,53
Olefins	4,61	3,92	2,00	4,29	2,08	2,66
Cyclic compounds	0,45	0,44	0,25	0,22	0,10	0,56
Compounds with oxygen	0,85	0,78	1,12	1,94	2,33	0,94
Hydrogen	0,52	79,24	82,19	77,91	90,26	79,67
Carbon monoxide	6,94	7,24	8,55	7,13	1,87	7,43
Carbon dioxide	2,35	2,14	2,61	2,18	0,63	4,11
Others	77,42	0,06	0,28	0,55	0,69	0,09

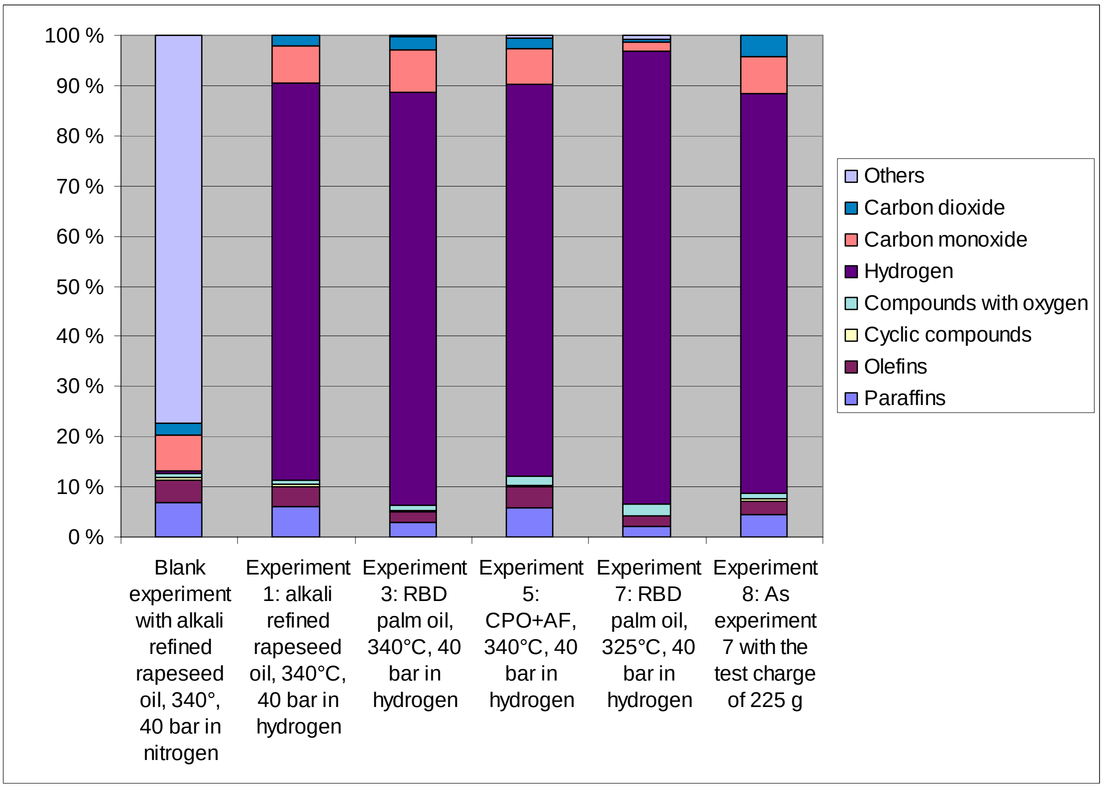


Figure 18. Mole percentages of certain groups of compounds in the second gas samples of blank experiment and experiments 1, 3, 5, 7 and 8.

In the second samples of experiments 1, 3, 5, 7 and 8 the pressure is higher than in the first samples, because the pressure was raised up to approximately 40 bar with hydrogen gas. Table 27 shows the compounds of all the gas samples of experiments carried out with air in certain categories. Because there are only three experiments carried out in air, both first and second gas samples fit into the same figure. Only the second sample of experiment 2 is shown as it was failed, and the first sample of experiment 4 may not be fully reliable. Figure 19 elucidates the mole percentages of table 27 in columns.

Table 27. The mole percentages of certain categories of compounds in all samples of experiments that were carried out in air sphere.

Group	**Exp.2, 2nd sample**	**Exp. 4, 1st sample**	**Exp. 4, 2nd sample**	**Exp. 6, 1st sample**	**Exp. 6, 2nd sample**
	[mol-%]	[mol-%]	[mol-%]	[mol-%]	[mol-%]
Paraffins	6,20	4,34	6,63	3,44	9,89
Olefins	3,81	2,82	3,82	3,03	7,38
Cyclic compounds	0,31	0,10	0,44	0,19	0,27
Compounds with oxygen	0,87	21,49	2,97	6,62	3,28
Hydrogen	5,06	9,50	3,50	2,32	3,56
Carbon monoxide	58,83	4,02	55,75	11,50	54,08
Carbon dioxide	16,43	3,75	17,51	6,59	16,34
Nitrogen	8,41	53,85	9,28	66,10	5,06
Others	0,04	0,09	0,03	0,13	0,07

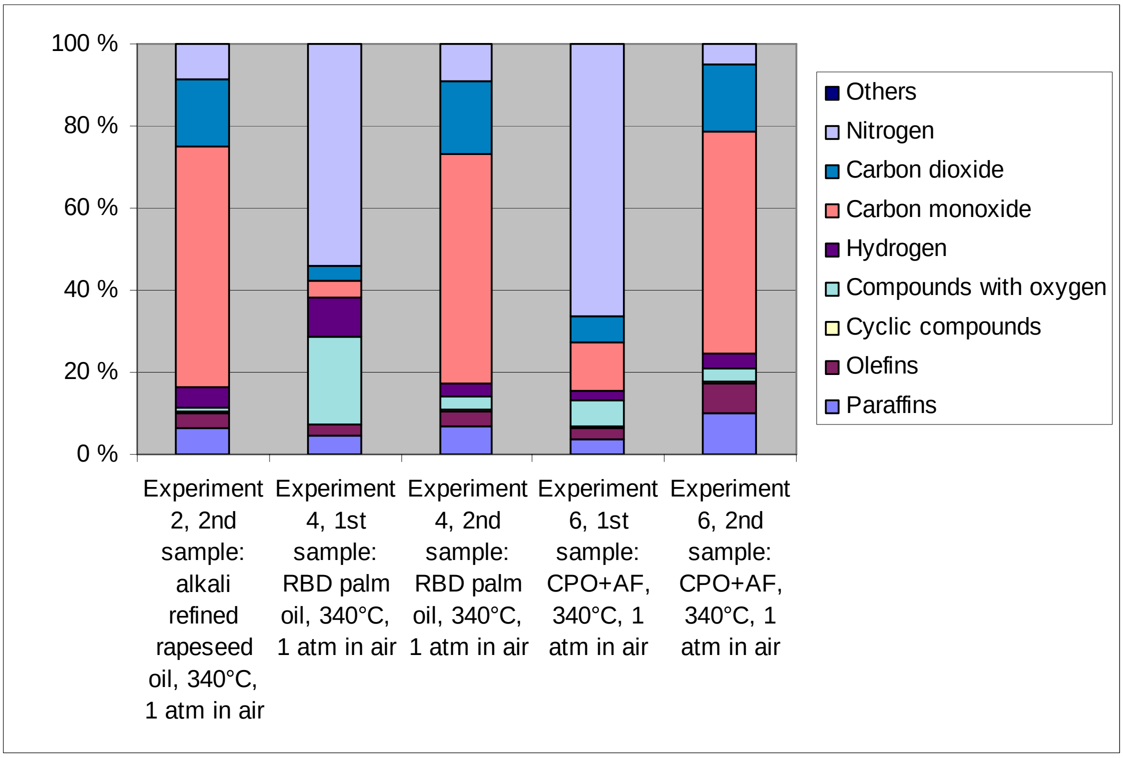


Figure 19. Mole percentages of certain groups of compounds in all the gas samples carried out with air.

From the basis of figures 17, 18 and 19 it can be said that compared to the first gas sample of all experiments the percentage of compounds with oxygen decreased in the second sample. This includes also acrolein. In contrast, in all experiments the percentage of carbon oxides increased in second gas samples, which sounds reasonable because carbon oxides are the products of incomplete combustion. In general, in experiments carried out with hydrogen the percentage of hydrogen decreased in second samples as more degradation products were formed when the residence time was longer.

Only in experiment 7 the percentage of hydrogen increased in the second sample. In experiments carried out with air the percentage of hydrogen decreased in experiment 4 and increased in experiment 6.

The percentage of paraffins increased in second samples in every experiment, except in experiment 7. Also the percentage of olefins increased in the second sample of all experiments except blank experiment and experiment 1. Cyclic compounds increased relatively or their percentages stayed the same in all experiments with the exception of blank experiment and experiment 1. In blank experiment and in those carried out with air the percentage of nitrogen decreased in the second sample. The percentage of ´Others' also decreased in second samples of every experiment.

In all experiments three of the 13 hazardous degradation products prevailed: carbon monoxide, acrolein and propanal (The gas analysis results of Appendix VI). Carbon monoxide prevailed especially in second samples as heating time was longer. Acrolein prevailed especially in first samples, when it had not yet reacted further. Propanal was present quite equally in first and second samples. The formation of hazardous gases, especially acrolein, is discussed in chapters 6.1 and 6.2.

5.2.1 Error sources of gas samples

When empirical information is required and therefore experiments are carried out, always some amount of error is generated. Also the analysis results of the gas samples are not without errors. Gas samples were taken in a temperature of 340°C or 325°C, but the analyses were carried out in a room temperature. This may result in the condensation of heavier compounds (>C_9) on inner wall of the sample cylinder. These compounds need a higher than a room temperature to be in a gaseous form. Hence they may not be all included in the analysis results, and this possibly concentrates the analysis results more than they really are. Also the first sample of experiment 4 may distort and concentrate the analysis result because of its unreliability due to too small amount of analysis gas. In addition, the first sample of experiment 2 was failed to be analyzed and is fully beyond conclusion making.

As different compounds of the gas samples were determined in the laboratory, a particular response coefficient was used for every compound. Unfortunately response coefficients for all compounds could not be found, which induced measurement inaccuracy. One of these compounds was acrolein, and it is estimated by Neste Oil's analytical laboratory that based on the molecular structure of acrolein, the true concentrations of the substance could be even 20 % higher. This means that the amounts of acrolein could be higher than presented in this thesis.

5.3 Calculations of the gas amounts

In the experiments the gas in the reactor is assumed to behave like an ideal gas, and the amount of gas for all nine (9) experiments is calculated by using the equation of a classical ideal gas:

$$pV = nRT \, , \tag{1}$$

where p is the absolute pressure of the gas
V is the volume of the gas
n is the number of moles of gas
R is the universal gas constant
T is the absolute temperature.

Calculated values of gas amounts were used in mass balance determination. Example calculations also help to understand the experiments from the start to the end. In this study the example calculations are done with parameters of experiment 8. The calculations are made according to the points of experiment where a change of state occurs. Figure 20 presents the pressure curve of experiment 8 as a function of time, where numbers from 1 to 5 denote the changing states. Pressure curves of experiments including experiment 8 are shown in Appendix VII. State 1 represents the starting situation, where the initial amount of gas has been added inside the reactor vessel (or left inside in the case of experiments carried out with air) and the warming of the autoclave starts. State 2 denotes the point where the set temperature has been achieved and the samples were taken after this state. State 3 is the point when samples have been taken and the pressure is lower than in state 2. State 4 denotes the point where pressure has been raised up to about 4 000 kPa and state 5 is the point when the residence time of two (2) hours has been achieved. At every changing state the ideal gas equation is used to determine the number of gas moles (n). Through the calculation, the number of added and developed gas moles can be determined. The number of states in experiments carried out in a hydrogen sphere is 5 and the ones carried out in air have 4 stages, because there is no gas input after achieving the set temperature, when air is not added to the system in the middle of the experiment.

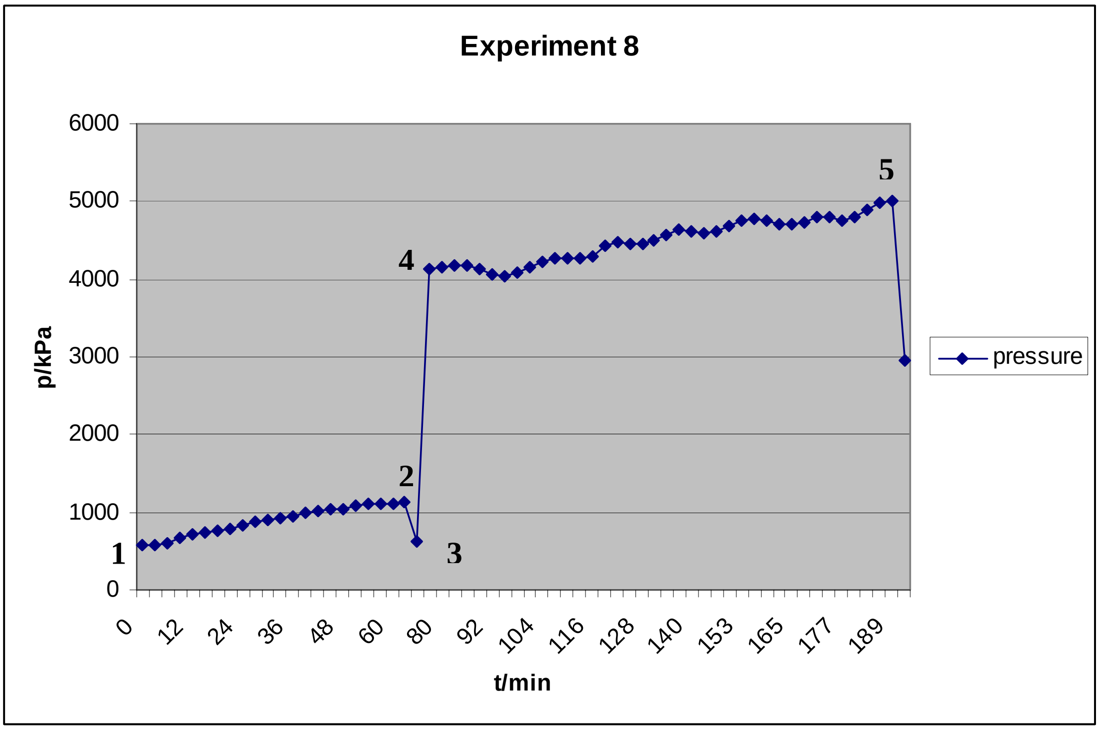


Figure 20. Pressure curve of experiment 8 as a function of time which was carried out with RBD palm oil in 340°C and in 40 bar with hydrogen. Indication of the calculation states are pointed with numbers from 1 to 5.

Every calculation state has its own experiment conditions which are retrieved from the measurement data that is the basis of figure 20 and similar figures in Appendix VII. The example calculation of the gas amounts of experiment 8 is presented in Appendix

VIII. In table 26 of Appendix VIII the numbers of gas moles of all states of every experiment are shown. State 2 corresponds to the situation before the first gas sample is taken, and the gas composition is the same as in the sample. State 4 or 5, depending on whether the experiment is carried out under air or hydrogen, corresponds to the situation before the second gas sample is taken. This state's gas composition is the same as in the second gas sample. As the numbers of moles of the states are known and their composition is known, the molar amounts of the gas components can be determined, when their percentages are shown in figures 17 to 19. Figures 21, 22 and 23 show the molar distribution of groups of compounds in the gas of the autoclave vessel in state 2 and state 4 or 5. Figure 21 shows the molar distribution of state 2 of the experiments carried out in a hydrogen sphere, and figure 22 shows the molar distribution of state 5 for the same experiments. It is important to notice that the scales in all three figures are different as the scale is determined by the molar amounts.

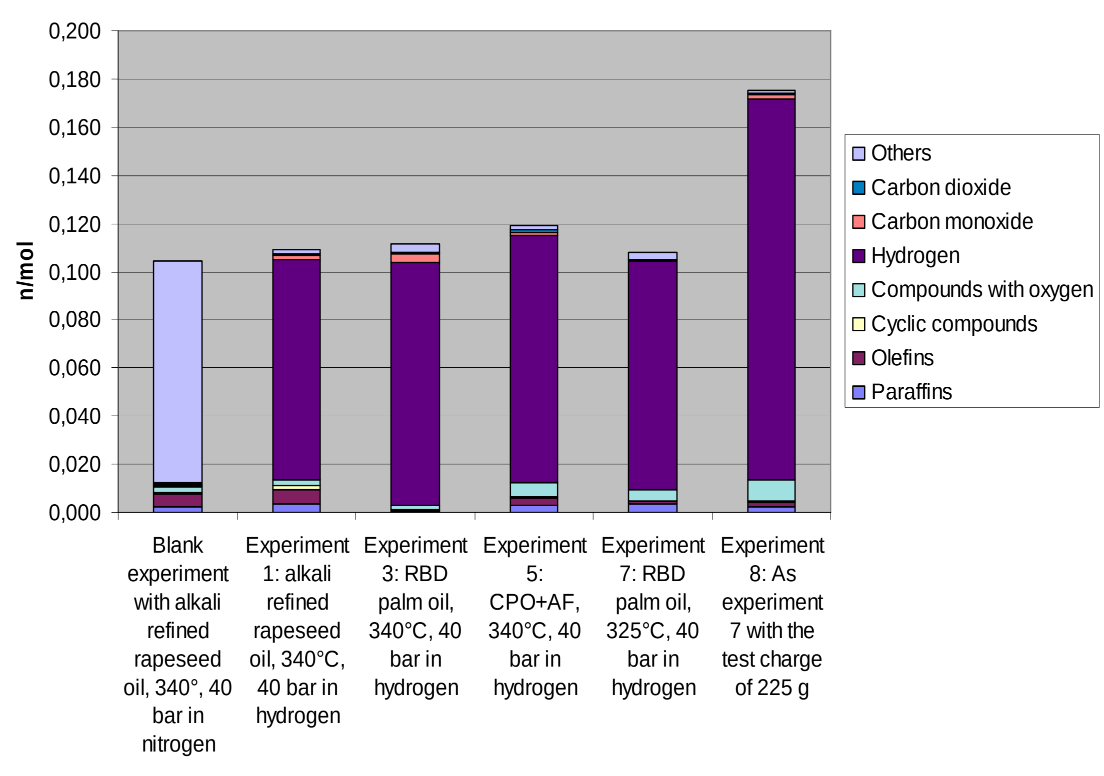


Figure 21. The molar amounts of the pyrolysis gas in state 2 in the blank experiment and in experiments 1, 3, 5, 7 and 8.

Figure 21 shows that in experiment 8 there were more developed gas in state 2 than in other experiments under hydrogen sphere. The gas moles in other experiments seem to be quite of the same scale, which is above 0,10 mol. This molar amount in experiment 8 is 0,176 mol (table 26 in Appendix VIII). Figure 22 shows the same kind of pattern; the molar amounts of state 2 are similar (more than 0,40 mol) in other experiments carried out under hydrogen than in experiment 8 (0,736 mol).

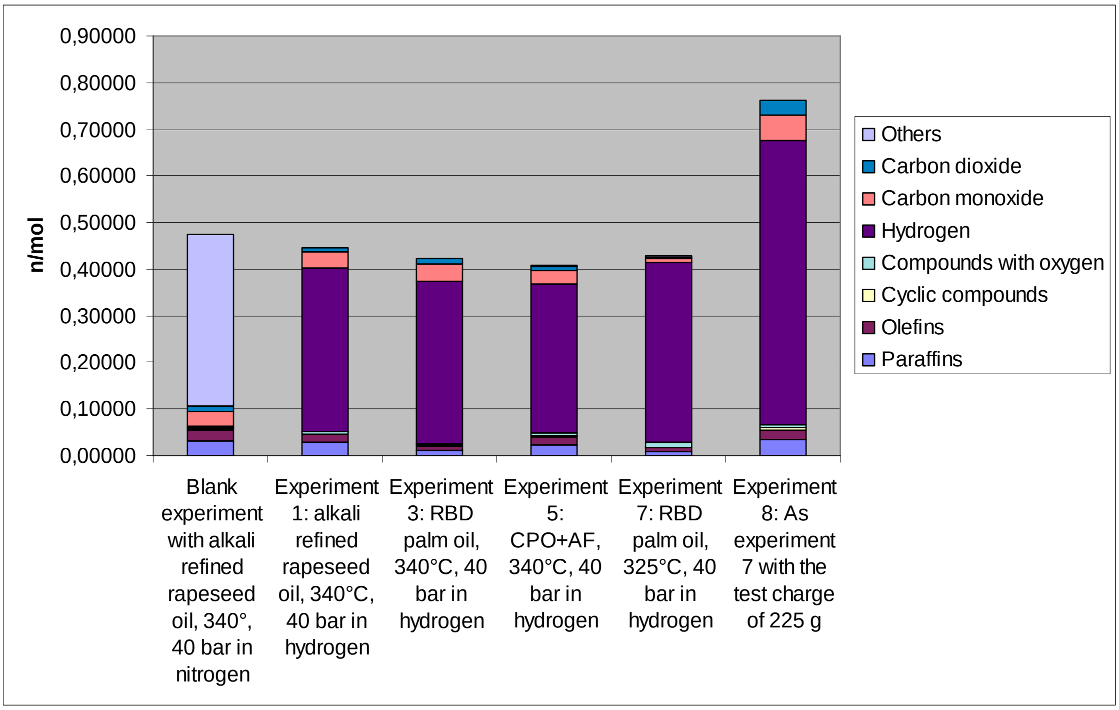


Figure 22. The molar amounts of the pyrolysis gas in state 5 in the blank experiment and in experiments 1, 3, 5, 7 and 8.

Figure 23 shows the molar amounts of the gas in states 2 and 4 of the experiments carried out in air.

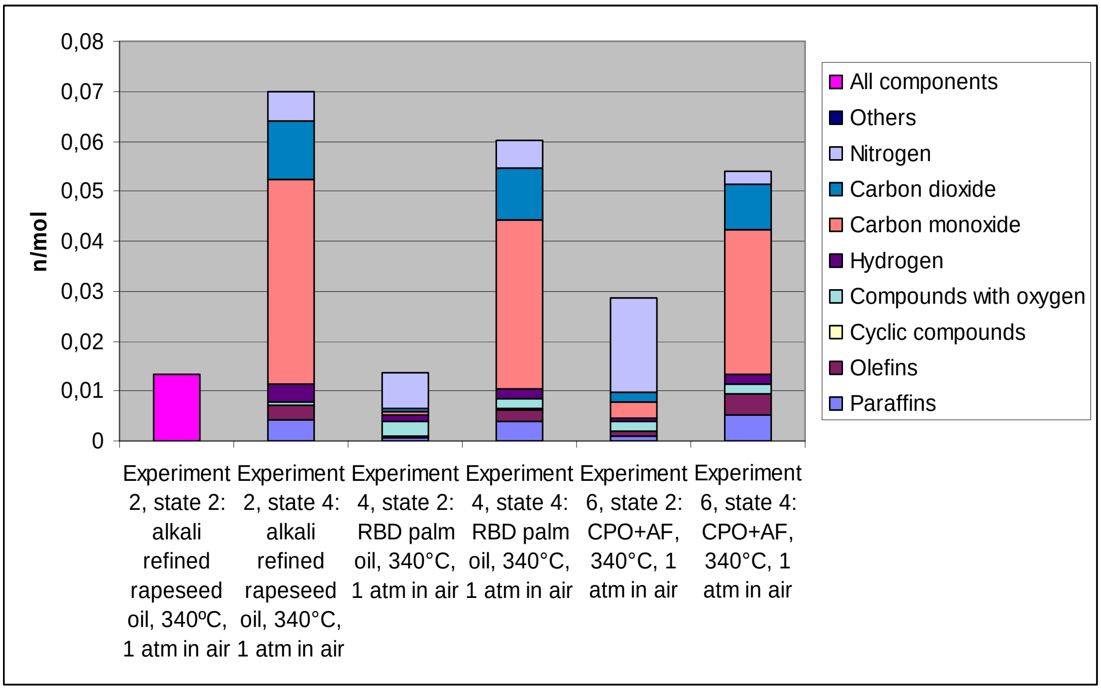


Figure 23. The molar amounts of the pyrolysis gas in state 2 and 4 in experiments 2, 4 and 6.

The molar amount of experiment 2 in state 2 is only showed as a whole. The molar proportions of certain groups of compounds are not known because of the analysis failure of the first gas sample of the experiment. Figure 23 shows that the molar gas amount in experiment 6 in state 2 is higher than the corresponding value in experiments 2 and 4 (both approximately 0,013 mol). When state 4 is compared, experiment 2 has the highest molar gas amount of the three experiments. The differences of the molar amounts in states 2 and 4 or 5 are discussed in the next chapter.

From the basis of the calculation shown in Appendix VIII, the numbers of developed gas moles for experiment 8 and others are presented in table 28. Table shows that the numbers of developed gas moles have been calculated in two different ways. Value n_{dev} was calculated based on the molar balance of the experiment, where the molar amount of added hydrogen into the system (n_{H2}) was subtracted from the sum of n_5 or n_4 (the number of moles in the end) and the molar amount of a gas sample $n_{\mathrm{sample,g}}$ (equation (7) in Appendix VIII). Developed gas $n_{\mathrm{dev1+2}}$ is the sum of n_{dev1} and n_{dev2}. n_{dev1} is the gas development between states 1 and 2 (n_2-n_1) and n_{dev2} is the gas development between states 4 and 5 (or 3 and 4 under air sphere) (n_5-n_4 or n_4-n_3).

Table 28. Numbers of developed gas moles of all experiments.

Experiment	Developed gas n_{dev} [mol]	Developed gas n_{dev1} [mol]	Developed gas n_{dev2} [mol]	Developed gas n_{dev1+2} [mol]
Blank	0,06603	-0,02495	0,08179	0,05684
1	0,31926	-0,02392	0,38427	0,36035
2	0,07458	0,00220	0,06267	0,06487
3	0,03968	-0,02203	0,01501	-0,00702
4	0,06090	0,00173	0,05100	0,05273
5	0,01264	-0,01770	0,03387	0,01617
6	0,06308	0,01284	0,03575	0,04859
7	-0,02409	-0,02571	0,00765	-0,01806
8	0,06036	-0,02795	0,11116	0,08321

The values n_{dev} and n_{dev1+2} should be theoretically the same, but in all experiments the amounts of gas calculated in two ways differ from each other. However, the results are in the same order of magnitude. Only in experiment 3 the results are totally different. In addition, developed gas moles are significantly higher in experiment 1 compared to others. The differences of the results are discussed in chapter 5.3.2.

5.3.1 The differences in the gas moles of states 2, 4 and 5

According to figures 21 and 22 experiment 8 is exceptional in that the molar gas amount is so much higher in both states 2 and 5 compared to other experiments carried out in a hydrogen sphere. Experimental conditions are the same, and experiment 3 is also carried out with RBD palm oil, but its number of gas moles is smaller. The only thing that is different is the amount of oil put into the vessel, since the mass of oil was 450 g in experiment 3 and 225 g in experiment 8. This means that the gas space is larger in the case of experiment 8 in the autoclave vessel, which has enabled the larger number of gas moles. There were also differences between the molar gas amounts in the experiments carried out in air sphere. The fluctuation may be due to small differences in experimental conditions at the time and the errors from the ideal gas assumption used in the calculation.

5.3.2 The differences in amounts of developed gases

Table 28 shows that the results varied to some extent; the largest gas amount was 20 times as much as the smallest. Although the amounts in general are very small and of laboratory scale, still the differences should be explained. The differences may mostly be due to the assumption that the mixture of analysis gas is ideal and that the calculations have been done based on the equation of classical ideal gas. In reality the calculations may be much more complex, some factors may be ignored and this causes error. In experiments 3 and 7 the gas development was negative, which may also be due to the error of using the ideal gas assumption. This could also be an indication of some hydrogen dissolution into the liquid.

5.4 Mass balance

Mass balance is done to the experimental system in order to check whether experiments have been carried out properly. If there are some differences between the start and end situations in mass balance this difference is considered as the error of a single experiment. In reality some error always occurs because so many factors influence on the experimental system.

The mass balance for experiment 8 is shown in table 29. The mass of added hydrogen is the calculated with equation (6) in Appendix VIII. The mass of the liquid discharged out of the reactor system is 178 g which is measured data as are the masses of samples and sample pipe flushing. Mass balances of other experiments are presented in Appendix IX.

Table 29. The mass balance of experiment 8.

	IN [g]	OUT [g]
Liquid oil	225,0	178,0
Added H_2	1,5	-
Samples		
liquid	-	37,3
gas	-	4,2
sample pipe flushing	-	8,2
Altogether	**226,5**	**227,7**

Mass balance shows that there is an error of 0,53 % between the start and end situations. Table 30 presents the errors of other experiments' mass balances. It shows that the error of the mass balance of blank experiment is notably larger than in other mass balances. The mass balance error of experiment 8 is the second most significant after blank experiment and the errors of experiments 5 and 2 are coming after this. Sources of error in mass balance and the differences in errors between different experiments are discussed in the next chapter.

Table 30. Errors in the start and end situations of mass balances.

Experiment	Error [%]
Blank	2,05
1	0,00
2	0,29
3	0,13
4	0,04
5	0,42
6	0,07
7	0,04
8	0,53

5.4.1 Errors of mass balance

In mass balance calculations some divergence between the errors of individual experiments were discovered. Blank experiment which was carried out in a nitrogen sphere had the most significant error (table 30). This may be due to the fact that the mass of added nitrogen was larger compared to the added amounts of air or hydrogen in other experiments, which distorted the mass balance in the starting situation. All in all the errors were quite small with the exceptions of experiments 2, 5 and 8 which had more significant errors in their mass balances (table 30). In the case of experiment

8 it is important to notice that the amount of oil in the experiment was only half of the amount used in other experiments. This means that the error is twice as large compared to the errors of other experiments.

Errors in mass balances show that some inaccuracies occur during carrying out experiments. One possible event where losses of oil are possible is sampling; in few experiments some oil droplets fell on the table, when the sample cylinder was disconnected from the experimental system because of the pressure which was in the assemblies. This may have decreased the amount of oil with one or two grams. In addition, some oil remained inside the connecting pieces of assemblies which were not included in the tare weight of the autoclave, and hence were not included in the mass balance. Also the fact that the scale used to weigh the gas cylinders had only an accuracy of 0,1 g, may cause an error because the accuracy may not be enough since such small amounts are in question. But as mentioned, in general most errors were small and in experiment 1 there was not even a distinguishable error.

6 DISCUSSION

Pyrolysis experiments were carried out and gas samples were analyzed to find out if any hazardous degradation products identified by danger symbols in table 13 in chapter 4 were present in the samples. It turned out that same hazardous pyrolysis products were present in the samples as in the studied literature (the analysis results of gas samples in Appendix VI). All except one substance of the 13 hazardous substances listed in table 13 were identified in the gas analyses: 2-heptanone was not identified in the samples, though five gas samples were identified to contain a ketone of 7 carbons but it was not known which ketone it is. On average every sample contained 10,3 hazardous compounds out of 13. The amounts formed in the experiments are difficult to compare with the literature as experimental conditions of different experiments varied a lot. Comparing of the quantities would require a complete repetition of a particular experiment and this is not the case.

When the first samples of all experiments are compared to the second samples, it seems that the changes have occurred similarly in every experiment, except in blank experiment and experiments 1 and 7 (tables 25 to 27 and figures 17 to 19). Blank experiment and experiment 1 were carried out with alkali refined rapeseed oil, but otherwise experimental conditions were similar as in other experiments carried out in a hydrogen sphere. This indicates that the used oil may have an impact on the experiments. The effect of the characteristics of the oil on pyrolysis is also supported by the literature (Dandik et al. (1998) and Schwab et al. (1988)).

Experiment 7 was carried out with RBD palm oil but in 325ºC instead of 340ºC. This indicates that the used temperature may also have an impact on the pyrolysis of triglycerides. Additionally, time may be one factor as well, because the heating period and the residence time of two hours were shorter than in other experiments, because less time was needed to gain the temperature of 325ºC than 340 ºC. Unfortunately only experiment 7 had a different temperature than others and this may not be enough to show the connection between temperature and pyrolysis products. However, according to Crossley et al. (1962) gross pyrolysis starts at a temperature of 300ºC so this gives some kind of indication about the influence of temperature on pyrolysis.

One factor that impacts on a reaction and reaction products is pressure. In the experiments under hydrogen sphere the pressure in the beginning of heating period was about 5 bar. After taking the first samples pressure was raised up to 40 bar with a hydrogen gas. However, due to the arrangement of experimental system, the set pressure of 40 bar was not easily achieved. The pressure in the beginning of 2-hour heating time varied between 36 and 41 bar in the experiments. This can be seen in the pressure curves of Appendix VII. If pressure has an influence on the reaction products, the pressure fluctuation in the experiments is one uncertainty factor.

Of the 13 hazardous degradation products carbon monoxide, acrolein and propanal were formed the most. The amounts of carbon monoxide increased in the second sample of all experiments. This makes sense as residence time was longer and no oxygen was present or it had run out. When the hazardous nature of these three compounds are compared, acrolein is the most harmful as its occupational exposure limit of 0,1 ppm is the lowest (chapter 4.1.1). Of all 13 hazardous degradation products benzene is the second most harmful substance having an occupational exposure limit of 2,5 ppm (chapter 4.1.2). In the experiments the formed amounts of benzene were so minor compared to acrolein formation that benzene is not the main concern.

6.1 The factors having an impact on acrolein formation

In general, first samples of all experiments included proportionally more acrolein than second samples. This is logical because acrolein is known to be highly reactive substance and it does not persist very long times. Relatively smaller amounts of acrolein in second samples indicate that acrolein has reacted further after the two-hour continued heating time. In many experiments (blank experiment and experiments 1, 3, 5 and 7) the amount of acrolein relatively decreased as the amount of propanal relatively increased. There may be a relation between these two substances in some of the experiments because Murillo & Chen (2008) have proposed that one pathway to hydrogenate acrolein is through propanal formation.

In order to understand why acrolein is formed in considerable amounts in some of the pyrolysis experiments, the factors that influence on the formation of the substance have to be examined. It appears that one factor is time. An evidence of this is that the proportion of acrolein decreases in the second gas samples, when in the first samples the proportion can be very remarkable. Figure 24A shows the mass fraction-% of acrolein and figure 24B the acrolein amount in moles of each experiment's gas phase carried out with air or hydrogen as a function of time.

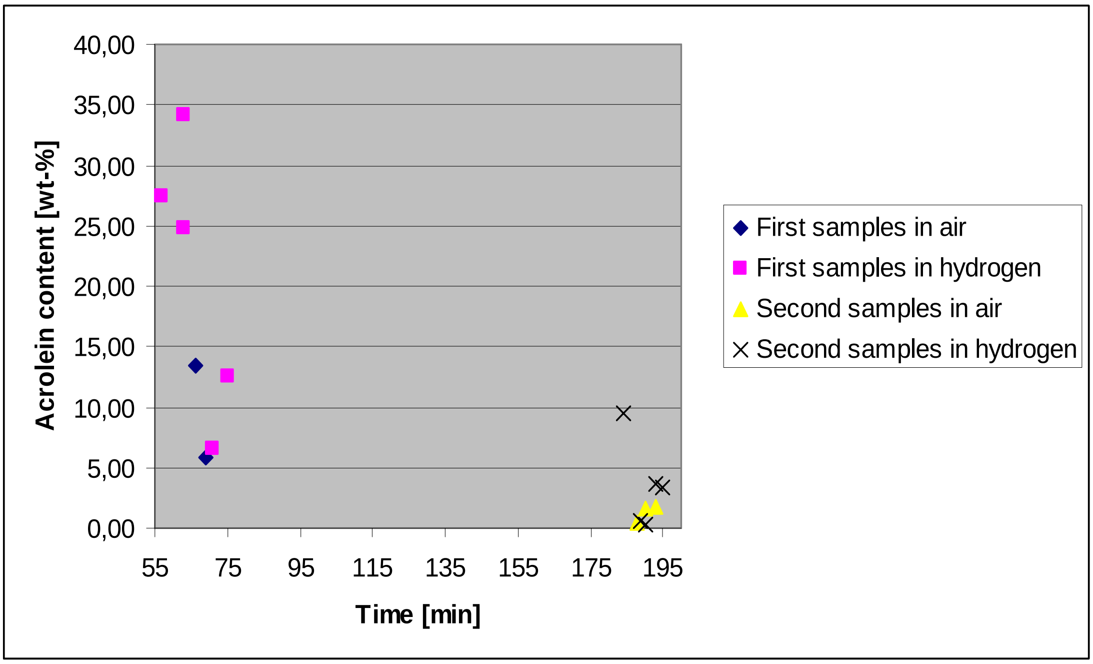


Figure 24A. Mass fraction-% of acrolein in the first and second gas samples as a function of time of the experiments.

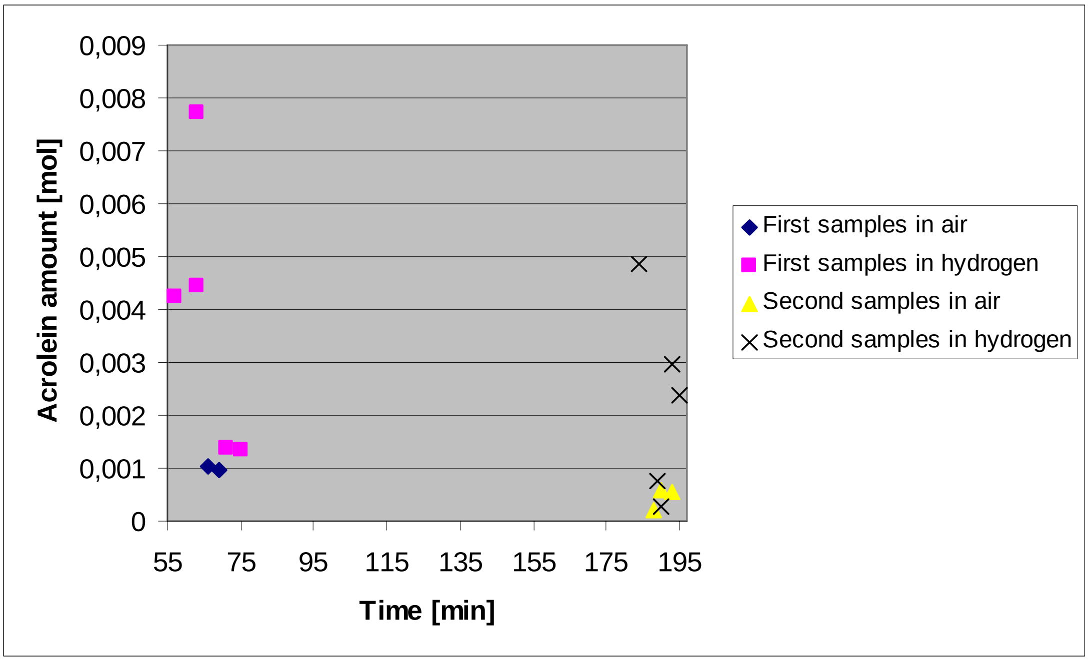


Figure 24B. Acrolein amount in moles in the first and second gas samples as a function of time of the experiments.

In the case of first samples the time is the heating time which was needed to achieve the wanted temperature of 340ºC or 325ºC. In the case of second samples the time is the heating time plus a residence time of two hours when temperature was kept the same. Figure 24A shows that acrolein content in the gas space of the autoclave vessel has decreased notably after two hours of further heating. In figure 24B the unit of acrolein is the number of moles and it is more absolute. The decrease of molar acrolein amounts is not so notable, but a particular direction towards decreasing can be observed.

Further examining of the analysis results show that second factor that has an effect on acrolein formation is oil. The oil used in the experiments appears to have two factors that impact on acrolein formation; the amount of triglycerides and the length of fatty acid chains in a triglyceride molecule of the oil. In addition, another factor is apparently the sphere where the experiments are carried out. Figures 25 and 26 elucidate the impact of these factors. The information in the figures is based on the analysis results of gas samples of Appendix VI and the liquid GPC-analysis results presented in tables 3 and 4 of Appendix V. In the case of the first gas samples, triglyceride contents in the beginning of the tests are used, and in the case of the second samples, the triglyceride contents in the beginning of the 2-hour heating period are used.

In the figures acrolein formation rate is described as a function of glycerides and they are identical except the categories of series are different. Figure 25 distinguishes the types of oils used, and whether a first or a second sample is in question. Figure 26 also separates the first and second samples, but it also separates the samples based on the sphere where the experiment was carried out. Figures show also the influence of time as the acrolein formation of second samples is smaller compared to first samples, as shown in figures 24A and 24B above.

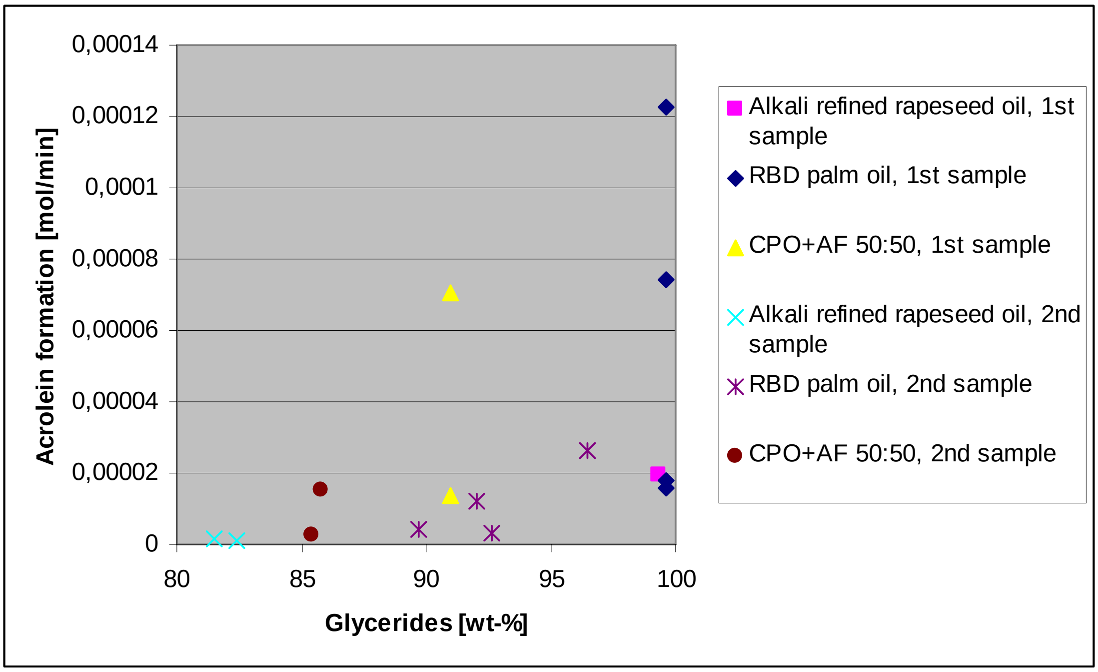


Figure 25. Acrolein formation rate as a function of mono-, di- and triglycerides present in the used oil.

Figure 25 shows that the first samples of palm oil and crude palm oil-animal fat-mixture (CPO+AF) have the highest acrolein formation rates. Acrolein formation is lower in rapeseed oil samples, especially in the second samples of which the glyceride content is the lowest of all. When figures 25 and 26 are examined as a whole, one can notice that the higher is the content of glycerides in the oil, the higher is acrolein formation rate.

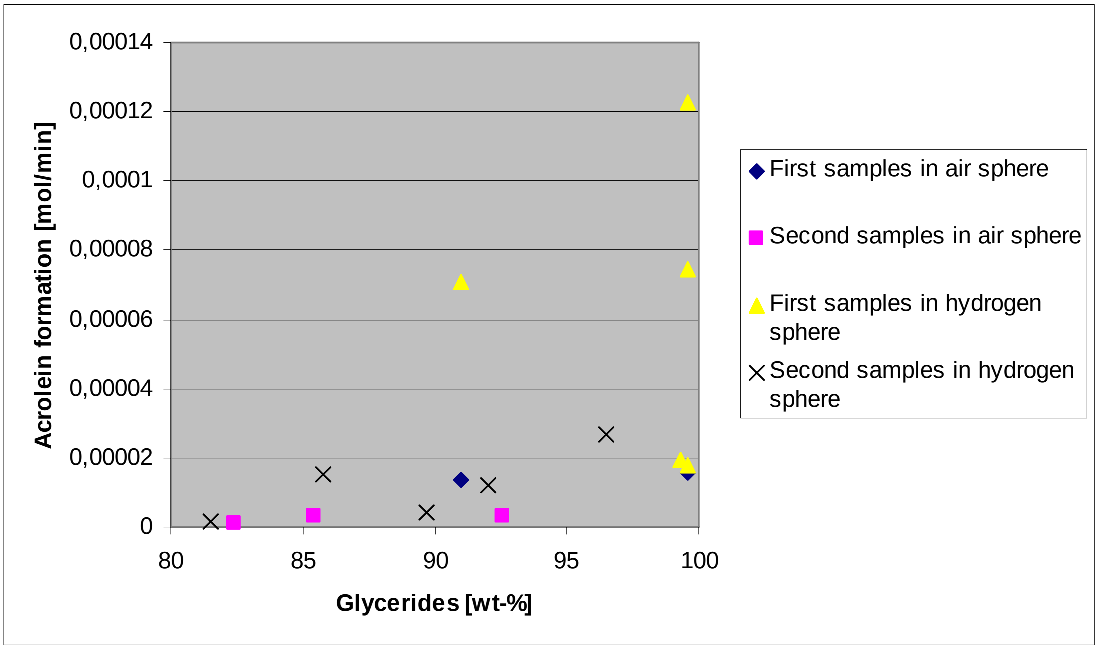


Figure 26. Acrolein formation rate as a function of mono-, di- and triglycerides present in the used oil. The categories of series are different from figure 25.

However, all samples in the figures can not be explained only by the glyceride content, because all sample results do not follow the logic that the more glycerides in the oil the higher is the acrolein formation rate. Such sample is especially the first sample of rapeseed oil (figure 25). It has high glyceride content but acrolein formation is low compared to other two oils. In my opinion this is because rapeseed oil has a very different fatty acid structure in the triglycerides than palm oil or animal fats. Table 31 presents the fatty acid compositions of palm oil and rapeseed (Canola) oil which are retrieved from literature. Fatty acid composition of animal fat used in the experiments is difficult to determine because the composition varies and it may be a mixture of different animal fats.

Table 31. Fatty acid composition of palm oil and rapeseed (Canola) oil (Basiron 2005, 340; Przybylski et al. 2005, 64).

	% of total	
Fatty acid	**Palm oil (Malaysia), mean**	**Rapeseed (Canola) oil**
12:0	0,23	-
14:0	1,09	0,1
16:0	44,02	3,6
16:1	0,12	0,2
18:0	4,54	1,5
18:1	39,15	61,6
18:2	10,12	21,7
18:3	0,37	9,6
20:0	0,38	0,6
20:1	-	1,4
22:0	-	0,3
22:1	-	0,2
24:0	-	0,2

In the case of palm oil and rapeseed oil table 31 shows that the fatty acid compositions differ greatly from each other; palm oil has a much larger proportion of shorter chained fatty acids while majority of fatty acids in rapeseed oil are longer chained fatty acids. In rapeseed oil the proportion of glycerol skeleton in glycerides and in oil is lower than in palm oil, which means that structurally more acrolein can be formed from palm oil, because acrolein is formed from the glycerol skeleton of a mono-, di- or triglyceride. The mechanism of acrolein formation from the glycerol skeleton hardly changes between different oils, so the fatty acid structure of triglycerides present in oil impacts on acrolein formation through the relative amount of glycerol.

Figure 26 shows that experiments that were carried out in hydrogen, they mostly have a higher acrolein formation in their samples. In some of the second samples the formation of acrolein is even higher, than the formation in the first samples of air sphere. In figure 25 two first samples of RBD palm oil (pink dots, these are experiments 3 and 4) have lower formations of acrolein than other two palm oil samples (these are experiments 7 and 8). Experiment 4 was carried out with air, so its acrolein formation rate is lower. But experiment 3 was carried out in a hydrogen sphere, and still its acrolein formation is lower, than that of a first sample of rapeseed oil from an experiment that was carried out with air (illustrated in figure 26). A question rises why the first sample of experiment 3 does not have acrolein formation rate as high as the first samples of experiments 8 and 7. This could be explained partly by the influence of time. When comparing the heating periods of these three experiments there are differences in them. Experiment 3 had the longest heating period of all nine experiments being 75 min, as those of experiments 8 and 7 were 63 min and 57 min, respectively (the times of heating periods are retrieved from the measurement data). This means that heating of RBD palm oil in experiment 3 has continued 12 and even 18 minutes longer than the heating in experiments 8 and 7. Figures 24A and 24B show that time has an impact on acrolein formation, and on the basis of experiments 3, 7 and 8, the differences in the formation rate can be noticed within 15 minutes or even less.

Experiment 8 was a repetition of experiment 3, where only the amount of oil was different (half of the amount of other experiments). The aim to carry out experiment 8 was to achieve a shorter heating period. This was achieved as explained in previous chapter. Experiment 7 was also a repetition of experiment 3, with the exception of the set temperature which was 325°C. According to figures 21 and 22 on pages 72 and 73 the molar amounts of gas in states 2 and 5 were the highest in experiment 8 of all experiments. This is due to the larger gas space in the reactor vessel. Also the molar amount of added hydrogen is higher than in other experiments.

The largest amount of acrolein was formed in the first sample of experiment 8 that was carried out in a hydrogen sphere at 340ºC with RBD palm oil. This sample had also the highest percentage of acrolein (table 21 in Appendix VI). This experiment seemed to have all the requirements that were needed to gain the highest proportion of acrolein of the nine (9) experiments; certain kinds of oil characteristics, hydrogen sphere and short heating time. The lowest proportion of acrolein in the experiments was not so obvious: the lowest acrolein formation was in the second sample of either blank experiment or experiment 1 depending on the unit used (wt-% or mole-%).

The oil characteristics as one factor influencing on acrolein formation are already supported by the literature in this study. In chapter 3.2.2 Kitamura (1971) concluded that the pyrolysis products are different when oxygen is present compared to the situation when oxygen is absent. To some extent this supports the idea that the sphere does matter in acrolein formation. Though none of the experiments of the literature presented in this study were carried out in a hydrogen sphere, but many were carried out under nitrogen or air. When examining the impact of residence time in the literature, Umano & Shibamoto (1987) concluded in chapter 3.3 that the longer corn oil was heated the more acrolein was formed at 300ºC. This conflicts with the conclusion of this study that the shorter the residence time, the more acrolein is formed. Umano & Shibamoto (1987) carried out this particular experiment in a nitrogen sphere which is an inert gas. As only blank experiment of the experiments related to this thesis was carried out in a nitrogen sphere it is not enough to make any deductions to one direction or another. In addition, the temperature was lower (300 ºC) in the experiment of Umano & Shibamoto (1987) than in blank experiment (340 ºC) and the influence of temperature could not be examined more closely because only one experiment was carried out in a different temperature than others.

6.2 Other hazardous degradation products

While the factors influencing on acrolein formation are widely discussed in previous chapter, the formation of other hazardous gaseous degradation products of plant oils and animal fats is only discussed shortly. This is because acrolein was stated to be the most hazardous gas in the context of this study. Additionally, this study was carried out within the frames of master's thesis, so examining the factors having an effect on the formation of all other 12 hazardous compounds would expand this study too much.

However, a couple of factors were noted to have an impact. Time seemed to be one factor that has an impact on other hazardous compounds: the proportion of aromatic hydrocarbons and 1,3-butadiene decreased in the second samples, though some of them were not always even present in the first samples (Appendix VI). Also carbon monoxide formation was influenced by residence time; the proportion of carbon monoxide increased the longer the residence time (figures 17 to 19). In addition, there seemed to be a potential factor for the formation of aromatics: theoretically rapeseed oil, that has more unsaturated fatty acids, has more potential to form aromatic compounds as the double bonds of the fatty acids enable benzene ring formation. This is supported by Idem et al. (1996, 1156) who stated that formation of aromatics is possible from linolenic acid which contains three double bonds. Rapeseed oil contains 9,6 % of linolenic acid according to table 31.

6.3 Further study

One objective of this master's thesis was to achieve more understanding about thermal degradation of plant oils and animal fats. A good deal of understanding was achieved from acrolein, its formation and the factors that impact on its formation. However, one very potential factor temperature was not examined enough in this thesis. That is why more thermal degradation experiments should be carried out in different temperatures in order to find out in which temperature acrolein formation starts and in which temperature it is the highest. This should be studied in similar experimental conditions where the experiments of this thesis were carried out. Especially when literature did not report any experiments carried out with hydrogen, own empirical knowledge in a hydrogen sphere is needed more. Additionally, pressure is known to have an impact on reactions. In own thermal degradation experiments pressure was not a variable. This is why also the influence of pressure on pyrolysis products should be examined.

In this thesis time was concluded to be one factor to influence on acrolein formation in the pyrolysis of triglycerides. However, time as one factor is not a simple issue. This is why further study should also concentrate on examining the reaction kinetics of acrolein. Additionally, the influence of catalytic action on acrolein formation is worth studying.

There is also a need for another subject of further study. If a leak occurred in the hydro treatment reactor, also the hazardous gases including acrolein would spread into the atmosphere. This dispersion of gases should be studied with the help of a dispersion model that would give an impression about the impacts of a leak of certain scale.

Dispersion models are used in order to understand individual atmospheric processes such as chemistry, transport and removal of substances. They help to integrate individual atmospheric processes so that their interactions can be studied. Mathematical equations of dispersion models describe the atmosphere, dispersion as well as chemical and physical processes in a certain space to calculate concentrations of a compound in different locations. A dispersion model can include descriptions of emission patterns, chemical transformations, meteorology and removal processes as the tools to describe the atmosphere. (Holmes & Morawska 2006, 5902; Seinfeld & Pandis 2006, 1092)

The gas formed in the thermal degradation of plant oils and animal fats is composed of various compounds and therefore it is not easy to model its dispersion. Computational fluid dynamic models (CFD-models) carry out complex analysis of fluid flow that is founded on conservation of mass and momentum. This is possible by resolving the Navier-Stokes equation that uses finite difference and volume procedures in three dimensions. (Holmes & Morawska 2006, 5909) CFD-model could be potential in modelling the dispersion of such a complex mixture of gas as a pyrolysis gas is. Perhaps this model could also be used to examine aerosol formation of the 13 hazardous substances, because if some proportion of the emissions forms aerosols it changes the dispersion and the characteristics of the gas cloud.

A dispersion model needs a lot of initial data to model such a complex mixture of compounds. These data among others are the composition of a dispersing gas, and some physical and chemical properties of the substances in the gas mixture. Usually these properties are already found from the databank of the model, unless a very unusual substance is in question. Also temperature and pressure of the dispersing substance in the initial point of dispersion is usually needed. When a proper dispersion model has been found to evaluate the impacts of the pyrolysis gas dispersion, the composition of a dispersing gas could be retrieved from the gas analysis results of the experiments carried out in this study. The hazardousness of the gas cloud could be determined in such a way that the hazardous degradation products would be the concern considering the spreading of the cloud.

7 CONCLUSIONS

This master’s thesis aimed to add more understanding about thermal degradation of plant oils and animal fats, and to identify possible gaseous hazardous compounds that are formed when these materials degrade thermally. The literature studied in this master’s thesis showed that thermal degradation of triglycerides is complex, and because plant oils and animal fats as raw materials are new compared to the conventional mineral based oils, more information is needed. Thermal degradation of triglycerides is different compared to that of mineral based oils, because of the mono-, di- or triglycerides which are not present in the fossil raw material.

In this thesis the mechanisms of the pyrolysis of triglycerides presented in literature were examined. The earliest researchers proposed a mechanism for thermal degradation of saturated triglycerides were Chang & Wan (1947). Their mechanism included 16 reaction equations that explained the decomposition of particular groups of compounds that originated from triglycerides containing saturated fatty acids. Much later Alencar et al. (1983) presented their own mechanism also for saturated triglycerides that was based on Chang & Wan’s (1947) equations. After this Schwab et al. (1988) stated their mechanism for thermal degradation of unsaturated triglycerides and Idem et al. (1996) presented their mechanism for both saturated and unsaturated triglycerides. The mechanisms do not exclude one another, but more like support each other, and the later ones are based on the equations of Chang & Wan (1947). The most complex mechanism was proposed by Idem et al. (1996). The proposed mechanisms are rational and applicable, but the one of Idem et al. (1996) requires a lot of understanding and knowledge of chemistry.

Based on the literature studies, the hazardous gas compounds of the pyrolysis of plant oils and animal fats were determined. *13 different hazardous substances were found* and as expected one of them was acrolein. In addition, six aromatic compounds, one olefin, two ketones, carbon monoxide, propanal and hydrogen were found to be hazardous. Based on its toxicity, acrolein turned out to be the most hazardous compound of all 13 substances. It also seems to be quite common pyrolysis product, because many studies reported about its formation.

In order to get an own perspective about the subject, thermal degradation experiments were carried out as a part of this thesis. In general, there were some differences between the gas analysis results. It seemed that these differences occurred due to the impact of *temperature, time and the characteristics of the oil used.* These factors influencing the pyrolysis products of the oil are supported by Dandik et al. (1998) and Idem et al. (1996). The thermal degradation experiments confirmed that at least 12 hazardous pyrolysis products do form and their existence is not only based on literature studies. While *acrolein* proved to be the most toxic of all, its amounts in the experiments carried out in the autoclave were also notable.

Largest acrolein amounts were formed with palm oil that was heated in 340ºC at a pressure of 40 bar, and under hydrogen sphere. The proportion decreased as heating was continued, and one factor impacting on the formation of acrolein and also other hazardous substances was concluded to be time. Also sphere and the characteristics of the oil had an impact on acrolein formation, but these factors may not be applicable to the formation of other 12 substances. The specific oil characteristics that had an influence on acrolein formation were the content of triglycerides in the oil, and the length of fatty acid chains that are attached to glycerol. Based on the experiments that were carried out rapeseed oil seemed to be the ´safest’ oil to be pyrolized if acrolein formation would be considered as a danger.

The literature and the thermal degradation experiments with autoclave showed that hazardous pyrolysis products are formed and acrolein is one of them. However, it is important to remember that pyrolysis was generated on purpose in the experiments with the autoclave. In the hydro treatment reactor of NExBTL-process other strictly controlled reactions prevail, and oxygen is pursued to remove totally in this reactor so that no undesirable substances can be formed. When oxygen is removed no acrolein can be formed either. Yet, theoretically there is a possibility that the hydrogen feed is lost for some reason or a leakage to the atmosphere occurs. Then process conditions are abnormal and the formation of hazardous compounds is possible. In this situation these substances including acrolein can pose a threat of some level. Especially in a leakage situation, if hot pyrolysis gas is released into the atmosphere, their behaviour may be difficult to determine. This is because the pyrolysis gas of plant oils and animal fats consists of many compounds which may also form aerosols. Impacts of aerosols shall be considered separately.

The gas analysis results of the pyrolysis experiments are not readily applicable to a large scale hydro treatment reactor. NExBTL process is based on other reactions than pyrolysis and do not maintain thermal degradation in the normal process conditions. In addition, catalytic action may or may not have an impact on the formation of hazardous compounds in abnormal conditions. The influence of catalysts to acrolein formation was not examined in the experiments with the autoclave. That is why it is suggested as one subject of further study.

To answer the question posed in chapter 1.2, hazardous degradation products, especially acrolein, can be formed in considerable amounts. Fortunately, acrolein is very reactive and tends to react further for example into propanal or 1-propanol (Murillo & Chen 2008, 919) which are less harmful than acrolein itself but yet not harmless. In addition, the proportional amounts of the hazardous substances are likely to be smaller than in the pyrolysis experiments with autoclave, because it was designed to develop experimental conditions that are favourable to thermal degradation. To find out more about the influence of hazardous substances in the hydro treatment reactor, further study subjects are suggested in chapter 6.3.

8 SUMMARY

This master's thesis was carried out as a part of Neste Oil's NExBTL renewable diesel-research program. To ensure that environmentally friendly traffic fuels can be produced, the raw materials must be of organic origin and carbon neutral. Neste Oil has introduced plant oils and animal fats as raw materials for making NExBTL renewable diesel. The objective of this thesis was to examine the thermal degradation of these organic oils and fats, and to identify the possible hazardous substances that are formed in their degradation. To achieve the objective a comprehensive literature survey and own thermal degradation experiments were carried out.

Plant oils such as palm oil, soy bean oil and rapeseed oil, and animal fats such as tallow and lard are used in the making of biodiesel, which is the commonly used name of a traffic fuel made of organic raw material. Rapeseed oil is the main raw material in Europe, but also the use of soy bean oil and especially palm oil has increased in the production of biodiesel. Plant oils and animal fats consist mostly of triglycerides that are large molecules where three fatty acids are attached to glycerol with ester bonds. They also contain some proportions of mono- and diglycerides, free fatty acids and minor compounds such as tocopherols.

As a part of the literature survey, the mechanisms of the pyrolysis of triglycerides were examined in this study. Mechanisms for saturated and unsaturated triglycerides were proposed separately, and later the mechanism for both saturated and unsaturated triglycerides were presented together. The pyrolysis of triglycerides is complex because so many compounds can be formed via different reaction paths. The studied mechanisms were rational and usable, but the last mechanism presented in this study proposed by Idem et al. (1996) was very complex and requires a good understanding of chemistry. Also the thermal degradation of some particular triglycerides and formation of aliphatic aldehydes such as acrolein were examined. All in all, many kinds of pyrolysis products were reported in the literature as follows: carboxylic and fatty acids, ketones and ketenes, aldehydes, alkanes, alkenes, light hydrocarbon gases, alcohols, carbon oxides and cyclic hydrocarbons. Generally the researchers carried out experiments and explained the formed pyrolysis products with the proposed pyrolysis mechanism.

The hazardous pyrolysis products were retrieved from the pyrolysis products reported in the studied literature. The identification was done with the help of hazardous labelling symbols that are used in the European Union and its Economic area and in some other countries. Substances labelled as toxic, harmful, irritating, flammable or environmentally dangerous were denoted as hazardous. Altogether 13 hazardous gaseous thermal degradation products of plant oils and animal fats were found. When comparing these 13 substances, acrolein had the lowest occupational exposure limit which was 0,1 ppm.

As a part of this master's thesis, thermal degradation experiments were carried out with RBD palm oil, alkali refined rapeseed oil and with a mixture of crude palm oil and animal fat. The experiments were carried out to retrieve own results and perspective to the pyrolysis of the used raw materials. In addition, none of the studies in the examined literature reported any experiments carried out in a hydrogen sphere. Because hydrogen is used in the hydro treatment reactor of NExBTL-process, own laboratory scale experiments in hydrogen seemed useful. Also some experiments were carried out in air for comparison, and the blank experiment was carried out with nitrogen. All the experiments were carried out in a system called autoclave that comprised of a vessel of 1 litre and a cover flange that were both made of stainless steel. The temperature used in the heating was 340ºC or 325ºC and the pressure was approximately 40 bar (in a hydrogen sphere) or 1 atm (in air experiments).

Gas and liquid samples were taken during the experiments and they were analyzed in the analytical laboratory of Neste Oil. Because this master's thesis concentrated on the gaseous degradation products, the liquid analysis results were not discussed. Similar gaseous pyrolysis products as in the literature were discovered, and 12 out of 13 hazardous compounds were reported in the experiments. Most predominant of them in all nine (9) experiments were acrolein, carbon monoxide and propanal. Based on its toxicity and the notable amounts formed in the experiments, acrolein was concluded to be the most hazardous degradation product.

The gas analysis results show different component proportions in each test run. This was concluded to be possibly due to the differences in oil, the used temperature and the heating time. Also literature supported these conclusions. Acrolein formation was examined more thoroughly as it turned out to be hazardous. The factors that had an influence on acrolein formation rate were heating time, the sphere where the experiment was carried out and the characteristics of the used oil. Two characteristics of the oil were examined to have an effect; the content of glycerides (the more glycerides the higher the acrolein formation rate) and the lengths of fatty acid chains in triglycerides of the oil. The shorter the fatty acid chains, the more glycerol the oil proportionally contains. Acrolein is formed from the glycerol skeleton of a mono- di or triglyceride.

The influence of temperature could not be examined more thoroughly, because only one experiment was carried out in a different temperature than others. Also the impact of catalytic action on acrolein formation was not studied. This is why these subjects should be examined in further studies. Additionally, reaction kinetics studies of acrolein can give more thorough information about the influence of time on acrolein formation. Dispersion modelling of gas emissions including possible aerosol formation in the case of hot raw material leakage is also one subject of further study.

The results of the experiments carried out in the autoclave are not readily applicable in the conditions of the hydro treatment reactor, because the experiments were carried out in laboratory scale batch type stirrer reactor, and the hydro treatment reactor is a true reactor of a large scale continuous flow catalytic reactor. In addition, the experiments were designed to maintain pyrolysis and in the hydro treatment reactor other reactions prevail. But when considering abnormal process conditions in the reactor, the phenomenon of thermal degradation may exist.

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LIST OF APPENDICES

Hazardous labelling symbols used in the European Union, the European Economic Area and some other countries

Toxic (T) substances and very toxic (T+) substances

Irritating (Xi) substances and harmful (Xn) substances

Environmentally dangerous (N) substances

Flammable (F) substances and extremely flammable (F+) substances

Production and use of acrolein

Isolated acrolein is manufactured in a closed system with gas-phase oxidation of propene and it is catalysed heterogeneously. It is also produced for the manufacture of acrylic acid in which acrolein is a non-isolated intermediate. (Gomes et al. 2002, 8) Figure 1 presents the flow chart of the manufacture of acrolein and acrylic acid.

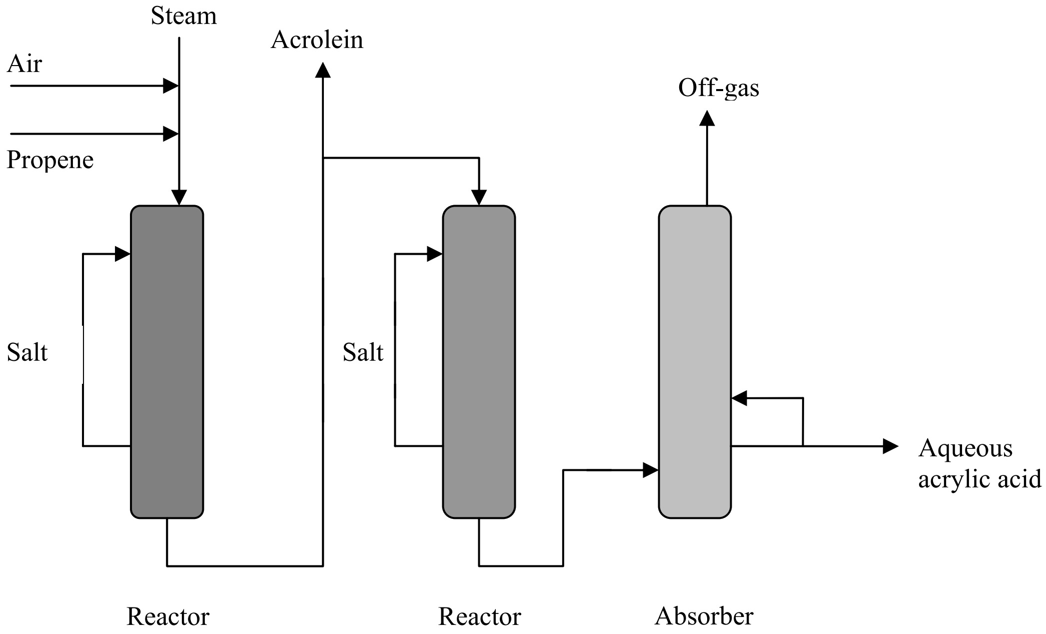

Figure 1. Production of acrolein and acrylic acid by propene oxidation (Speight 2002, 2.24).

The oxidation of propene is usually conducted in a fixed-bed multitube reactor where the pressure is near atmospheric pressure, temperature is approximately 350°C and melted salt is used to control the temperature. Air is usually used as the source of oxygen, and steam is added to prevent the development of flammable gas mixtures. Process can be a single pass or it can be equipped with a recycle. The effluent gases of the reactor are cooled so that acrolein can be condensed and separated from unreacted propene, oxygen and other components that have low boiling points (principally nitrogen). This is usually conducted in two absorption steps; first aqueous acrylic acid is separated from the reaction effluent by condensation and is then absorbed in a stream of water-base. The same is done to acrolein to separate it from propene, oxygen, nitrogen and carbon oxides. The main side reactions generate acrylic acid, acetic acid, acetaldehyde, carbon monoxide and carbon dioxide, also small amounts of other aldehydes and acids are formed. (Speight 2002, 2.23-2.24; Gomes et al. 2002, 8) Reported production amounts of acrolein between 1980 and early 1990’s were as follows:

• The United States	27 000-35 000 t/a
• Japan (several sites)	20 000 t/a
• European Union	60 000 t/a (France and Germany)
• Russia	10 500 t/a.

In year 2002 there were three producers of acrolein in the United States, and more recent production figure is available from that year when the production of acrolein was estimated to be 45 000-227 000 tons. In the EU countries, chemical industry produces and uses acrolein only as an intermediate in the manufacture of substances that are used as biocides, animal additives and leather tanning agents. Other countries such as Canada, Australia, the United States, Egypt and Argentina release acrolein into the environment on purpose, because acrolein is used mainly as a biocide in water treatment basins, cooling water towers, irrigation canals and process water circuits. In Canada acrolein is also used as an active ingredient in a product that oil companies use to purify hydrogen sulphide from the fluids produced in petroleum operations. Acrolein is also used in the production of pyridines, allyl alcohol, tetrahydrobenzaldehyde, modified starch, acrolein polymers, polyurethanes, polyester resins and synthetic glycerine. (Gomes et al. 2002, 8; Stevens et al. 2006, 1)

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Experimental instructions of thermal degradation tests with autoclave

Experimental arrangement

• Autoclave used in the tests:	PARR5, K. RA. 055
• Total volume of the vessel of the autoclave:	1000 ml
• The amount of test charge used in one test:	450 g or 225 g

- Pressure test done with nitrogen (N_2)
- Parameters monitored in the tests:
  - test charge material
  - pressure; 1 atm and 40 bar
  - temperature; 340°C and 325°C
  - RT (residence time); the heating time + 2 h
  - sphere; nitrogen (blank experiment), air and hydrogen (H_2)

Procedures before starting the experiment

Before weighing the autoclave reactor, it is important to recognize which parts belong to the tare weight so that the tare is always the same during one experiment. A graphite seal and the mixer that also belong to the tare weight are installed to the cover flange of autoclave. The vortex breaker is put in to the vessel to prevent the swirls that mixing causes. The autoclave is weighed and the tare weight is written down, after which test charge of 450 g or 225 g is weighed and put into the autoclave. The full weight is now measured and written down.

The autoclave is put in to a screw vice and separate cover flange parts are installed around the cover flange, and the six screws on top of the parts are screwed across, so that the cover flange is as horizontal as possible to prevent leakage. The autoclave is taken out of the screw vice, and installed into an electrically heated body that surrounds the autoclave and is situated in a fume cupboard. The magnetic stirrer is installed on to the cover flange of the autoclave. The heater and pressure gauge instruments are installed to the cover flange of the autoclave.

The power of the heater is switched on. The pressure test is done by opening the nitrogen valves one by one and spraying some foam on them to see if they have a leak. If no leak is observed, nitrogen is let to enter the autoclave and the pressure is let to rise to 580 psi which corresponds 40 bar. The pressure is let to stay in the reactor about 20 min and if the pressure has not dropped notably, the reactor system is tight enough. Then nitrogen is let out through the gas discharge valve.

Blank experiment with nitrogen

Nitrogen gas valve is opened and nitrogen is let to flow into the autoclave. The reactor vessel is depressurised by opening the discharge valve. This flush with nitrogen is done a few times and finally nitrogen is allowed to stay in the autoclave, so that the initial pressure of the experiment is 5 bar. Then all the instruments are uninstalled from the autoclave which is taken from the fume cupboard and weighted once more, so that the gas inside will be in the measurement. After this all the instruments are installed back including the two cooling water hose pipes and the water tap is turned on, so that water barely circulates in the system to cool the bearing of the magnetic stirrer. High temperature limit is set for 360°C. The heating of the autoclave is started and temperature is let to rise gradually to 340°C or 325°C. The pressure and temperature are monitored and values are written down every few minutes. Start-up values for the experiments with hydrogen and air are presented in the experiment matrix.

Sampling after temperature rise period

Two gas sample cylinders of 300 ml and one liquid sample cylinder of 50 ml are vacuumed to be ready for the sample taking. The tare weights of the vacuumed cylinders are measured. When the temperature of 340°C is achieved, a pipe connection where liquid sample will be taken is aerated by opening the valve and letting few grams of the test charge to a tared waste bottle, so that the amount leaving the system can be weighted. Liquid sample is then taken by installing the vacuumed 50 ml cylinder to the pipe connection and by opening the sample taking valve. When pressure drop no longer occurs, the valve is closed and the cylinder is disconnected from the pipe connection and then weighted.

After taking the liquid sample a gas sample is taken to one cylinder by installing the cylinder to the pipe connection and by opening the valve. When the pressure does not decrease anymore, this means that the pressure is equalized between the reactor and the cylinder. Then the valve is closed and the cylinder is taken out of the pipe connection and weighted. Now the heating is continued at 340°C for two hours. The pressure and temperature are monitored and values are written down every few minutes.

The end of the experiment

When the residence time has passed, a gas sample is taken to the other vacuumed and tared cylinder and then weighted. The heating is switched off when rapeseed oil is used as raw material. In other two cases of oil heating is lowered to 70°C, so that oil remains liquid in the vessel. When temperature is only 100°C the mixing is switched off and the cooling water tap is turned off. The information about the samples is input in Neste Oil’s laboratory system on the internet and sample tags are printed and placed on the samples. Then the samples are taken to the analysis. The autoclave is allowed to cool down until the next morning.

Procedures after cooling

On the following morning the heater is switched off and heater and pressure gauge instruments are uninstalled from the cover flange of the autoclave, and the cooling water hose pipes are uninstalled. Autoclave is taken from the fume cupboard and from the heating body and weighted, so that the remaining gas inside the vessel is taken into account in weighing. Then the autoclave is put back into the fume cupboard to release the remaining pressure through the discharge valve. After this the autoclave is put into the screw vice to open the screws. The cover flange is removed and the pyrolysis oil is poured to a centrifuge bottle and centrifuged for 30 minutes. After centrifugation if any precipitation has occurred, it is decanted from the liquid pyrolysis oil. The information about the two samples is input to the laboratory system and sample tag numbers are printed out and placed on the samples. Then they are taken to the analysis.

Cleaning of the equipment

After finishing the experiment the graphite seal and the mixer are removed from the cover flange. The autoclave vessel, the mixer and vortex breaker are washed with liquid detergent and dried with paper towels. The rest of the pyrolysis oil is removed with toluene or xylene and after that with acetone, and then the equipment is dried with nitrogen gas. The cover flange assemblies are sprayed with toluene or xylene so that there is no pyrolysis oil left in them. Finally they are treated with acetone and nitrogen is used to dry the assemblies. The used sample cylinders are cleaned by spraying acetone inside so that there are no leftovers from the samples. Then they are dried with a nitrogen spray of about 10 to 15 min.

Appendix IV

Experiment matrix of pyrolysis experiments 21.1.-5.3.2009

Parameters

Feed	• Alkali refined rapeseed oil • Refined, bleached and deodorized palm oil (RBD palm oil) • Crude palm oil and animal fat (CPO+AF) 50:50
T	• T_1= 340°C • T_2= 325°C
p	• p_1= 40 bar • p_2= 1 atm
Sphere	• air • hydrogen
Residence time	warming period (approximately 1 h) + 2 h

Individual experiments

Experiment day		
7.1.2009	**0**	Blank experiment, alkali refined rapeseed oil, 340°, 40 bar in nitrogen
21.1.2009	**1**	Alkali refined rapeseed oil, 340°C, 40 bar in hydrogen
27.1.2009	**2**	Alkali refined rapeseed oil, 340°C, 1 atm in air
2.2.2009	**3**	RBD palm oil, 340°C, 40 bar in hydrogen
9.2.2009	**4**	RBD palm oil, 340°C, 1 atm in air
11.2.2009	**5**	CPO+AF, 340°C, 40 bar in hydrogen
17.2.2009	**6**	CPO+AF, 340°C, 1 atm in air
2.3.2009	**7**	RBD palm oil, 325°C, 40 bar in hydrogen
5.3.2009	**8**	As the experiment 7 with the test charge of 225 g

Notion

The magnetic stirrer of the autoclave is used at slow rotation in the experiments so that the oil composition stays uniform.

The analysis results of liquid product analysis of thermal degradation experiments

Table 1. Total acid number and iodine value of raw materials used in the experiments.

Oili-number	**Raw material**	**Total acid number [mgKOH/g]**	**Iodine value [-]**
00998965	Alkaline refined rapeseed oil	3,1	116
01119841	RBD palm oil	1,3	51
01134597	Crude palm oil and animal fat	25,0	57

Table 2. Total acid number and iodine value of liquid samples and product of the experiments.

Oili-number	**Experiment**	**Total acid number [mgKOH/g]**	**Iodine value [-]**
	1		
01023013	Sample	8,9	105
01023012	Product	57,0	85
	2		
01049868	Sample	9,5	106
01049867	Product	60,0	83
	3		
01081224	Sample	8,3	50
01081226	Product	59,0	45
	4		
01119816	Sample	7,4	49
01119817	Product	58,0	45
	5		
01134596	Sample	31,0	54
01134593	Product	87,0	47
	6		
01170435	Sample	34,0	53
01170432	Product	82,0	47
	7		
01270948	Sample	4,0	51
01270949	Product	20,0	48
	8		
01299243	Sample	9,3	50
01299245	Product	130,0	43

Table 3. The GPC analysis results of raw materials used in the experiments.

Oili-number	**Raw material**	**Oligomers [area-%]**	**Triglycerides [area-%]**	**Diglycerides [area-%]**	**Monoglycerides [area-%]**	**Fatty acids [area-%]**	**Cracking products [area-%]**
00998965	Alkaline refined rapeseed oil	0,1	96,7	2,6	0,1	0,6	-
01119841	RBD palm oil	0,2	93,4	5,9	0,3	0,2	-
01134597	Crude palm oil and animal fat	0,3	74,4	15,7	0,9	5,8	3,0

Table 4. The GPC analysis results of liquid samples and products of the experiments carried out.

Oili-number	**Experiment**	**Oligomers [area-%]**	**Triglycerides [area-%]**	**Diglycerides [area-%]**	**Monoglycerides [area-%]**	**Fatty acids [area-%]**	**Cracking products [area-%]**
	Blank experiment						
00998966	Sample	9,5	83,4	3,0	0,5	2,2	1,4
00998969	Product	50,7	23,5	4,0	5,7	12,3	3,9
	1						
01023013	Sample	13,7	78,1	2,6	0,8	3,0	1,8
01023012	Product	49,6	24,4	4,4	5,7	12,5	3,5
	2						
01049868	Sample	13,2	78,9	2,9	0,6	2,8	1,7
01049867	Product	49,4	24,0	4,4	5,6	12,8	3,8
	3						
01081224	Sample	4,8	87,3	4,4	0,3	3,2	-
01081226	Product	19,8	51,7	3,3	5,2	19,4	0,6
	4						
01119816	Sample	5,4	87,8	4,5	0,3	0,2	1,9
01119817	Product	19,8	54,7	2,9	5,0	17,7	-
	5						
01134596	Sample	2,5	72,6	12,6	0,6	8,5	3,2
01134593	Product	8,6	52,7	5,4	1,7	26,2	5,4
	6						
01170435	Sample	3,9	74,1	10,9	0,3	8,1	2,6
01170432	Product	9,5	58,1	1,6	1,8	23,5	5,4
	7						
01270948	Sample	2,5	90,1	6,1	0,3	1,0	-
01270949	Product	13,7	75,9	1,3	1,3	7,8	-
	8						
01299243	Sample	6,5	86,1	3,1	0,5	3,7	-
01299245	Product	14,2	23,0	11,1	11,1	36,6	4,1

Table 5. The research report of fatty acid composition of the end oil of experiment 5 (in Finnish only).

NESTE OIL **Tutkimustiedote**

1(1)

Tutkimus ja Teknologia / Riitta Pulkki 16.3.2009

Aihe: Rasvahappokoostumus, Orgaaniset Komponentit
Tilaaja: Jukka-Pekka Myllyoja
Proj.numero: HAAA
Jakelu: Raila Heiskanen **c.c.** Maija Kaasinen

Viivakoodi:
Näytteet: 1. Koe 5, neste 2h 1134593

Saapumispäivä: 12.2.2009 4.3.2009
Tekijä: Riitta Pulkki, Maija Kaasinen, Kim Wickström
Tehtävä: Rasvahapot (saippuoidut + vapaat)
Menetelmä: NM 413: Saippuointi, metylointi, GC, GC-MS (DB-WAX)

Tulokset:

	1	yksikkö	1	yksikkö
C7:0	0,07	wt-%	0,09	norm-%
C7:1	0,03	wt-%	0,05	norm-%
C8:0	0,09	wt-%	0,12	norm-%
C8:1	0,02	wt-%	0,03	norm-%
C9:0	0,13	wt-%	0,18	norm-%
C9:1	0,01	wt-%	0,02	norm-%
C10:0	0,35	wt-%	0,48	norm-%
C10:1	0,02	wt-%	0,02	norm-%
C11:0	0,04	wt-%	0,06	norm-%
C11:1	0,08	wt-%	0,11	norm-%
C12:0	0,09	wt-%	0,12	norm-%
C12:1	0,03	wt-%	0,04	norm-%
C13:0	0,01	wt-%	0,01	norm-%
C14:0	1,16	wt-%	1,61	norm-%
C14:1	0,08	wt-%	0,11	norm-%
C15:0	0,10	wt-%	0,14	norm-%
C15:1	0,04	wt-%	0,06	norm-%
C16:0	28,01	wt-%	38,91	norm-%
C16:1	1,19	wt-%	1,65	norm-%
C17:0	0,62	wt-%	0,85	norm-%
C17:1	0,24	wt-%	0,34	norm-%
C18:0	9,46	wt-%	13,14	norm-%
C18:1	26,86	wt-%	37,31	norm-%
C18:2	1,61	wt-%	2,24	norm-%
C20:0	0,35	wt-%	0,48	norm-%
C20:1	0,61	wt-%	0,85	norm-%
C21:0	0,06	wt-%	0,09	norm-%

C22:0	0,08	wt-%	0,11	norm-%
C20:2	0,06	wt-%	0,08	norm-%
C20:3		wt-%	0,00	norm-%
C20:4		wt-%	0,00	norm-%
C20:5		wt-%	0,00	norm-%
C22:0	0,08	wt-%	0,11	norm-%
10-okso-C18:0	0,06	wt-%	0,08	norm-%
C22:1		wt-%	0,00	norm-%
C23:0		wt-%	0,00	norm-%
C22:4		wt-%	0,00	norm-%
C22:5		wt-%	0,00	norm-%
C24:0	0,05	wt-%	0,06	norm-%
C24:1	0,30	wt-%	0,42	norm-%
		wt-%	0,00	norm-%
Tunnistetut rasvahapot yhteensä	71,99	wt-%	100,00	norm-%
C4-alkyylibentseeni	0,02	wt-%		
C15-olefiini	0,03	wt-%		
C16-olefiini	0,04	wt-%		
n-C17	0,04	wt-%		
C18-olefiini	0,03	wt-%		
palmitonitriili	0,20	wt-%		
C26-olefiini	0,12	wt-%		
C26-dieeni	0,13	wt-%		
mp 334	0,16	wt-%		
mp 368	0,11	wt-%		
asetaalit	0,70	wt-%		
Tunnistamattomat	2,43	wt-%		
Total	75,99	wt-%		
Tot. FA > C20	1,58			

Huom.:
Total -tulos riippuu hydrolyysin onnistumisesta.
Rasvahappojen kokonaismäärää voi verrata saippuoimaton-osuuden tulokseen.

The analysis results of gas samples of thermal degradation experiments (in Finnish only)

Table 6. The components and their relative amounts of the first gas sample of blank experiment. The F is a correction factor for individual compounds in all tables of this appendix.

Näyte:	Nollakoe, kaasu, 0h
Analys.pvm:	8.1.2009
Tekijä:	TKZ
Menetelmä:	NM428/NM291
Oili-koodi:	998967

NRO	KOMPONENTTI	mol-%	p-%	F
	METAANI	0,34	0,17	1,0000
	ETEENI	0,21	0,19	0,8743
	ETAANI	0,53	0,50	0,9371
	PROPEENI	0,16	0,21	0,8743
	PROPAANI	0,17	0,23	0,9162
	I+1-BUTEENI	1,46	2,55	0,8743
	N-BUTAANI	0,24	0,43	0,9057
	TRANS-2-BUTEENI	0,09	0,17	0,8743
	CIS-2-BUTEENI	0,07	0,13	0,8743
	3-ME-1-BUTEENI	0,01	0,03	0,8743
	1-PENTEENI	0,44	0,96	0,8743
	2-ME-1-BUTEENI	0,01	0,01	0,8743
	N-PENTAANI	0,36	0,81	0,8994
	TRANS-2-PENTEENI	0,45	0,98	0,8743
	CIS-2-PENTEENI	0,22	0,48	0,8743
	2-ME-2-BUTEENI	0,09	0,20	0,8743
	SYKLOPENTAANI	0,01	0,02	0,8743
	2,3-DIME-BUTAANI	0,01	0,04	0,8952
	2-ME-PENTAANI	0,06	0,17	0,8952
	3-ME-PENTAANI	0,07	0,18	0,8952
	N-HEKSAANI	0,28	0,76	0,8952
	TRANS-2-HEKSEENI	0,02	0,05	0,8743
	CIS-2-HEKSEENI	0,01	0,02	0,8743
	ME-SYKLOPENTAANI	0,23	0,59	0,8743
	BENTSEENI	0,08	0,20	0,8114
	SYKLOHEKSAANI	0,10	0,26	0,8743
	N-HEPTAANI	0,07	0,22	0,8922
	ME-SYKLOHEKSAANI	0,00	0,01	0,8743
	ET-SYKLOPENTAANI	0,00	0,01	0,8743
	TOLUEENI	0,05	0,13	0,8204
	3-ME-HEPTAANI	0,00	0,01	0,8900
	N-OKTAANI	0,05	0,19	0,8900
	N-NONAANI	0,02	0,06	0,8882
	AKROLEIINI	1,74	3,04	1,0000
	PROPANAALI	0,41	0,74	1,0000
	TRANS-1,3-BUTADIEENI	0,02	0,04	0,8429
	2-ME-1,3-BUTADIEENI	0,02	0,04	0,8491
	SYKLOPENTEENI	0,10	0,22	0,8491

TRANS-1,3-PENTADIEENI	0,03	0,06	0,8491
CIS-1,3-PENTADIEENI	0,85	1,80	0,8491
2,3-PENTADIEENI	0,02	0,04	0,8491
BUTANAALI	0,03	0,08	1,0000
2-BUTENAALI	0,01	0,01	1,0000
PENTANAALI	0,00	0,01	1,0000
3-ME-3-BUTEENINITRIILI	0,01	0,03	1,0000
1-HEKSEENI	0,09	0,25	0,8743
TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,03	0,08	0,8743
2-ME-2-PENTEENI	0,00	0,01	0,8743
3-ME-SYKLOPENTEENI	0,00	0,01	0,8533
ME-SYKLOPENTADIEENI	0,00	0,01	0,8324
1-ME-SYKLOPENTEENI	0,01	0,02	0,8533
SYKLOHEKSEENI	0,01	0,03	0,8533
4-ME-1-HEKSEENI	0,01	0,02	0,8952
C6H10-DIEENI	0,05	0,12	0,8533
C6H8-SYKLODIEENI	0,06	0,16	0,8324
HEKSANAALI	0,03	0,09	1,0000
2-HEKSENAALI	0,01	0,03	1,0000
1-HEPTEENI	0,36	1,10	0,8743
TRANS-3-HEPTEENI	0,01	0,02	0,8743
TRANS-2-HEPTEENI	0,03	0,09	0,8743
CIS-2-HEPTEENI	0,02	0,05	0,8743
CIS-3-HEPTEENI	0,00	0,01	0,8743
ET-SYKLOPENTEENI	0,00	0,01	0,8563
1-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
C7H12-DIEENI	0,09	0,28	0,8563
C7H12-SYKLODIEENI	0,01	0,03	0,8563
1-OKTEENI	0,10	0,35	0,8743
C8H16-NAFTEENI	0,00	0,01	0,8743
C8H16-OLEFIINI	0,01	0,03	0,8743
TRANS-2-OKTEENI	0,12	0,44	0,8743
CIS-2-OKTEENI	0,07	0,23	0,8743
SYKLO-OKTEENI	0,05	0,17	0,8586
C8H14-SYKLO-OLEFIINI	0,02	0,06	0,8586
C8H14-DIEENI	0,13	0,45	0,8586
C8H12-OLEFIININEN NAFTEENI	0,11	0,36	0,8429
ETYYLIBENTSEENI	0,02	0,05	0,8272
META-KSYLEENI	0,00	0,01	0,8272
PARA-KSYLEENI	0,00	0,01	0,8272
HEPTANAALI	0,04	0,13	1,0000
4-HEPTENAALI	0,00	0,01	1,0000
OKTANAALI	0,01	0,03	1,0000
ORTO-KSYLEENI	0,00	0,02	0,8272
1-NONEENI	0,01	0,04	0,8743
4-NONEENI	0,01	0,04	0,8743
C9H18-OLEFIINI	0,01	0,04	0,8743
TRANS-2-NONEENI	0,01	0,02	0,8743
CIS-2-NONEENI	0,00	0,01	0,8743
C9H16-DIEENI	0,03	0,10	0,8603
C9H14-SYKLO-OLEFIINI	0,00	0,01	0,8464

N-PROPYYLIBENTSEENI	0,01	0,02	0,8324
vety	0,11	0,01	
typpi	87,74	76,49	
hiilidioksidi	0,38	0,52	
hiilimonoksidi	1,02	0,89	
YHTEENSÄ	100,00	100,00	
LUKUKESKIM. MOLEKYYLIPAINO =		32,13	
ORG. mol-%	10,75		

Näyte sisältää jälkiä seuraavasta komponentista: 2-BUTANONI

Table 7. The components and their relative amounts of the second gas sample of blank experiment.

Näyte:	Nollakoe, kaasu, 2h
Analys.pvm:	9.1.2009
Tekijä:	TKZ
Menetelmä:	NM428/NM291
Oili-koodi:	998968

NRO	KOMPONENTTI	mol-%	p-%	F
	METAANI	1,24	0,63	1,0000
	ETEENI	0,78	0,69	0,8743
	ETAANI	2,01	1,92	0,9371
	PROPEENI	0,66	0,89	0,8743
	PROPAANI	1,00	1,40	0,9162
	I+1-BUTEENI	0,98	1,74	0,8743
	N-BUTAANI	0,97	1,79	0,9057
	TRANS-2-BUTEENI	0,15	0,26	0,8743
	CIS-2-BUTEENI	0,10	0,18	0,8743
	3-ME-1-BUTEENI	0,01	0,02	0,8743
	1-PENTEENI	0,61	1,36	0,8743
	2-ME-1-BUTEENI	0,02	0,04	0,8743
	N-PENTAANI	0,88	2,02	0,8994
	TRANS-2-PENTEENI	0,30	0,68	0,8743
	CIS-2-PENTEENI	0,14	0,32	0,8743
	2-ME-2-BUTEENI	0,05	0,11	0,8743
	SYKLOPENTAANI	0,01	0,01	0,8743
	2,3-DIME-BUTAANI	0,00	0,01	0,8952
	2-ME-PENTAANI	0,01	0,03	0,8952
	3-ME-PENTAANI	0,01	0,03	0,8952
	N-HEKSAANI	0,49	1,33	0,8952
	TRANS-2-HEKSEENI	0,04	0,10	0,8743
	CIS-2-HEKSEENI	0,02	0,04	0,8743
	ME-SYKLOPENTAANI	0,03	0,09	0,8743
	BENTSEENI	0,05	0,12	0,8114
	SYKLOHEKSAANI	0,01	0,03	0,8743
	2,3-DIME-PENTAANI	0,00	0,01	0,8922
	N-HEPTAANI	0,16	0,50	0,8922

ME-SYKLOHEKSAANI	0,00	0,02	0,8743
ET-SYKLOPENTAANI	0,00	0,01	0,8743
TOLUEENI	0,01	0,03	0,8204
N-OKTAANI	0,05	0,19	0,8900
N-NONAANI	0,02	0,07	0,8882
AKROLEIINI	0,07	0,12	1,0000
ASETONI	0,07	0,12	1,0000
PROPANAALI	0,71	1,32	1,0000
TRANS-1,3-BUTADIEENI	0,00	0,01	0,8429
SYKLOPENTEENI	0,29	0,62	0,8491
CIS-1,3-PENTADIEENI	0,00	0,01	0,8491
2,3-DIME-1-BUTEENI	0,00	0,01	0,8743
1-HEKSEENI	0,27	0,73	0,8743
TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,02	0,04	0,8743
2-ME-2-PENTEENI	0,00	0,01	0,8743
3-ME-SYKLOPENTEENI	0,00	0,01	0,8533
1-ME-SYKLOPENTEENI	0,01	0,02	0,8533
SYKLOHEKSEENI	0,04	0,11	0,8533
CIS-4-ME-2-HEKSEENI	0,00	0,01	0,8952
C6H10-DIEENI	0,01	0,01	0,8533
C6H8O	0,00	0,01	1,0000
1-HEPTEENI	0,26	0,82	0,8743
TRANS-3-HEPTEENI	0,01	0,02	0,8743
DIME-SYKLOPENTEENI	0,00	0,01	0,8563
TRANS-2-HEPTEENI	0,04	0,13	0,8743
CIS-2-HEPTEENI	0,02	0,07	0,8743
1-ET-SYKLOPENTEENI	0,00	0,01	0,8563
3-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
4-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
ET-SYKLOPENTEENI	0,00	0,01	0,8563
1-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
C7H12-SYKLO-OLEFIINI	0,00	0,01	0,8563
C7H12-DIEENI	0,00	0,01	0,8563
1-OKTEENI	0,04	0,15	0,8743
C8H16-OLEFIINI	0,00	0,02	0,8743
TRANS-2-OKTEENI	0,04	0,14	0,8743
CIS-2-OKTEENI	0,02	0,07	0,8743
C8H14-SYKLO-OLEFIINI	0,03	0,11	0,8586
ETYYLIBENTSEENI	0,00	0,01	0,8272
HEPTANAALI	0,00	0,01	1,0000
ORTO-KSYLEENI	0,00	0,01	0,8272
1-NONEENI	0,01	0,03	0,8743
C9H18-OLEFIINI	0,00	0,01	0,8743
TRANS-2-NONEENI	0,00	0,01	0,8743
CIS-2-NONEENI	0,00	0,01	0,8743
C9H16-SYKLO-OLEFIINI	0,00	0,01	0,8603
C9H14-OLEFIININEN NAFTEENI	0,00	0,01	0,8464
N-PROPYYLIBENTSEENI	0,00	0,02	0,8324
vety	0,52	0,03	
typpi	77,35	68,91	
hiilidioksidi	2,35	3,29	

hiilimonoksidi	6,94	6,18
YHTEENSÄ	100,00	100,00
LUKUKESKIM. MOLEKYYLIPAINO =		31,44
ORG. mol-%	12,84	

Näyte sisältää jälkiä seuraavista komponenteista	2,3-PENTADIEENI BUTANAALI 2-BUTANONI PENTANAALI

Table 8. The components and their relative amounts of the first gas sample of experiment 1.

Näyte:	Koe 1, H2, kaasu 0h
Analys.pvm:	22.1.2009
Tekijä:	RHX
Menetelmä:	NM428/NM291
Oili-koodi:	1023011

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	0,49	0,73	1,0000
2	ETEENI	0,33	0,88	0,8743
3	ETAANI	0,85	2,38	0,9371
4	PROPEENI	0,26	1,01	0,8743
5	PROPAANI	0,29	1,18	0,9162
10	I-BUTAANI	0,00	0,01	0,9057
12	I+1-BUTEENI	1,88	9,88	0,8743
13	1,3-BUTADIEENI	0,03	0,16	0,8429
14	N-BUTAANI	0,39	2,11	0,9057
16	TRANS-2-BUTEENI	0,14	0,71	0,8743
19	CIS-2-BUTEENI	0,10	0,52	0,8743
22	3-ME-1-BUTEENI	0,02	0,11	0,8743
28	1-PENTEENI	0,64	4,23	0,8743
31	2-ME-1-BUTEENI	0,01	0,05	0,8743
32	N-PENTAANI	0,55	3,73	0,8994
34	TRANS-2-PENTEENI	0,64	4,17	0,8743
36	CIS-2-PENTEENI	0,32	2,08	0,8743
37	ME-SYKLOBUTAANI	0,00	0,01	0,8743
39	2-ME-2-BUTEENI	0,12	0,78	0,8743
48	SYKLOPENTAANI	0,01	0,06	0,8743
49	2,3-DIME-BUTAANI	0,01	0,10	0,8952
53	2-ME-PENTAANI	0,07	0,53	0,8952
54	TRANS-4-ME-2-PENTEENI	0,00	0,01	0,8743
58	3-ME-PENTAANI	0,07	0,58	0,8952
63	N-HEKSAANI	0,34	2,72	0,8952
66	TRANS-2-HEKSEENI	0,02	0,19	0,8743
71	CIS-2-HEKSEENI	0,01	0,09	0,8743
77	ME-SYKLOPENTAANI	0,22	1,72	0,8743
93	BENTSEENI	0,11	0,83	0,8114

104	SYKLOHEKSAANI	0,09	0,72	0,8743
135	N-HEPTAANI	0,08	0,79	0,8922
147	ME-SYKLOHEKSAANI	0,00	0,04	0,8743
152	ET-SYKLOPENTAANI	0,00	0,02	0,8743
174	TOLUEENI	0,03	0,25	0,8204
188	2-ME-HEPTAANI	0,00	0,01	0,8900
194	3-ME-HEPTAANI	0,00	0,02	0,8900
214	N-OKTAANI	0,03	0,35	0,8900
238	C8-NAFTEENI	0,01	0,05	0,8743
287	N-NONAANI	0,00	0,05	0,8882
	AKROLEIINI	1,26	6,61	1,0000
	ASETALDEHYDI	0,00	0,01	1,0000
24	ASETONI	0,02	0,12	1,0000
	PROPANAALI	1,08	5,88	1,0000
	FURAANI	0,00	0,03	1,0000
33	2-ME-1,3-BUTADIEENI	0,02	0,12	0,8491
45	SYKLOPENTEENI	0,18	1,17	0,8491
41	SYKLOPENTADIEENI	0,76	4,71	0,8240
40	TRANS-1,3-PENTADIEENI	0,03	0,18	0,8491
43	CIS-1,3-PENTADIEENI	0,02	0,13	0,8491
50	2,3-DIME-1-BUTEENI	0,00	0,02	0,8743
	BUTANAALI	0,04	0,25	1,0000
	2-BUTENAALI	0,01	0,03	1,0000
	C5-KETONI	0,00	0,01	1,0000
61	1-HEKSEENI	0,15	1,14	0,8743
64	TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,04	0,29	0,8743
67	2-ME-2-PENTEENI	0,00	0,02	0,8743
46	4-ME-1-PENTEENI	0,00	0,01	0,8743
47	3-ME-1-PENTEENI	0,00	0,01	0,8743
68	3-ME-SYKLOPENTEENI	0,00	0,02	0,8533
70	4-ME-SYKLOPENTEENI	0,00	0,01	0,8533
69	CIS-3-ME-2-PENTEENI	0,00	0,01	0,8743
82	2,3-DIME-2-BUTEENI	0,00	0,02	0,8743
94	1-ME-SYKLOPENTEENI	0,01	0,04	0,8533
118	SYKLOHEKSEENI	0,01	0,12	0,8533
96	3-ME-1-HEKSEENI	0,00	0,01	0,8952
113	CIS-4-ME-2-HEKSEENI	0,00	0,02	0,8952
91	HEKSADIEENI	0,00	0,01	0,8533
95	C6H10-DIEENI	0,04	0,32	0,8533
107	C6H8-SYKLODIEENI	0,05	0,36	0,8324
	C6H10O-ALDEHYDI	0,00	0,01	1,0000
	HEKSANAALI	0,01	0,09	1,0000
127	1-HEPTEENI	0,42	3,88	0,8743
133	TRANS-3-HEPTEENI	0,01	0,08	0,8743
139	TRANS-2-HEPTEENI	0,03	0,29	0,8743
144	CIS-2-HEPTEENI	0,02	0,16	0,8743
136	CIS-3-HEPTEENI	0,00	0,02	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,01	0,8563
154	3-ME-SYKLOHEKSEENI	0,00	0,02	0,8563
155	4-ME-SYKLOHEKSEENI	0,00	0,02	0,8563
172	ET-SYKLOPENTEENI	0,00	0,02	0,8563

	SYKLOHEPTEENI	0,00	0,03	0,8563
185	1-ME-SYKLOHEKSEENI	0,00	0,04	0,8563
166	C7H12-DIEENI	0,07	0,65	0,8563
160	C7H10-SYKLODIEENI	0,01	0,05	0,8384
	1-OKTEENI	0,07	0,69	0,8743
207	C8H16-NAFTEENI	0,00	0,02	0,8743
221	C8H16-OLEFIINI	0,01	0,08	0,8743
216	TRANS-2-OKTEENI	0,07	0,77	0,8743
222	CIS-2-OKTEENI	0,04	0,38	0,8743
	SYKLO-OKTEENI	0,02	0,17	0,8586
223	C8H14-SYKLO-OLEFIINI	0,04	0,37	0,8586
218	C8H14-DIEENI	0,03	0,30	0,8586
	C8H12-OLEFIININEN NAFTEENI	0,03	0,33	0,8429
250	ETYYLIBENTSEENI	0,01	0,06	0,8272
257	META-KSYLEENI	0,00	0,01	0,8272
258	PARA-KSYLEENI	0,00	0,01	0,8272
	HEPTANAALI	0,00	0,04	1,0000
276	ORTO-KSYLEENI	0,00	0,01	0,8272
281	1-NONEENI	0,00	0,04	0,8743
283	4-NONEENI	0,00	0,02	0,8743
284	C9H18-OLEFIINI	0,00	0,02	0,8743
	TRANS-2-NONEENI	0,00	0,02	0,8743
	CIS-2-NONEENI	0,00	0,01	0,8743
292	C9H16-DIEENI	0,00	0,01	0,8603
	C9H16	0,00	0,02	0,8603
	C9H14	0,00	0,06	0,8464
312	N-PROPYYLIBENTSEENI	0,00	0,01	0,8324
	vety	83,68	15,78	
	typpi	1,28	3,35	
	hiilidioksidi	0,48	1,96	
	hiilimonoksidi	1,75	4,58	
	YHTEENSÄ	100,00	100,00	

LUKUKESKIM.
MOLEKYYLIPAINO = 10,69

ORG. mol-% 12,82

Näytteessä on jälkiä seuraavista yhdisteistä:

2-ME-PROPANAALI
C4H6O
2-BUTANONI
PENTANAALI

Table 9. The components and their relative amounts of the second gas sample of experiment 1.

Näyte: Koe 1, H2, kaasu 2h
Analys.pvm: 22.1.2009
Tekijä: RHX
Menetelmä: NM428/NM291
Oili-koodi: 1023010

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	1,14	1,73	1,0000
2	ETEENI	0,68	1,80	0,8743
3	ETAANI	1,89	5,38	0,9371
4	PROPEENI	0,56	2,22	0,8743
5	PROPAANI	0,96	4,00	0,9162
10	I-BUTAANI	0,00	0,01	0,9057
12	I+1-BUTEENI	0,82	4,36	0,8743
13	1,3-BUTADIEENI	0,01	0,04	0,8429
14	N-BUTAANI	0,85	4,67	0,9057
16	TRANS-2-BUTEENI	0,13	0,70	0,8743
19	CIS-2-BUTEENI	0,09	0,47	0,8743
22	3-ME-1-BUTEENI	0,01	0,04	0,8743
24	ASETONI	0,21	1,17	1,0000
28	1-PENTEENI	0,50	3,33	0,8743
31	2-ME-1-BUTEENI	0,01	0,09	0,8743
32	N-PENTAANI	0,75	5,09	0,8994
34	TRANS-2-PENTEENI	0,25	1,66	0,8743
36	CIS-2-PENTEENI	0,12	0,79	0,8743
39	2-ME-2-BUTEENI	0,04	0,26	0,8743
48	SYKLOPENTAANI	0,00	0,03	0,8743
49	2,3-DIME-BUTAANI	0,00	0,02	0,8952
53	2-ME-PENTAANI	0,01	0,07	0,8952
54	TRANS-4-ME-2-PENTEENI	0,00	0,01	0,8743
57	C6-H10-DIEENI	0,00	0,01	0,8533
58	3-ME-PENTAANI	0,01	0,07	0,8952
63	N-HEKSAANI	0,37	2,98	0,8952
66	TRANS-2-HEKSEENI	0,03	0,23	0,8743
71	CIS-2-HEKSEENI	0,01	0,10	0,8743
	C6-H12-NAFTEENI	0,00	0,01	0,8743
77	ME-SYKLOPENTAANI	0,02	0,19	0,8743
93	BENTSEENI	0,03	0,22	0,8114
104	SYKLOHEKSAANI	0,01	0,07	0,8743
115	2,3-DIME-PENTAANI	0,00	0,01	0,8922
120	C7-H14-OLEFIINI	0,00	0,02	0,8743
135	N-HEPTAANI	0,10	0,99	0,8922
147	ME-SYKLOHEKSAANI	0,00	0,03	0,8743
148	1,1,3-TRIME-SYKLOPENTAANI	0,00	0,00	0,8747
152	ET-SYKLOPENTAANI	0,00	0,01	0,8743
174	TOLUEENI	0,01	0,09	0,8204
238	C8-NAFTEENI	0,00	0,04	0,8743
198	TRANS-1,3-DIME-SYKLOHEKSAANI	0,00	0,01	0,8743
214	N-OKTAANI	0,08	0,88	0,8900
235	N-PROPYYLI-SYKLOPENTAANI	0,00	0,04	0,8747

236	ET-SYKLOHEKSAANI	0,00	0,02	0,8747
287	N-NONAANI	0,03	0,33	0,8882
	AKROLEIINI	0,06	0,33	1,0000
	ASETALDEHYDI	0,00	0,01	1,0000
	PROPANAALI	0,50	2,74	1,0000
45	SYKLOPENTEENI	0,26	1,65	0,8491
41	SYKLOPENTADIEENI	0,01	0,04	0,8240
40	TRANS-1,3-PENTADIEENI	0,00	0,01	0,8491
43	CIS-1,3-PENTADIEENI	0,00	0,01	0,8491
50	2,3-DIME-1-BUTEENI	0,00	0,01	0,8743
	C5-KETONI	0,00	0,01	1,0000
	PENTANAALI	0,00	0,01	1,0000
61	1-HEKSEENI	0,20	1,60	0,8743
64	TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,01	0,11	0,8743
67	2-ME-2-PENTEENI	0,00	0,03	0,8743
46	4-ME-1-PENTEENI	0,00	0,01	0,8743
47	3-ME-1-PENTEENI	0,00	0,01	0,8743
68	3-ME-SYKLOPENTEENI	0,00	0,03	0,8533
70	4-ME-SYKLOPENTEENI	0,00	0,01	0,8533
69	CIS-3-ME-2-PENTEENI	0,00	0,02	0,8743
72	TRANS-3-ME-2-PENTEENI	0,00	0,01	0,8743
82	2,3-DIME-2-BUTEENI	0,00	0,01	0,8743
89	3,4-DIME-1-PENTEENI	0,00	0,01	0,8743
94	1-ME-SYKLOPENTEENI	0,01	0,04	0,8533
118	SYKLOHEKSEENI	0,03	0,23	0,8533
96	3-ME-1-HEKSEENI	0,00	0,01	0,8952
109	2-ME-TRANS-3-HEKSEENI	0,00	0,01	0,8743
112	4-ME-1-HEKSEENI	0,00	0,01	0,8952
113	CIS-4-ME-2-HEKSEENI	0,00	0,01	0,8952
95	C6H10-DIEENI	0,00	0,01	0,8533
	C6H8O	0,00	0,02	1,0000
	HEKSANAALI	0,00	0,01	1,0000
	C6-KETONI	0,00	0,02	1,0000
127	1-HEPTEENI	0,17	1,59	0,8743
129	C7-H12-DIEENI	0,00	0,01	0,8563
133	TRANS-3-HEPTEENI	0,00	0,04	0,8743
134	DIME-SYKLOPENTEENI	0,00	0,03	0,8563
139	TRANS-2-HEPTEENI	0,03	0,27	0,8743
144	CIS-2-HEPTEENI	0,02	0,14	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,03	0,8563
154	3-ME-SYKLOHEKSEENI	0,00	0,02	0,8563
155	4-ME-SYKLOHEKSEENI	0,00	0,02	0,8563
172	ET-SYKLOPENTEENI	0,00	0,01	0,8563
185	1-ME-SYKLOHEKSEENI	0,00	0,04	0,8563
166	C7H12-DIEENI	0,00	0,02	0,8563
	C7H10-SYKLODIEENI	0,00	0,01	0,8384
	SYKLOHEPTEENI	0,00	0,04	0,8563
	1-OKTEENI	0,06	0,63	0,8743
207	C8H16-NAFTEENI	0,00	0,01	0,8743
221	C8H16-OLEFIINI	0,01	0,11	0,8743
216	TRANS-2-OKTEENI	0,07	0,70	0,8743
222	CIS-2-OKTEENI	0,03	0,35	0,8743

	SYKLO-OKTEENI	0,03	0,29	0,8586
223	C8H14-SYKLO-OLEFIINI	0,03	0,35	0,8586
218	C8H14-DIEENI	0,01	0,16	0,8586
	C8H12-OLEFIININEN NAFTEENI	0,00	0,02	0,8429
250	ETYYLIBENTSEENI	0,01	0,08	0,8272
257	META-KSYLEENI	0,00	0,01	0,8272
258	PARA-KSYLEENI	0,00	0,01	0,8272
	HEPTANAALI	0,00	0,02	1,0000
276	ORTO-KSYLEENI	0,00	0,02	0,8272
281	1-NONEENI	0,01	0,14	0,8743
283	4-NONEENI	0,00	0,01	0,8743
284	C9H18-OLEFIINI	0,00	0,02	0,8743
	TRANS-2-NONEENI	0,00	0,06	0,8743
	CIS-2-NONEENI	0,00	0,03	0,8743
288	C9H16-SYKLO-OLEFIINI	0,01	0,08	0,8603
306	PROPYYLISYKLOHEKSAANI	0,00	0,01	0,8743
312	N-PROPYYLIBENTSEENI	0,00	0,03	0,8324
	vety	79,24	15,13	
	hiilidioksidi	2,14	8,92	
	hiilimonoksidi	7,24	19,20	
	YHTEENSÄ	100,00	100,00	
	LUKUKESKIM. MOLEKYYLIPAINO =		10,56	
	ORG. mol-%	11,39		

Näytteessä on jälkiä seuraavista yhdisteistä:	2-ME-PROPANAALI BUTANAALI 2-BUTANONI ETIKKAHAPPO PROPIONIHAPPO C4-HAPPO

Table 10. The components and their relative amounts of the second gas sample of experiment 2.

Näyte:	Koe 2, kaasu 2h
Analys.pvm:	28.1.2009
Tekijä:	RHX
Menetelmä:	NM428/NM291
Oili-koodi:	1049865

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	1,21	0,61	1,0000
2	ETEENI	0,74	0,65	0,8743
3	ETAANI	1,97	1,86	0,9371
4	PROPEENI	0,60	0,80	0,8743
5	PROPAANI	0,90	1,25	0,9162
12	I+1-BUTEENI	0,84	1,48	0,8743
13	1,3-BUTADIEENI	0,00	0,01	0,8429

14	N-BUTAANI	0,86	1,56	0,9057
16	TRANS-2-BUTEENI	0,13	0,23	0,8743
19	CIS-2-BUTEENI	0,09	0,16	0,8743
22	3-ME-1-BUTEENI	0,01	0,01	0,8743
28	1-PENTEENI	0,49	1,07	0,8743
29	IPA=ISOPROPANOLI	0,06	0,10	1,0000
31	2-ME-1-BUTEENI	0,01	0,03	0,8743
32	N-PENTAANI	0,75	1,71	0,8994
34	TRANS-2-PENTEENI	0,24	0,54	0,8743
36	CIS-2-PENTEENI	0,11	0,25	0,8743
39	2-ME-2-BUTEENI	0,04	0,08	0,8743
48	SYKLOPENTAANI	0,00	0,01	0,8743
49	2,3-DIME-BUTAANI	0,00	0,01	0,8952
53	2-ME-PENTAANI	0,01	0,03	0,8952
54	TRANS-4-ME-2-PENTEENI	0,00	0,00	0,8743
58	3-ME-PENTAANI	0,01	0,02	0,8952
63	N-HEKSAANI	0,33	0,90	0,8952
66	TRANS-2-HEKSEENI	0,03	0,07	0,8743
71	CIS-2-HEKSEENI	0,01	0,03	0,8743
77	ME-SYKLOPENTAANI	0,02	0,06	0,8743
93	BENTSEENI	0,03	0,07	0,8114
104	SYKLOHEKSAANI	0,01	0,02	0,8743
114	2-ME-HEKSAANI	0,01	0,02	0,8922
119	3-ME-HEKSAANI	0,00	0,01	0,8922
135	N-HEPTAANI	0,10	0,33	0,8922
147	ME-SYKLOHEKSAANI	0,00	0,01	0,8743
174	TOLUEENI	0,01	0,02	0,8204
188	2-ME-HEPTAANI	0,00	0,01	0,8900
214	N-OKTAANI	0,03	0,11	0,8900
287	N-NONAANI	0,01	0,03	0,8882
	AKROLEIINI	0,28	0,49	1,0000
	ASETALDEHYDI	0,03	0,04	1,0000
	PROPANAALI	0,48	0,88	1,0000
	ETIKKAHAPPO	0,02	0,04	1,0000
45	SYKLOPENTEENI	0,21	0,45	0,8491
41	SYKLOPENTADIEENI	0,01	0,03	0,8240
	PENTANAALI	0,00	0,01	1,0000
61	1-HEKSEENI	0,18	0,48	0,8743
64	TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,01	0,03	0,8743
67	2-ME-2-PENTEENI	0,01	0,01	0,8743
68	3-ME-SYKLOPENTEENI	0,00	0,01	0,8533
94	1-ME-SYKLOPENTEENI	0,01	0,01	0,8533
118	SYKLOHEKSEENI	0,02	0,07	0,8533
127	1-HEPTEENI	0,15	0,47	0,8743
133	TRANS-3-HEPTEENI	0,00	0,01	0,8743
	SYKLOHEPTEENI	0,00	0,01	0,8563
134	DIME-SYKLOPENTEENI	0,00	0,01	0,8563
139	TRANS-2-HEPTEENI	0,03	0,08	0,8743
144	CIS-2-HEPTEENI	0,01	0,04	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,01	0,8563
154	3-ME-SYKLOHEKSEENI	0,00	0,01	0,8563

185	1-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
166	C7H12-DIEENI	0,00	0,01	0,8563
	1-OKTEENI	0,02	0,09	0,8743
221	C8H16-OLEFIINI	0,01	0,02	0,8743
216	TRANS-2-OKTEENI	0,02	0,08	0,8743
222	CIS-2-OKTEENI	0,01	0,04	0,8743
	SYKLO-OKTEENI	0,01	0,02	0,8586
223	C8H14-SYKLO-OLEFIINI	0,01	0,03	0,8586
	C8H12-OLEFIININEN NAFTEENI	0,00	0,01	0,8429
250	ETYYLIBENTSEENI	0,00	0,01	0,8272
281	1-NONEENI	0,00	0,01	0,8743
	vety	5,06	0,32	
	typpi	8,41	7,41	
	hiilidioksidi	16,43	22,72	
	hiilimonoksidi	58,83	51,78	
	YHTEENSÄ	100,00	100,00	
	LUKUKESKIM. MOLEKYYLIPAINO =		31,82	
	ORG. mol-%	11,27		

Table 11. The components and their relative amounts of the first gas sample of experiment 3.

Näyte:	Koe 3, kaasu 0h
Analys.pvm:	5.2.2009
Tekijä:	RHX
Menetelmä:	NM428/NM291
Oili-koodi:	1081225

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	0,10	0,31	1,0000
2	ETEENI	0,08	0,39	0,8743
3	ETAANI	0,05	0,30	0,9371
4	PROPEENI	0,04	0,30	0,8743
5	PROPAANI	0,04	0,29	0,9162
10	I-BUTAANI	0,00	0,01	0,9057
12	I+1-BUTEENI	0,14	1,43	0,8743
14	N-BUTAANI	0,09	0,93	0,9057
16	TRANS-2-BUTEENI	0,00	0,02	0,8743
17	2,2-DIME-PROPAANI	0,00	0,02	0,8994
22	3-ME-1-BUTEENI	0,01	0,07	0,8743
28	1-PENTEENI	0,07	0,94	0,8743
31	2-ME-1-BUTEENI	0,00	0,02	0,8743
32	N-PENTAANI	0,21	2,80	0,8994
34	TRANS-2-PENTEENI	0,00	0,06	0,8743
36	CIS-2-PENTEENI	0,00	0,03	0,8743
39	2-ME-2-BUTEENI	0,05	0,62	0,8743
53	2-ME-PENTAANI	0,00	0,01	0,8952
58	3-ME-PENTAANI	0,00	0,01	0,8952
63	N-HEKSAANI	0,04	0,68	0,8952

66	TRANS-2-HEKSEENI	0,00	0,01	0,8743
71	CIS-2-HEKSEENI	0,00	0,01	0,8743
77	ME-SYKLOPENTAANI	0,00	0,01	0,8743
93	BENTSEENI	0,00	0,03	0,8114
	C7H14-OLEFIINI	0,00	0,03	0,8743
135	N-HEPTAANI	0,03	0,47	0,8922
147	ME-SYKLOHEKSAANI	0,00	0,02	0,8743
174	TOLUEENI	0,00	0,03	0,8204
238	C8-NAFTEENI	0,00	0,01	0,8743
188	2-ME-HEPTAANI	0,00	0,01	0,8900
194	3-ME-HEPTAANI	0,00	0,01	0,8900
214	N-OKTAANI	0,01	0,20	0,8900
287	N-NONAANI	0,00	0,02	0,8882
	AKROLEIINI	1,21	12,55	1,0000
	ASETALDEHYDI	0,02	0,20	1,0000
24	ASETONI	0,00	0,05	1,0000
	PROPANAALI	0,11	1,19	1,0000
	1,3-BUTADIEENI	0,00	0,01	0,8429
33	2-ME-1,3-BUTADIEENI	0,00	0,05	0,8491
	FURAANI	0,00	0,02	1,0000
45	SYKLOPENTEENI	0,00	0,05	0,8491
41	SYKLOPENTADIEENI	0,01	0,08	0,8240
	PENTANAALI	0,00	0,03	1,0000
61	1-HEKSEENI	0,04	0,59	0,8743
94	1-ME-SYKLOPENTEENI	0,00	0,01	0,8533
118	SYKLOHEKSEENI	0,00	0,01	0,8533
113	CIS-4-ME-2-HEKSEENI	0,00	0,01	0,8952
95	C6H10-DIEENI	0,00	0,02	0,8533
107	C6H8-SYKLODIEENI	0,00	0,01	0,8324
	HEKSANAALI	0,01	0,22	1,0000
127	1-HEPTEENI	0,10	1,87	0,8743
134	DIME-SYKLOPENTEENI	0,00	0,01	0,8563
139	TRANS-2-HEPTEENI	0,01	0,09	0,8743
144	CIS-2-HEPTEENI	0,00	0,05	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,01	0,8563
155	4-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
185	1-ME-SYKLOHEKSEENI	0,00	0,02	0,8563
166	C7H12-DIEENI	0,00	0,01	0,8563
	1-OKTEENI	0,01	0,27	0,8743
207	C8H16-NAFTEENI	0,00	0,01	0,8743
221	C8H16-OLEFIINI	0,00	0,01	0,8743
216	TRANS-2-OKTEENI	0,01	0,20	0,8743
222	CIS-2-OKTEENI	0,00	0,10	0,8743
	SYKLO-OKTEENI	0,00	0,02	0,8586
223	C8H14-SYKLO-OLEFIINI	0,00	0,02	0,8586
218	C8H14-DIEENI	0,00	0,02	0,8586
234	C9-PARAFIINI	0,00	0,01	0,8882
250	ETYYLIBENTSEENI	0,00	0,01	0,8272
257	META-KSYLEENI	0,00	0,05	0,8272
258	PARA-KSYLEENI	0,00	0,01	0,8272
268		0,00	0,01	0,8882
276	ORTO-KSYLEENI	0,00	0,01	0,8272

281	1-NONEENI	0,00	0,02	0,8743
	vety	90,49	33,84	
	typpi	3,22	16,71	
	hiilidioksidi	0,63	5,16	
	hiilimonoksidi	3,12	16,22	
	YHTEENSÄ	100,00	100,00	
	LUKUKESKIM. MOLEKYYLIPAINO =		5,39	
	ORG. mol-%	2,54		

Näytteessä on jälkiä yhdisteistä butanaali ja MEK.

Table 12. The components and their relative amounts of the second gas sample of experiment 3.

Näyte:	Koe 3, kaasu 2 h
Analys.pvm:	4.2.2009
Tekijä:	RHX
Menetelmä:	NM428/NM291
Oili-koodi:	1081227

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	0,45	0,80	1,0000
2	ETEENI	0,39	1,22	0,8743
3	ETAANI	0,66	2,18	0,9371
4	PROPEENI	0,21	0,98	0,8743
5	PROPAANI	0,29	1,42	0,9162
10	I-BUTAANI	0,00	0,02	0,9057
12	I+1-BUTEENI	0,31	1,93	0,8743
14	N-BUTAANI	0,42	2,70	0,9057
16	TRANS-2-BUTEENI	0,03	0,16	0,8743
19	CIS-2-BUTEENI	0,02	0,11	0,8743
22	3-ME-1-BUTEENI	0,01	0,05	0,8743
28	1-PENTEENI	0,22	1,69	0,8743
31	2-ME-1-BUTEENI	0,02	0,12	0,8743
32	N-PENTAANI	0,51	4,08	0,8994
34	TRANS-2-PENTEENI	0,03	0,20	0,8743
36	CIS-2-PENTEENI	0,01	0,09	0,8743
39	2-ME-2-BUTEENI	0,05	0,41	0,8743
48	SYKLOPENTAANI	0,00	0,02	0,8743
53	2-ME-PENTAANI	0,00	0,02	0,8952
58	3-ME-PENTAANI	0,00	0,01	0,8952
63	N-HEKSAANI	0,35	3,35	0,8952
66	TRANS-2-HEKSEENI	0,02	0,16	0,8743
71	CIS-2-HEKSEENI	0,01	0,08	0,8743
77	ME-SYKLOPENTAANI	0,00	0,04	0,8743
93	BENTSEENI	0,01	0,09	0,8114
104	SYKLOHEKSAANI	0,00	0,01	0,8743
116	1,1-DIME-SYKLOPENTAANI	0,00	0,01	0,8743
135	N-HEPTAANI	0,19	2,11	0,8922

147	ME-SYKLOHEKSAANI	0,01	0,08	0,8743
152	ET-SYKLOPENTAANI	0,00	0,01	0,8743
174	TOLUEENI	0,01	0,07	0,8204
188	2-ME-HEPTAANI	0,00	0,01	0,8900
194	3-ME-HEPTAANI	0,00	0,01	0,8900
206?	1-ME-TRANS-2-ET-SYKLOPENTAANI	0,00	0,02	0,8747
214	N-OKTAANI	0,07	0,94	0,8900
238	C8-NAFTEENI	0,00	0,03	0,8743
236	ET-SYKLOHEKSAANI	0,00	0,01	0,8747
268	2-ME-OKTAANI	0,00	0,01	0,8882
267	4-ME-OKTAANI	0,00	0,01	0,8882
	C8H10-OLEFIININEN NAFTEENI	0,00	0,01	0,8272
287	N-NONAANI	0,02	0,21	0,8882
	AKROLEIINI	0,56	3,43	1,0000
	ASETALDEHYDI	0,03	0,16	1,0000
24	ASETONI	0,01	0,05	1,0000
	ETIKKAHAPPO	0,03	0,21	1,0000
	PROPANAALI	0,47	3,00	1,0000
	PROPIONIHAPPO	0,00	0,01	1,0000
45	SYKLOPENTEENI	0,16	1,17	0,8491
41	SYKLOPENTADIEENI	0,00	0,01	0,8240
43	CIS-1,3-PENTADIEENI	0,00	0,01	0,8491
	FURAANI	0,00	0,02	1,0000
	C2-FURAANI C6H8O	0,00	0,04	1,0000
	PENTANAALI	0,01	0,06	1,0000
	1-ASETOKSIASETONI	0,00	0,02	1,0000
61	1-HEKSEENI	0,17	1,62	0,8743
64	TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,00	0,02	0,8743
67	2-ME-2-PENTEENI	0,00	0,01	0,8743
68	3-ME-SYKLOPENTEENI	0,00	0,02	0,8533
70	4-ME-SYKLOPENTEENI	0,00	0,01	0,8533
72	TRANS-3-ME-2-PENTEENI	0,00	0,01	0,8743
94	1-ME-SYKLOPENTEENI	0,01	0,06	0,8533
118	SYKLOHEKSEENI	0,02	0,22	0,8533
112	4-ME-1-HEKSEENI	0,00	0,01	0,8952
107	C6H8-SYKLODIEENI	0,00	0,01	0,8324
	C6-KETONI	0,00	0,01	1,0000
	C6H12O	0,00	0,01	1,0000
	HEKSANAALI	0,00	0,05	1,0000
	HEKSADIONI	0,00	0,02	1,0000
	HEKSENONI	0,00	0,01	1,0000
	C7-KETONI C7H14O	0,00	0,01	1,0000
120	C7H14-OLEFIINI	0,00	0,02	0,8743
127	1-HEPTEENI	0,30	3,24	0,8743
133	TRANS-3-HEPTEENI	0,00	0,03	0,8743
134	DIME-SYKLOPENTEENI	0,00	0,03	0,8563
139	TRANS-2-HEPTEENI	0,04	0,44	0,8743
144	CIS-2-HEPTEENI	0,02	0,21	0,8743
136	CIS-3-HEPTEENI	0,00	0,01	0,8743
	SYKLOHEPTEENI	0,00	0,04	0,8563
145	1-ET-SYKLOPENTEENI	0,00	0,03	0,8563

130	ME-SYKLOHEKSEENI	0,00	0,01	0,8563
146	1-CIS-2-DIME-SYKLOPENTAANI	0,00	0,01	0,8743
154	3-ME-SYKLOHEKSEENI	0,00	0,03	0,8563
155	4-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
172	ET-SYKLOPENTEENI	0,00	0,01	0,8563
185	1-ME-SYKLOHEKSEENI	0,01	0,08	0,8563
166	C7H12-DIEENI	0,00	0,02	0,8563
	BENTSALDEHYDI	0,00	0,01	1,0000
	1-OKTEENI	0,05	0,66	0,8743
207	C8H16-NAFTEENI	0,00	0,01	0,8743
221	C8H16-OLEFIINI	0,00	0,06	0,8743
216	TRANS-2-OKTEENI	0,04	0,50	0,8743
222	CIS-2-OKTEENI	0,02	0,23	0,8743
	SYKLO-OKTEENI	0,01	0,16	0,8586
223	C8H14-SYKLO-OLEFIINI	0,00	0,04	0,8586
218	C8H14-DIEENI	0,00	0,01	0,8586
	C8H16O	0,00	0,01	1,0000
250	ETYYLIBENTSEENI	0,00	0,01	0,8272
257	META-KSYLEENI	0,00	0,03	0,8272
258	PARA-KSYLEENI	0,00	0,01	0,8272
	HEPTANAALI	0,00	0,02	1,0000
276	ORTO-KSYLEENI	0,00	0,01	0,8272
281	1-NONEENI	0,01	0,11	0,8743
	TRANS-2-NONEENI	0,00	0,03	0,8743
	CIS-2-NONEENI	0,00	0,01	0,8743
	C9H16	0,00	0,04	0,8603
306	PROPYYLISYKLOHEKSAANI	0,00	0,01	0,8743
312	N-PROPYYLIBENTSEENI	0,00	0,01	0,8324
	vety	82,19	18,24	
	typpi	0,26	0,79	
	hiilidioksidi	2,61	12,63	
	hiilimonoksidi	8,55	26,37	
	YHTEENSÄ	100,00	100,00	

LUKUKESKIM.
MOLEKYYLIPAINO = 9,09

ORG. mol-% 6,39

Näytteessä on jälkiä yhdisteistä butanaali ja MEK.

Table 13. The components and their relative amounts of the first gas sample of experiment 4.

Näyte:	Koe 4, kaasu 0 h
Analys.pvm:	11.2.2009
Tekijä:	TKZ, RHX
Menetelmä:	NM428/NM291
Oili-koodi:	1119814

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	0,76	0,39	1,0000
2	ETEENI	0,33	0,29	0,8743
3	ETAANI	0,39	0,37	0,9371
4	PROPEENI	0,18	0,25	0,8743
5	PROPAANI	0,23	0,33	0,9162
10	I-BUTAANI	0,01	0,01	0,9057
12	I+1-BUTEENI	0,76	1,36	0,8743
13	1,3-BUTADIEENI	0,01	0,01	0,8429
14	N-BUTAANI	0,55	1,01	0,9057
16	TRANS-2-BUTEENI	0,01	0,02	0,8743
19	CIS-2-BUTEENI	0,01	0,02	0,8743
22	3-ME-1-BUTEENI	0,03	0,07	0,8743
28	1-PENTEENI	0,36	0,81	0,8743
31	2-ME-1-BUTEENI	0,01	0,02	0,8743
32	N-PENTAANI	1,93	4,43	0,8994
34	TRANS-2-PENTEENI	0,03	0,06	0,8743
36	CIS-2-PENTEENI	0,01	0,03	0,8743
37	ME-SYKLOBUTAANI	0,00	0,01	0,8743
39	2-ME-2-BUTEENI	0,27	0,61	0,8743
54	TRANS-4-ME-2-PENTEENI	0,00	0,01	0,8994
63	N-HEKSAANI	0,22	0,60	0,8952
66	TRANS-2-HEKSEENI	0,00	0,01	0,8743
71	CIS-2-HEKSEENI	0,00	0,01	0,8743
77	ME-SYKLOPENTAANI	0,01	0,01	0,8743
93	BENTSEENI	0,01	0,03	0,8114
120	C7H14-OLEFIINI	0,01	0,02	0,8743
135	N-HEPTAANI	0,18	0,59	0,8922
147	ME-SYKLOHEKSAANI	0,00	0,02	0,8743
174	TOLUEENI	0,01	0,02	0,8204
188	2-ME-HEPTAANI	0,00	0,01	0,8900
194	3-ME-HEPTAANI	0,00	0,01	0,8900
214	N-OKTAANI	0,06	0,21	0,8900
287	N-NONAANI	0,00	0,01	0,8882
	AKROLEIINI	7,59	13,48	1,0000
	ASETALDEHYDI	0,23	0,33	1,0000
24	ASETONI	0,01	0,01	1,0000
	PROPANAALI	0,45	0,83	1,0000
33	2-ME-1,3-BUTADIEENI	0,05	0,10	0,8491
45	SYKLOPENTEENI	0,01	0,02	0,8491
41	SYKLOPENTADIEENI	0,05	0,10	0,8240
40	TRANS-1,3-PENTADIEENI	0,00	0,01	0,8491
43	CIS-1,3-PENTADIEENI	0,00	0,01	0,8491
	FURAANI	0,01	0,03	1,0000
	BUTANAALI	0,02	0,05	1,0000

	ISO-BUTANAALI	0,00	0,01	1,0000
	PENTANAALI	0,03	0,08	1,0000
61	1-HEKSEENI	0,19	0,51	0,8743
67	2-ME-2-PENTEENI	0,00	0,01	0,8743
94	1-ME-SYKLOPENTEENI	0,00	0,01	0,8533
118	SYKLOHEKSEENI	0,00	0,01	0,8533
95	C6H10-DIEENI	0,01	0,02	0,8533
107	C6H8-SYKLODIEENI	0,00	0,01	0,8324
	HEKSANAALI	0,07	0,21	1,0000
127	1-HEPTEENI	0,40	1,24	0,8743
134	DIME-SYKLOPENTEENI	0,00	0,01	0,8563
139	TRANS-2-HEPTEENI	0,02	0,06	0,8743
144	CIS-2-HEPTEENI	0,01	0,03	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,01	0,8563
160	C7H10-SYKLODIEENI	0,00	0,01	0,8384
185	1-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
166	C7H12-DIEENI	0,00	0,01	0,8563
	1-OKTEENI	0,04	0,15	0,8743
207	C8H16-NAFTEENI	0,00	0,01	0,8743
221	C8H16-OLEFIINI	0,00	0,01	0,8743
216	TRANS-2-OKTEENI	0,03	0,10	0,8743
222	CIS-2-OKTEENI	0,01	0,05	0,8743
	SYKLO-OKTEENI	0,00	0,01	0,8586
223	C8H14-SYKLO-OLEFIINI	0,01	0,02	0,8586
218	C8H14-DIEENI	0,00	0,02	0,8586
257	META-KSYLEENI	0,00	0,01	0,8272
258	PARA-KSYLEENI	0,00	0,01	0,8272
268	2-ME-OKTAANI	0,00	0,01	0,8882
276	ORTO-KSYLEENI	0,00	0,01	0,8272
281	1-NONEENI	0,00	0,01	0,8743
292	C9H16-DIEENI	0,00	0,01	0,8603
	TUNTEMATON	0,06	0,13	0,8743
	vety	9,50	0,61	
	happi	13,08	13,27	
	typpi	53,85	47,82	
	hiilidioksidi	3,75	5,24	
	hiilimonoksidi	4,02	3,57	
	YHTEENSÄ	100,00	100,00	
	LUKUKESKIM. MOLEKYYLIPAINO =		31,54	
	ORG. mol-%	15,80		

Näytteessä on jälkiä yhdisteestä C5H8O.

Näytettä ei riittänyt tarpeeksi epäorgaanisten kaasujen määritykseen
ja MS-tunnistukseen.

Todennäköisesti näytteen loppupää on samanlainen kuin 2 tunnin näytteellä, mutta piikit on laitettu tuntemattomiin, koska varmuutta siitä ei ole.

Table 14. The components and their relative amounts of the second gas sample of experiment 4.

Näyte:	Koe 4, kaasu 2h
Analys.pvm:	16.2.2009
Tekijä:	TKZ
Menetelmä:	NM428/NM291
Oili-koodi:	1119815

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	1,15	0,55	1,0000
2	ETEENI	1,09	0,90	0,8743
3	ETAANI	1,39	1,24	0,9371
4	PROPEENI	0,57	0,72	0,8743
5	PROPAANI	0,59	0,78	0,9162
10	I-BUTAANI	0,01	0,01	0,9057
12	I+1-BUTEENI	0,83	1,38	0,8743
14	N-BUTAANI	1,09	1,89	0,9057
16	TRANS-2-BUTEENI	0,06	0,10	0,8743
19	CIS-2-BUTEENI	0,04	0,07	0,8743
22	3-ME-1-BUTEENI	0,02	0,03	0,8743
25	I-PENTAANI	0,08	0,17	0,8994
28	1-PENTEENI	0,00	0,01	0,8743
31	2-ME-1-BUTEENI	0,04	0,08	0,8743
32	N-PENTAANI	1,31	2,80	0,8994
34	TRANS-2-PENTEENI	0,06	0,12	0,8743
36	CIS-2-PENTEENI	0,02	0,05	0,8743
39	2-ME-2-BUTEENI	0,13	0,26	0,8743
48	SYKLOPENTAANI	0,00	0,01	0,8743
53	2-ME-PENTAANI	0,00	0,01	0,8952
58	3-ME-PENTAANI	0,00	0,01	0,8952
63	N-HEKSAANI	0,71	1,82	0,8952
66	TRANS-2-HEKSEENI	0,03	0,09	0,8743
71	CIS-2-HEKSEENI	0,02	0,04	0,8743
77	ME-SYKLOPENTAANI	0,01	0,02	0,8743
93	BENTSEENI	0,02	0,06	0,8114
104	SYKLOHEKSAANI	0,00	0,01	0,8743
119	3-ME-HEKSAANI	0,00	0,01	0,8922
124	CIS-1,3-DIME-SYKLOPENTAANI	0,00	0,01	0,8743
135	N-HEPTAANI	0,24	0,72	0,8922
147	ME-SYKLOHEKSAANI	0,01	0,02	0,8743
174	TOLUEENI	0,00	0,01	0,8204
214	N-OKTAANI	0,04	0,14	0,8900
287	N-NONAANI	0,00	0,01	0,8882
	AKROLEIINI	0,96	1,59	1,0000
	ASETALDEHYDI	0,13	0,18	1,0000
	PROPANAALI	1,16	1,99	1,0000
	C4H4O	0,67	1,36	1,0000
45	SYKLOPENTEENI	0,34	0,69	0,8491
	BUTANAALI	0,01	0,01	1,0000
	ETIKKAHAPPO	0,03	0,06	1,0000
	PENTANAALI	0,01	0,02	1,0000
61	1-HEKSEENI	0,39	0,97	0,8743
68	3-ME-SYKLOPENTEENI	0,00	0,01	0,8533

94	1-ME-SYKLOPENTEENI	0,01	0,03	0,8533
118	SYKLOHEKSEENI	0,03	0,08	0,8533
	C6H8O	0,00	0,01	1,0000
	HEKSANAALI	0,00	0,01	1,0000
	SYKLOHEPTEENI	0,00	0,01	0,8563
127	1-HEPTEENI	0,40	1,16	0,8743
134	DIME-SYKLOPENTEENI	0,00	0,01	0,8563
139	TRANS-2-HEPTEENI	0,05	0,13	0,8743
144	CIS-2-HEPTEENI	0,02	0,06	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,01	0,8563
154	3-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
155	4-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
185	1-ME-SYKLOHEKSEENI	0,01	0,02	0,8563
	1-OKTEENI	0,03	0,10	0,8743
221	C8H16-OLEFIINI	0,00	0,01	0,8743
216	TRANS-2-OKTEENI	0,02	0,06	0,8743
222	CIS-2-OKTEENI	0,01	0,03	0,8743
	SYKLO-OKTEENI	0,00	0,01	0,8586
223	C8H14-SYKLO-OLEFIINI	0,00	0,01	0,8586
281	1-NONEENI	0,00	0,01	0,8743
	vety	3,50	0,21	
	typpi	9,28	7,71	
	hiilidioksidi	17,51	22,85	
	hiilimonoksidi	55,75	46,31	
	YHTEENSÄ	100,00	100,00	
	LUKUKESKIM. MOLEKYYLIPAINO =		33,73	
	ORG. mol-%	13,96		

Table 15. The components and their relative amounts of the first gas sample of experiment 5.

Näyte:	Koe 5, kaasu 0 h
Analys.pvm:	16.2.2009
Tekijä:	RHX, TKZ
Menetelmä:	NM428/NM291
Oili-koodi:	1134595

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	1,24	2,37	1,0000
2	ETEENI	0,40	1,32	0,8743
3	ETAANI	0,31	1,10	0,9371
4	PROPEENI	0,22	1,12	0,8743
5	PROPAANI	0,21	1,12	0,9162
10	I-BUTAANI	0,03	0,18	0,9057
11	METANOLI	0,00	0,02	1,0000
12	I+1-BUTEENI	0,64	4,29	0,8743
13	1,3-BUTADIEENI	0,01	0,09	0,8429
14	N-BUTAANI	0,34	2,32	0,9057
16	TRANS-2-BUTEENI	0,02	0,16	0,8743

19	CIS-2-BUTEENI	0,02	0,10	0,8743
21	ETANOLI	0,01	0,05	1,0000
22	3-ME-1-BUTEENI	0,03	0,25	0,8743
28	1-PENTEENI	0,28	2,36	0,8743
31	2-ME-1-BUTEENI	0,01	0,11	0,8743
32	N-PENTAANI	0,32	2,75	0,8994
34	TRANS-2-PENTEENI	0,08	0,64	0,8743
36	CIS-2-PENTEENI	0,04	0,34	0,8743
39	2-ME-2-BUTEENI	0,19	1,61	0,8743
53	2-ME-PENTAANI	0,00	0,02	0,8952
63	N-HEKSAANI	0,13	1,33	0,8952
66	TRANS-2-HEKSEENI	0,01	0,05	0,8743
71	CIS-2-HEKSEENI	0,01	0,05	0,8743
77	ME-SYKLOPENTAANI	0,00	0,03	0,8743
93	BENTSEENI	0,08	0,73	0,8114
135	N-HEPTAANI	0,06	0,73	0,8922
147	ME-SYKLOHEKSAANI	0,00	0,04	0,8743
160	C7H10-SYKLODIEENI	0,00	0,01	0,8384
174	TOLUEENI	0,02	0,26	0,8204
188	2-ME-HEPTAANI	0,00	0,02	0,8900
190	4-ME-HEPTAANI	0,00	0,00	0,8900
194	3-ME-HEPTAANI	0,00	0,02	0,8900
214	N-OKTAANI	0,01	0,19	0,8900
	ASETONITRIILI	0,01	0,05	1,0000
	AKROLEIINI	3,73	24,80	1,0000
	ASETALDEHYDI	0,42	2,20	1,0000
24	ASETONI	0,06	0,43	1,0000
	ETIKKAHAPPO	0,00	0,02	1,0000
	PROPANAALI	0,70	4,82	1,0000
	N-PROPANOLI	0,00	0,01	1,0000
33	2-ME-1,3-BUTADIEENI	0,06	0,50	0,8491
45	SYKLOPENTEENI	0,02	0,19	0,8491
41	SYKLOPENTADIEENI	0,07	0,53	0,8240
40	TRANS-1,3-PENTADIEENI	0,01	0,11	0,8491
43	CIS-1,3-PENTADIEENI	0,01	0,07	0,8491
	FURAANI	0,01	0,11	1,0000
	ME-FURAANI	0,00	0,02	1,0000
	ISO-BUTANAALI	0,09	0,75	1,0000
	3-ME-BUTANAALI	0,14	1,47	1,0000
	2-ME-BUTANAALI	0,03	0,33	1,0000
61	1-HEKSEENI	0,10	1,02	0,8743
64	TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,01	0,05	0,8743
67	2-ME-2-PENTEENI	0,00	0,02	0,8743
46	4-ME-1-PENTEENI	0,00	0,01	0,8743
47	3-ME-1-PENTEENI	0,00	0,01	0,8743
68	3-ME-SYKLOPENTEENI	0,00	0,02	0,8533
94	1-ME-SYKLOPENTEENI	0,00	0,02	0,8533
118	SYKLOHEKSEENI	0,01	0,07	0,8533
96	3-ME-1-HEKSEENI	0,00	0,02	0,8952
95	C6H10-DIEENI	0,01	0,09	0,8533
107	C6H8-SYKLODIEENI	0,03	0,33	0,8324

	HEKSANAALI	0,01	0,06	1,0000
97	TIOFEENI	0,00	0,04	1,0000
120	C7H14-OLEFIINI	0,00	0,01	0,8743
127	1-HEPTEENI	0,21	2,49	0,8743
134	DIME-SYKLOPENTEENI	0,00	0,02	0,8563
139	TRANS-2-HEPTEENI	0,01	0,16	0,8743
144	CIS-2-HEPTEENI	0,01	0,08	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,02	0,8563
185	1-ME-SYKLOHEKSEENI	0,00	0,03	0,8563
166	C7H12-DIEENI	0,00	0,04	0,8563
	1-OKTEENI	0,02	0,22	0,8743
216	TRANS-2-OKTEENI	0,01	0,13	0,8743
222	CIS-2-OKTEENI	0,00	0,06	0,8743
257	META-KSYLEENI	0,00	0,06	0,8272
258	PARA-KSYLEENI	0,00	0,02	0,8272
	vety	86,23	20,63	
	typpi	1,50	4,98	
	hiilidioksidi	0,78	4,05	
	hiilimonoksidi	0,90	3,00	
	YHTEENSÄ	100,00	100,00	
	LUKUKESKIM. MOLEKYYLIPAINO =		8,43	
	ORG. mol-%	10,59		

Näytteessä on jälkiä yhdisteistä kloorimetaani, pentanaali ja etyylibentseeni.

MS-tunnistuksessa on näkynyt enemmän piikkejä kuin GC-ajossa.

Table 16. The components and their relative amounts of the second gas sample of experiment 5.

Näyte:	Koe 5, kaasu 2 h
Analys.pvm:	17.2.2009
Tekijä:	RHX
Menetelmä:	NM428/NM291
Oili-koodi:	1134594

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	1,36	1,92	1,0000
2	ETEENI	1,28	3,16	0,8743
3	ETAANI	1,46	3,88	0,9371
4	PROPEENI	0,45	1,68	0,8743
5	PROPAANI	0,56	2,19	0,9162
10	I-BUTAANI	0,08	0,41	0,9057
12	I+1-BUTEENI	0,59	2,91	0,8743
13	1,3-BUTADIEENI	0,00	0,01	0,8429
14	N-BUTAANI	0,72	3,70	0,9057
16	TRANS-2-BUTEENI	0,08	0,38	0,8743

19	CIS-2-BUTEENI	0,05	0,26	0,8743
22	3-ME-1-BUTEENI	0,02	0,11	0,8743
28	1-PENTEENI	0,40	2,48	0,8743
31	2-ME-1-BUTEENI	0,03	0,18	0,8743
32	N-PENTAANI	0,65	4,17	0,8994
34	TRANS-2-PENTEENI	0,10	0,59	0,8743
36	CIS-2-PENTEENI	0,04	0,27	0,8743
39	2-ME-2-BUTEENI	0,08	0,49	0,8743
48	SYKLOPENTAANI	0,00	0,03	0,8743
53	2-ME-PENTAANI	0,00	0,04	0,8952
54	TRANS-4-ME-2-PENTEENI	0,00	0,01	0,8743
58	3-ME-PENTAANI	0,00	0,02	0,8952
63	N-HEKSAANI	0,54	4,14	0,8952
66	TRANS-2-HEKSEENI	0,04	0,32	0,8743
71	CIS-2-HEKSEENI	0,02	0,15	0,8743
77	ME-SYKLOPENTAANI	0,01	0,05	0,8743
93	BENTSEENI	0,04	0,27	0,8114
101	C7H14-OLEFIINI	0,00	0,01	0,8743
104	SYKLOHEKSAANI	0,00	0,01	0,8743
114	2-ME-HEKSAANI	0,00	0,01	0,8922
116	1,1-DIME-SYKLOPENTAANI	0,00	0,01	0,8743
135	N-HEPTAANI	0,28	2,52	0,8922
147	ME-SYKLOHEKSAANI	0,01	0,09	0,8743
152	ET-SYKLOPENTAANI	0,00	0,02	0,8743
174	TOLUEENI	0,02	0,18	0,8204
198	TRANS-1,3-DIME-SYKLOHEKSAANI	0,00	0,01	0,8743
238	C8-NAFTEENI	0,00	0,03	0,8743
188	2-ME-HEPTAANI	0,00	0,02	0,8900
194	3-ME-HEPTAANI	0,00	0,01	0,8900
217	1-CIS-3-DIME-SYKLOHEKSAANI	0,00	0,01	0,8747
214	N-OKTAANI	0,09	0,92	0,8900
235	N-PROPYYLI-SYKLOPENTAANI	0,00	0,01	0,8747
236	ET-SYKLOHEKSAANI	0,00	0,01	0,8747
267	4-ME-OKTAANI	0,00	0,01	0,8882
268	2-ME-OKTAANI	0,00	0,01	0,8882
287	N-NONAANI	0,01	0,08	0,8882
	AKROLEIINI	0,73	3,63	1,0000
	ASETALDEHYDI	0,14	0,55	1,0000
24	ASETONI	0,02	0,10	1,0000
	ETIKKAHAPPO	0,00	0,01	1,0000
	PROPANAALI	0,95	4,85	1,0000
45	SYKLOPENTEENI	0,11	0,64	0,8491
40	TRANS-1,3-PENTADIEENI	0,00	0,01	0,8491
43	CIS-1,3-PENTADIEENI	0,00	0,01	0,8491
	BUTANAALI	0,00	0,01	1,0000
	ISO-BUTANAALI	0,02	0,10	1,0000
56	2-BUTANONI	0,00	0,01	1,0000
	FURAANI	0,00	0,01	1,0000
	ME-FURAANI	0,00	0,02	1,0000
	C2-FURAANI	0,01	0,07	1,0000
97	TIOFEENI	0,00	0,01	1,0000

	PENTANAALI	0,01	0,07	1,0000
	3-ME-BUTANAALI	0,03	0,26	1,0000
	2-ME-BUTANAALI	0,01	0,07	1,0000
	C5H8O	0,01	0,05	1,0000
61	1-HEKSEENI	0,29	2,12	0,8743
64	TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,00	0,03	0,8743
67	2-ME-2-PENTEENI	0,00	0,01	0,8743
46	4-ME-1-PENTEENI	0,00	0,03	0,8743
47	3-ME-1-PENTEENI	0,00	0,01	0,8743
68	3-ME-SYKLOPENTEENI	0,00	0,02	0,8533
70	4-ME-SYKLOPENTEENI	0,00	0,01	0,8533
69	CIS-3-ME-2-PENTEENI	0,00	0,01	0,8743
72	TRANS-3-ME-2-PENTEENI	0,00	0,02	0,8743
94	1-ME-SYKLOPENTEENI	0,01	0,07	0,8533
118	SYKLOHEKSEENI	0,03	0,20	0,8533
96	3-ME-1-HEKSEENI	0,00	0,01	0,8952
112	4-ME-1-HEKSEENI	0,00	0,01	0,8952
113	CIS-4-ME-2-HEKSEENI	0,00	0,01	0,8952
95	C6H10-DIEENI	0,00	0,01	0,8533
107	C6H8-SYKLODIEENI	0,00	0,01	0,8324
	C6H10O	0,00	0,01	1,0000
	C6H12O	0,00	0,01	1,0000
	HEKSANAALI	0,00	0,02	1,0000
	HEKSADIONI	0,00	0,03	1,0000
	SYKLOHEPTEENI	0,00	0,03	0,8563
127	1-HEPTEENI	0,47	4,06	0,8743
133	TRANS-3-HEPTEENI	0,01	0,05	0,8743
134	DIME-SYKLOPENTEENI	0,01	0,06	0,8563
139	TRANS-2-HEPTEENI	0,10	0,84	0,8743
144	CIS-2-HEPTEENI	0,05	0,40	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,04	0,8563
154	3-ME-SYKLOHEKSEENI	0,01	0,04	0,8563
155	4-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
172	ET-SYKLOPENTEENI	0,00	0,02	0,8563
185	1-ME-SYKLOHEKSEENI	0,01	0,08	0,8563
166	C7H12-DIEENI	0,00	0,02	0,8563
	C7-KETONI	0,00	0,01	1,0000
	1-OKTEENI	0,07	0,72	0,8743
207	C8H16-NAFTEENI	0,00	0,01	0,8743
221	C8H16-OLEFIINI	0,01	0,14	0,8743
216	TRANS-2-OKTEENI	0,06	0,56	0,8743
222	CIS-2-OKTEENI	0,03	0,27	0,8743
	SYKLO-OKTEENI	0,00	0,04	0,8586
223	C8H14-SYKLO-OLEFIINI	0,01	0,08	0,8586
218	C8H14-DIEENI	0,00	0,02	0,8586
	C8H12-OLEFIININEN NAFTEENI	0,00	0,01	0,8429
	C8H16O	0,00	0,01	1,0000
250	ETYYLIBENTSEENI	0,00	0,04	0,8272
257	META-KSYLEENI	0,01	0,13	0,8272
258	PARA-KSYLEENI	0,00	0,05	0,8272
	HEPTANAALI	0,00	0,01	1,0000

272	3-ET-HEPTAANI	0,00	0,01	0,8882
273	3-ME-OKTAANI	0,00	0,01	0,8882
276	ORTO-KSYLEENI	0,00	0,03	0,8272
281	1-NONEENI	0,00	0,05	0,8743
284	C9H18-OLEFIINI	0,00	0,01	0,8743
	TRANS-2-NONEENI	0,00	0,02	0,8743
	CIS-2-NONEENI	0,00	0,01	0,8743
	C9H14-OLEFIININEN NAFTEENI	0,00	0,01	0,8464
	vety	77,91	13,88	
	typpi	0,46	1,13	
	hiilidioksidi	2,18	8,46	
	hiilimonoksidi	7,13	17,64	
	YHTEENSÄ	100,00	100,00	
	LUKUKESKIM. MOLEKYYLIPAINO =		11,32	
	ORG. mol-%	12,33		

Näytteessä on jälkiä yhdisteistä metanoli,
asetonitriili ja C4H6O.

Table 17. The components and their relative amounts of the first gas sample of experiment 6.

Näyte:	Koe 6, kaasu #2, 0h
Analys.pvm:	18.2.2009
Tekijä:	TKZ
Menetelmä:	NM428/NM291
Oili-koodi:	1170436

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	0,96	0,48	1,0000
2	ETEENI	0,54	0,48	0,8743
3	ETAANI	0,53	0,50	0,9371
4	PROPEENI	0,26	0,34	0,8743
5	PROPAANI	0,30	0,41	0,9162
10	I-BUTAANI	0,04	0,07	0,9057
12	I+1-BUTEENI	0,71	1,25	0,8743
13	1,3-BUTADIEENI	0,01	0,02	0,8429
14	N-BUTAANI	0,49	0,88	0,9057
16	TRANS-2-BUTEENI	0,03	0,05	0,8743
19	CIS-2-BUTEENI	0,02	0,03	0,8743
22	3-ME-1-BUTEENI	0,03	0,07	0,8743
25	I-PENTAANI	0,00	0,01	0,8994
28	1-PENTEENI	0,37	0,80	0,8743
31	2-ME-1-BUTEENI	0,02	0,04	0,8743
32	N-PENTAANI	0,66	1,50	0,8994
34	TRANS-2-PENTEENI	0,09	0,19	0,8743
36	CIS-2-PENTEENI	0,04	0,10	0,8743
39	2-ME-2-BUTEENI	0,19	0,41	0,8743

53	2-ME-PENTAANI	0,00	0,01	0,8952
63	N-HEKSAANI	0,24	0,65	0,8952
66	TRANS-2-HEKSEENI	0,01	0,03	0,8743
71	CIS-2-HEKSEENI	0,01	0,01	0,8743
77	ME-SYKLOPENTAANI	0,00	0,01	0,8743
93	BENTSEENI	0,09	0,22	0,8114
97	TIOFEENI	0,00	0,01	1,0000
120	C7H14-OLEFIINI	0,00	0,01	0,8743
135	N-HEPTAANI	0,16	0,51	0,8922
147	ME-SYKLOHEKSAANI	0,00	0,01	0,8743
160	C7H10-SYKLODIEENI	0,00	0,01	0,8384
174	TOLUEENI	0,02	0,06	0,8204
214	N-OKTAANI	0,04	0,15	0,8900
238	C8-NAFTEENI	0,00	0,01	0,8743
287	N-NONAANI	0,00	0,01	0,8882
	AKROLEIINI	3,31	5,79	1,0000
	ASETALDEHYDI	0,49	0,68	1,0000
24	ASETONI	0,12	0,22	1,0000
	PROPANAALI	1,19	2,15	1,0000
	I-PROPANAALI	0,08	0,17	1,0000
	FURAANI,C4H4O	0,02	0,03	1,0000
33	2-ME-1,3-BUTADIEENI	0,03	0,06	0,8491
45	SYKLOPENTEENI	0,03	0,06	0,8491
41	SYKLOPENTADIEENI	0,11	0,24	0,8240
40	TRANS-1,3-PENTADIEENI	0,02	0,04	0,8491
43	CIS-1,3-PENTADIEENI	0,01	0,02	0,8491
	BUTANAALI	0,02	0,05	1,0000
	ETIKKAHAPPO	0,00	0,01	1,0000
	ME-FURAANI	0,00	0,01	1,0000
	2-ME-BUTANAALI	0,04	0,10	1,0000
	3-ME-BUTANAALI	0,18	0,49	1,0000
	PENTANAALI	0,01	0,04	1,0000
61	1-HEKSEENI	0,17	0,46	0,8743
64	TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,00	0,01	0,8743
67	2-ME-2-PENTEENI	0,00	0,01	0,8743
46	4-ME-1-PENTEENI	0,00	0,01	0,8743
68	3-ME-SYKLOPENTEENI	0,00	0,01	0,8533
118	SYKLOHEKSEENI	0,01	0,03	0,8533
95	C6H10-DIEENI	0,01	0,03	0,8533
107	C6H8-SYKLODIEENI	0,03	0,07	0,8324
	C6H10O	0,00	0,01	1,0000
	HEKSANAALI	0,01	0,02	1,0000
127	1-HEPTEENI	0,34	1,04	0,8743
134	DIME-SYKLOPENTEENI	0,00	0,01	0,8563
139	TRANS-2-HEPTEENI	0,02	0,07	0,8743
144	CIS-2-HEPTEENI	0,01	0,03	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,01	0,8563
185	1-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
166	C7H12-DIEENI	0,01	0,04	0,8563
	1-OKTEENI	0,03	0,11	0,8743
207	C8H16-NAFTEENI	0,00	0,01	0,8743

221	C8H16-OLEFIINI	0,00	0,01	0,8743
216	TRANS-2-OKTEENI	0,02	0,08	0,8743
222	CIS-2-OKTEENI	0,01	0,04	0,8743
223	C8H14-SYKLO-OLEFIINI	0,01	0,03	0,8586
218	C8H14-DIEENI	0,00	0,01	0,8586
250	ETYYLIBENTSEENI	0,00	0,01	0,8272
257	META-KSYLEENI	0,00	0,01	0,8272
258	PARA-KSYLEENI	0,00	0,01	0,8272
281	1-NONEENI	0,00	0,01	0,8743
292	C9H16-DIEENI	0,00	0,01	0,8603
288	C9H16-SYKLO-OLEFIINI	0,00	0,01	0,8603
	C9H14-OLEFIININEN NAFTEENI	0,00	0,01	0,8464
	vety	2,32	0,15	
	happi	1,15	1,15	
	typpi	66,10	57,79	
	hiilidioksidi	6,59	9,05	
	hiilimonoksidi	11,50	10,06	
	YHTEENSÄ	100,00	100,00	
	LUKUKESKIM. MOLEKYYLIPAINO =	32,04		
	ORG. mol-%	12,34		

Näyte sisältää jälkiä seuraavista komponenteista: SYKLOBUTAANI, KLOORI-ETAANI, C2H5Cl, PROPIONINITRIILI, C3H5N, 2-ME-TIOFEENI, 3-ME-TIOFEENI

Table 18. The components and their relative amounts of the second gas sample of experiment 6.

Näyte: Koe 6, kaasu 2 h
Analys.pvm: 19.2.2009
Tekijä: RHX
Menetelmä: NM428/NM291
Oili-koodi: 1170433

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	2,35	1,10	1,0000
2	ETEENI	2,59	2,11	0,8743
3	ETAANI	2,53	2,21	0,9371
4	PROPEENI	0,86	1,06	0,8743
5	PROPAANI	1,05	1,34	0,9162
10	I-BUTAANI	0,13	0,23	0,9057
12	I+1-BUTEENI	1,17	1,90	0,8743
13	1,3-BUTADIEENI	0,00	0,01	0,8429
14	N-BUTAANI	1,40	2,36	0,9057
16	TRANS-2-BUTEENI	0,13	0,22	0,8743
19	CIS-2-BUTEENI	0,09	0,15	0,8743
22	3-ME-1-BUTEENI	0,03	0,07	0,8743
28	1-PENTEENI	0,77	1,57	0,8743
31	2-ME-1-BUTEENI	0,05	0,09	0,8743
32	N-PENTAANI	1,25	2,62	0,8994

34	TRANS-2-PENTEENI	0,16	0,32	0,8743
36	CIS-2-PENTEENI	0,07	0,14	0,8743
39	2-ME-2-BUTEENI	0,13	0,26	0,8743
48	SYKLOPENTAANI	0,01	0,01	0,8743
53	2-ME-PENTAANI	0,01	0,02	0,8952
58	3-ME-PENTAANI	0,00	0,01	0,8952
63	N-HEKSAANI	0,80	2,01	0,8952
66	TRANS-2-HEKSEENI	0,06	0,15	0,8743
71	CIS-2-HEKSEENI	0,03	0,07	0,8743
77	ME-SYKLOPENTAANI	0,01	0,02	0,8743
93	BENTSEENI	0,05	0,11	0,8114
104	SYKLOHEKSAANI	0,00	0,01	0,8743
120	C7H14-OLEFIINI	0,00	0,01	0,8743
135	N-HEPTAANI	0,30	0,86	0,8922
147	ME-SYKLOHEKSAANI	0,01	0,03	0,8743
152	ET-SYKLOPENTAANI	0,00	0,01	0,8743
174	TOLUEENI	0,01	0,04	0,8204
214	N-OKTAANI	0,06	0,20	0,8900
287	N-NONAANI	0,00	0,02	0,8882
	AKROLEIINI	1,03	1,68	1,0000
	ASETALDEHYDI	0,28	0,35	1,0000
24	ASETONI	0,21	0,36	1,0000
	PROPANAALI	1,65	2,78	1,0000
	I-PROPANAALI	0,03	0,05	1,0000
	FURAANI,C4H4O	0,00	0,01	1,0000
45	SYKLOPENTEENI	0,18	0,35	0,8491
40	TRANS-1,3-PENTADIEENI	0,00	0,01	0,8491
	BUTANAALI	0,01	0,02	1,0000
	ME-FURAANI	0,01	0,01	1,0000
	2-ME-BUTANAALI	0,01	0,03	1,0000
	3-ME-BUTANAALI	0,04	0,11	1,0000
	PENTANAALI	0,00	0,01	1,0000
61	1-HEKSEENI	0,46	1,12	0,8743
64	TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,01	0,02	0,8743
67	2-ME-2-PENTEENI	0,00	0,01	0,8743
46	4-ME-1-PENTEENI	0,01	0,01	0,8743
68	3-ME-SYKLOPENTEENI	0,00	0,01	0,8533
72	TRANS-3-ME-2-PENTEENI	0,00	0,01	0,8743
94	1-ME-SYKLOPENTEENI	0,01	0,03	0,8533
118	SYKLOHEKSEENI	0,03	0,08	0,8533
95	C6H10-DIEENI	0,00	0,01	0,8533
	C6H10O	0,00	0,01	1,0000
	HEKSANAALI	0,00	0,01	1,0000
	C2-FURAANI	0,01	0,02	1,0000
127	1-HEPTEENI	0,50	1,42	0,8743
133	TRANS-3-HEPTEENI	0,01	0,02	0,8743
134	DIME-SYKLOPENTEENI	0,01	0,02	0,8563
139	TRANS-2-HEPTEENI	0,09	0,25	0,8743
144	CIS-2-HEPTEENI	0,04	0,12	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,01	0,8563
154	3-ME-SYKLOHEKSEENI	0,00	0,01	0,8563

155	4-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
185	1-ME-SYKLOHEKSEENI	0,01	0,02	0,8563
166	C7H12-DIEENI	0,00	0,01	0,8563
	C7-KETONI	0,00	0,01	1,0000
	1-OKTEENI	0,05	0,15	0,8743
207	C8H16-NAFTEENI	0,00	0,01	0,8743
221	C8H16-OLEFIINI	0,01	0,02	0,8743
216	TRANS-2-OKTEENI	0,03	0,11	0,8743
222	CIS-2-OKTEENI	0,02	0,05	0,8743
223	C8H14-SYKLO-OLEFIINI	0,00	0,01	0,8586
218	C8H14-DIEENI	0,00	0,01	0,8586
281	1-NONEENI	0,00	0,01	0,8743
	TRANS-2-NONEENI	0,00	0,01	0,8743
288	C9H16-SYKLO-OLEFIINI	0,00	0,01	0,8603
	vety	3,56	0,21	
	typpi	5,06	4,11	
	hiilidioksidi	16,34	20,88	
	hiilimonoksidi	54,08	43,97	
	YHTEENSÄ	100,00	100,00	

LUKUKESKIM.
MOLEKYYLIPAINO = 34,45

ORG. mol-% 20,95

Näytteessä on jälkiä yhdisteistä kloorietaani, etanoli, asetonitriili, propionitriili ja C4H6O.

Table 19. The components and their relative amounts of the first gas sample of experiment 7.

Näyte: Koe 7, kaasu 0 h
Analys.pvm: 2.3.2009
Tekijä: RHX
Menetelmä: NM428/NM291
Oili-koodi: 1270950

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	0,45	0,90	1,0000
2	ETEENI	0,06	0,20	0,8743
3	ETAANI	0,18	0,69	0,9371
4	PROPEENI	0,04	0,23	0,8743
5	PROPAANI	0,05	0,28	0,9162
12	I+1-BUTEENI	0,26	1,84	0,8743
13	1,3-BUTADIEENI	0,03	0,19	0,8429
14	N-BUTAANI	0,14	0,98	0,9057
16	TRANS-2-BUTEENI	0,01	0,04	0,8743
19	CIS-2-BUTEENI	0,00	0,02	0,8743
22	3-ME-1-BUTEENI	0,02	0,13	0,8743
28	1-PENTEENI	0,11	1,00	0,8743
31	2-ME-1-BUTEENI	0,00	0,02	0,8743
32	N-PENTAANI	2,16	19,42	0,8994

34	TRANS-2-PENTEENI	0,02	0,16	0,8743
36	CIS-2-PENTEENI	0,01	0,07	0,8743
37	ME-SYKLOBUTAANI	0,00	0,04	0,8743
39	2-ME-2-BUTEENI	0,12	1,08	0,8743
58	3-ME-PENTAANI	0,00	0,01	0,8952
63	N-HEKSAANI	0,05	0,58	0,8952
66	TRANS-2-HEKSEENI	0,00	0,02	0,8743
71	CIS-2-HEKSEENI	0,00	0,01	0,8743
91	HEKSADIEENI	0,00	0,01	0,8533
93	BENTSEENI	0,01	0,07	0,8114
114	2-ME-HEKSAANI	0,00	0,02	0,8922
120	C7H14-OLEFIINI	0,00	0,02	0,8743
135	N-HEPTAANI	0,07	0,82	0,8922
147	ME-SYKLOHEKSAANI	0,00	0,02	0,8743
152	ET-SYKLOPENTAANI	0,00	0,01	0,8743
153	2,5-DIME-HEKSAANI	0,00	0,01	0,8900
156	2,4-DIME-HEKSAANI	0,00	0,01	0,8900
160	C7H10-SYKLODIEENI	0,00	0,04	0,8384
174	TOLUEENI	0,01	0,15	0,8204
188	2-ME-HEPTAANI	0,00	0,07	0,8900
190	4-ME-HEPTAANI	0,00	0,02	0,8900
194	3-ME-HEPTAANI	0,00	0,06	0,8900
195	3-ET-HEKSAANI	0,00	0,01	0,8900
214	N-OKTAANI	0,04	0,62	0,8900
228	C9-PARAFIINI	0,00	0,04	0,8882
237	2,6-DIME-HEPTAANI	0,00	0,03	0,8882
242	3,5-DIME-HEPTAANI	0,00	0,05	0,8882
267	4-ME-OKTAANI	0,00	0,05	0,8882
268	2-ME-OKTAANI	0,01	0,08	0,8882
273	3-ME-OKTAANI	0,01	0,09	0,8882
287	N-NONAANI	0,00	0,07	0,8882
	AKROLEIINI	3,92	27,40	1,0000
	ASETALDEHYDI	0,01	0,03	1,0000
24	ASETONI	0,03	0,24	1,0000
	PROPANAALI	0,03	0,24	1,0000
	FURAANI,C4H4O	0,00	0,04	1,0000
	ALLYYLIALKOHOLI=2-PROPENOLI	0,00	0,02	1,0000
33	2-ME-1,3-BUTADIEENI	0,09	0,73	0,8491
45	SYKLOPENTEENI	0,00	0,02	0,8491
41	SYKLOPENTADIEENI	0,06	0,50	0,8240
40	TRANS-1,3-PENTADIEENI	0,00	0,02	0,8491
	BUTANAALI	0,00	0,02	1,0000
	ETIKKAHAPPO	0,00	0,01	1,0000
	ME-FURAANI	0,00	0,00	1,0000
	HYDROKSIASETONI	0,00	0,02	1,0000
	2-BUTENAALI	0,00	0,02	1,0000
56	2-BUTANONI	0,00	0,04	1,0000
	PENTANAALI	0,01	0,12	1,0000
61	1-HEKSEENI	0,04	0,47	0,8743
64	TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,00	0,01	0,8743
84	ME-SYKLOPENTADIEENI	0,00	0,01	0,8324

118	SYKLOHEKSEENI	0,00	0,01	0,8533
95	C6H10-DIEENI	0,01	0,06	0,8533
107	C6H8-SYKLODIEENI	0,00	0,03	0,8324
	HEKSANAALI	0,18	2,24	1,0000
127	1-HEPTEENI	0,15	1,79	0,8743
134	DIME-SYKLOPENTEENI	0,00	0,01	0,8563
139	TRANS-2-HEPTEENI	0,01	0,11	0,8743
144	CIS-2-HEPTEENI	0,00	0,06	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,03	0,8563
185	1-ME-SYKLOHEKSEENI	0,00	0,02	0,8563
166	C7H12-DIEENI	0,00	0,02	0,8563
	C7-KETONI	0,00	0,05	1,0000
	1-OKTEENI	0,03	0,48	0,8743
221	C8H16-OLEFIINI	0,00	0,02	0,8743
216	TRANS-2-OKTEENI	0,02	0,34	0,8743
222	CIS-2-OKTEENI	0,01	0,16	0,8743
	SYKLO-OKTEENI	0,00	0,03	0,8586
223	C8H14-SYKLO-OLEFIINI	0,00	0,02	0,8586
218	C8H14-DIEENI	0,01	0,10	0,8586
250	ETYYLIBENTSEENI	0,00	0,04	0,8272
257	META-KSYLEENI	0,01	0,14	0,8272
258	PARA-KSYLEENI	0,01	0,10	0,8272
	BENTSALDEHYDI, C7H6O	0,00	0,00	1,0000
	HEPTANAALI	0,00	0,03	1,0000
276	ORTO-KSYLEENI	0,00	0,04	0,8272
281	1-NONEENI	0,00	0,03	0,8743
	TRANS-2-NONEENI	0,00	0,01	0,8743
292	C9H16-DIEENI	0,00	0,04	0,8603
288	C9H16-SYKLO-OLEFIINI	0,01	0,15	0,8603
	vety	88,25	22,17	
	typpi	2,89	10,10	
	hiilidioksidi	0,25	1,34	
	YHTEENSÄ	100,00	100,00	

LUKUKESKIM.
MOLEKYYLIPAINO = 8,03

ORG. mol-% 8,61

Näytteessä on jälkiä yhdisteestä formaldehydi.

Table 20. The components and their relative amounts of the second gas sample of experiment 7.

Näyte:	Koe 7, kaasu 2h
Analys.pvm:	4.3.2009
Tekijä:	TKZ
Menetelmä:	NM428/NM291
Oili-koodi:	1270951

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	0,36	0,85	1,0000
2	ETEENI	0,32	1,31	0,8743
3	ETAANI	0,30	1,35	0,9371
4	PROPEENI	0,14	0,85	0,8743
5	PROPAANI	0,17	1,10	0,9162
10	I-BUTAANI	0,00	0,03	0,9057
12	I+1-BUTEENI	0,45	3,75	0,8743
14	N-BUTAANI	0,32	2,74	0,9057
16	TRANS-2-BUTEENI	0,01	0,09	0,8743
19	CIS-2-BUTEENI	0,01	0,07	0,8743
22	3-ME-1-BUTEENI	0,02	0,16	0,8743
28	1-PENTEENI	0,28	2,92	0,8743
31	2-ME-1-BUTEENI	0,01	0,13	0,8743
32	N-PENTAANI	0,55	5,88	0,8994
34	TRANS-2-PENTEENI	0,02	0,17	0,8743
36	CIS-2-PENTEENI	0,01	0,08	0,8743
37	ME-SYKLOBUTAANI	0,00	0,01	0,8743
39	2-ME-2-BUTEENI	0,13	1,37	0,8743
53	2-ME-PENTAANI	0,00	0,01	0,8952
58	3-ME-PENTAANI	0,00	0,01	0,8952
63	N-HEKSAANI	0,19	2,38	0,8952
66	TRANS-2-HEKSEENI	0,01	0,07	0,8743
71	CIS-2-HEKSEENI	0,00	0,04	0,8743
77	ME-SYKLOPENTAANI	0,00	0,03	0,8743
81	2,4-DIME-PENTAANI	0,00	0,01	0,8922
93	BENTSEENI	0,01	0,08	0,8114
114	2-ME-HEKSAANI	0,00	0,01	0,8922
115	2,3-DIME-PENTAANI	0,00	0,01	0,8922
116	1,1-DIME-SYKLOPENTAANI	0,00	0,01	0,8743
124	CIS-1,3-DIME-SYKLOPENTAANI	0,00	0,01	0,8743
135	N-HEPTAANI	0,10	1,47	0,8922
137	2-ME-2-HEKSEENI	0,00	0,01	0,8743
147	ME-SYKLOHEKSAANI	0,01	0,09	0,8743
152	ET-SYKLOPENTAANI	0,00	0,01	0,8743
160	C7H10-SYKLODIEENI	0,00	0,01	0,8384
174	TOLUEENI	0,00	0,06	0,8204
238	C8-NAFTEENI	0,00	0,01	0,8743
188	2-ME-HEPTAANI	0,00	0,01	0,8900
190	4-ME-HEPTAANI	0,00	0,01	0,8900
194	3-ME-HEPTAANI	0,00	0,01	0,8900
214	N-OKTAANI	0,04	0,61	0,8900
242	3,5-DIME-HEPTAANI	0,00	0,01	0,8882
267	4-ME-OKTAANI	0,00	0,01	0,8882
268	2-ME-OKTAANI	0,00	0,01	0,8882

273	3-ME-OKTAANI	0,00	0,01	0,8882
287	N-NONAANI	0,00	0,05	0,8882
	AKROLEIINI	1,14	9,45	1,0000
	ASETALDEHYDI	0,08	0,50	1,0000
24	ASETONI	0,04	0,36	1,0000
	PROPANAALI	1,03	8,82	1,0000
	FURAANI,C4H4O	0,00	0,03	1,0000
33	2-ME-1,3-BUTADIEENI	0,00	0,03	0,8491
45	SYKLOPENTEENI	0,04	0,44	0,8491
41	SYKLOPENTADIEENI	0,01	0,07	0,8240
40	TRANS-1,3-PENTADIEENI	0,00	0,01	0,8491
43	CIS-1,3-PENTADIEENI	0,00	0,01	0,8491
	C4H6O	0,00	0,01	1,0000
	C4H6O2	0,00	0,01	1,0000
	ETIKKAHAPPO	0,00	0,01	1,0000
	ME-FURAANI	0,00	0,01	1,0000
	2-ME-BUTANAALI	0,00	0,01	1,0000
	C5H8O	0,01	0,10	1,0000
	PENTANAALI	0,01	0,11	1,0000
61	1-HEKSEENI	0,15	1,82	0,8743
64	TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,00	0,01	0,8743
67	2-ME-2-PENTEENI	0,00	0,02	0,8743
68	3-ME-SYKLOPENTEENI	0,00	0,02	0,8533
70	4-ME-SYKLOPENTEENI	0,00	0,01	0,8533
72	TRANS-3-ME-2-PENTEENI	0,00	0,01	0,8743
94	1-ME-SYKLOPENTEENI	0,00	0,04	0,8533
118	SYKLOHEKSEENI	0,00	0,06	0,8533
96	3-ME-1-HEKSEENI	0,00	0,01	0,8952
113	CIS-4-ME-2-HEKSEENI	0,00	0,01	0,8952
95	C6H10-DIEENI	0,00	0,02	0,8533
107	C6H8-SYKLODIEENI	0,00	0,01	0,8324
	C6H8O	0,00	0,02	1,0000
	C6H12O	0,00	0,01	1,0000
	HEKSANAALI	0,02	0,23	1,0000
	SYKLOHEPTEENI	0,00	0,02	0,8563
127	1-HEPTEENI	0,37	5,36	0,8743
133	TRANS-3-HEPTEENI	0,00	0,01	0,8743
134	DIME-SYKLOPENTEENI	0,00	0,06	0,8563
139	TRANS-2-HEPTEENI	0,02	0,34	0,8743
144	CIS-2-HEPTEENI	0,01	0,17	0,8743
136	CIS-3-HEPTEENI	0,00	0,01	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,05	0,8563
154	3-ME-SYKLOHEKSEENI	0,00	0,02	0,8563
155	4-ME-SYKLOHEKSEENI	0,00	0,02	0,8563
172	ET-SYKLOPENTEENI	0,00	0,01	0,8563
185	1-ME-SYKLOHEKSEENI	0,01	0,08	0,8563
166	C7H12-DIEENI	0,00	0,01	0,8563
	C7-KETONI	0,00	0,04	1,0000
	C7H14O	0,00	0,01	1,0000
	1-OKTEENI	0,05	0,76	0,8743
207	C8H16-NAFTEENI	0,00	0,01	0,8743

221	C8H16-OLEFIINI	0,00	0,07	0,8743
216	TRANS-2-OKTEENI	0,04	0,63	0,8743
222	CIS-2-OKTEENI	0,02	0,29	0,8743
	SYKLO-OKTEENI	0,00	0,07	0,8586
223	C8H14-SYKLO-OLEFIINI	0,00	0,04	0,8586
218	C8H14-DIEENI	0,00	0,06	0,8586
250	ETYYLIBENTSEENI	0,00	0,03	0,8272
257	META-KSYLEENI	0,00	0,03	0,8272
	HEPTANAALI	0,00	0,01	1,0000
276	ORTO-KSYLEENI	0,00	0,02	0,8272
281	1-NONEENI	0,00	0,05	0,8743
	TRANS-2-NONEENI	0,00	0,01	0,8743
	CIS-2-NONEENI	0,00	0,01	0,8743
288	C9H16-SYKLO-OLEFIINI	0,00	0,03	0,8603
306	PROPYYLISYKLOHEKSAANI	0,00	0,01	0,8743
	vety	90,26	26,87	
	typpi	0,67	2,78	
	hiilidioksidi	0,63	4,11	
	hiilimonoksidi	1,87	7,71	
	YHTEENSÄ	100,00	100,00	
	LUKUKESKIM. MOLEKYYLIPAINO =	6,77		
	ORG. mol-%	6,57		

Näyte sisältää jälkiä seuraavista komponenteista:

I-PROPANAALI
BUTANAALI

Table 21. The components and their relative amounts of the first gas sample of experiment 8.

Näyte:	Koe 8, kaasu 0h
Analys.pvm:	10.3.2009
Tekijä:	TKZ
Menetelmä:	NM428/NM291
Oili-koodi:	1299242

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	0,15	0,33	1,0000
2	ETEENI	0,09	0,35	0,8743
3	ETAANI	0,07	0,29	0,9371
4	PROPEENI	0,06	0,32	0,8743
5	PROPAANI	0,06	0,36	0,9162
10	I-BUTAANI	0,00	0,01	0,9057
12	I+1-BUTEENI	0,24	1,84	0,8743
13	1,3-BUTADIEENI	0,00	0,03	0,8429
14	N-BUTAANI	0,15	1,18	0,9057
16	TRANS-2-BUTEENI	0,00	0,03	0,8743
19	CIS-2-BUTEENI	0,00	0,02	0,8743
22	3-ME-1-BUTEENI	0,01	0,10	0,8743

28	1-PENTEENI	0,12	1,17	0,8743
31	2-ME-1-BUTEENI	0,00	0,02	0,8743
32	N-PENTAANI	0,55	5,51	0,8994
34	TRANS-2-PENTEENI	0,01	0,10	0,8743
36	CIS-2-PENTEENI	0,01	0,05	0,8743
37	ME-SYKLOBUTAANI	0,00	0,01	0,8743
39	2-ME-2-BUTEENI	0,10	0,98	0,8743
53	2-ME-PENTAANI	0,00	0,01	0,8952
58	3-ME-PENTAANI	0,00	0,02	0,8952
63	N-HEKSAANI	0,09	1,03	0,8952
66	TRANS-2-HEKSEENI	0,00	0,03	0,8743
71	CIS-2-HEKSEENI	0,00	0,01	0,8743
77	ME-SYKLOPENTAANI	0,00	0,02	0,8743
93	BENTSEENI	0,01	0,05	0,8114
104	SYKLOHEKSAANI	0,00	0,01	0,8743
114	2-ME-HEKSAANI	0,00	0,01	0,8922
115	2,3-DIME-PENTAANI	0,00	0,01	0,8922
120	C7H14-OLEFIINI	0,00	0,01	0,8743
124	CIS-1,3-DIME-SYKLOPENTAANI	0,00	0,01	0,8743
135	N-HEPTAANI	0,08	1,04	0,8922
147	ME-SYKLOHEKSAANI	0,00	0,06	0,8743
152	ET-SYKLOPENTAANI	0,00	0,01	0,8743
160	C7H10-SYKLODIEENI	0,00	0,02	0,8384
174	TOLUEENI	0,01	0,10	0,8204
188	2-ME-HEPTAANI	0,00	0,04	0,8900
190	4-ME-HEPTAANI	0,00	0,01	0,8900
194	3-ME-HEPTAANI	0,00	0,03	0,8900
214	N-OKTAANI	0,05	0,82	0,8900
238	C8-NAFTEENI	0,00	0,06	0,8743
237	2,6-DIME-HEPTAANI	0,00	0,03	0,8882
236	ET-SYKLOHEKSAANI	0,00	0,03	0,8747
242	3,5-DIME-HEPTAANI	0,00	0,03	0,8882
300	C10-PARAFIINI	0,00	0,06	0,8868
261	C9-PARAFIINI	0,00	0,01	0,8882
267	4-ME-OKTAANI	0,00	0,04	0,8882
268	2-ME-OKTAANI	0,00	0,07	0,8882
272	3-ET-HEPTAANI	0,00	0,01	0,8882
273	3-ME-OKTAANI	0,00	0,06	0,8882
280	C9H18-NAFTEENI	0,00	0,02	0,8743
287	N-NONAANI	0,03	0,54	0,8882
	AKROLEIINI	4,41	34,15	1,0000
	ASETALDEHYDI	0,04	0,22	1,0000
24	ASETONI	0,03	0,24	1,0000
	PROPANAALI	0,43	3,42	1,0000
	FURAANI,C4H4O	0,00	0,03	1,0000
33	2-ME-1,3-BUTADIEENI	0,03	0,29	0,8491
45	SYKLOPENTEENI	0,00	0,04	0,8491
41	SYKLOPENTADIEENI	0,00	0,05	0,8240
40	TRANS-1,3-PENTADIEENI	0,00	0,01	0,8491
43	CIS-1,3-PENTADIEENI	0,00	0,01	0,8491
	BUTANAALI	0,00	0,03	1,0000
	C4H6O	0,00	0,01	1,0000

	ETIKKAHAPPO	0,00	0,01	1,0000
	2-ME-BUTANAALI	0,00	0,01	1,0000
	3-ME-BUTANAALI	0,00	0,01	1,0000
	C5H8O	0,01	0,07	1,0000
	PENTANAALI	0,01	0,07	1,0000
	PROPIONIHAPPO	0,00	0,01	1,0000
	C4-HAPPO	0,00	0,01	1,0000
61	1-HEKSEENI	0,08	0,89	0,8743
64	TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,00	0,02	0,8743
67	2-ME-2-PENTEENI	0,00	0,01	0,8743
68	3-ME-SYKLOPENTEENI	0,00	0,01	0,8533
72	TRANS-3-ME-2-PENTEENI	0,00	0,01	0,8743
94	1-ME-SYKLOPENTEENI	0,00	0,02	0,8533
118	SYKLOHEKSEENI	0,00	0,01	0,8533
96	3-ME-1-HEKSEENI	0,00	0,01	0,8952
113	CIS-4-ME-2-HEKSEENI	0,00	0,01	0,8952
95	C6H10-DIEENI	0,00	0,03	0,8533
107	C6H8-SYKLODIEENI	0,00	0,04	0,8324
	C6H12O	0,00	0,01	1,0000
	C6H10O	0,00	0,01	1,0000
	HEKSANAALI	0,07	1,01	1,0000
	SYKLOHEPTEENI	0,00	0,02	0,8563
127	1-HEPTEENI	0,27	3,60	0,8743
133	TRANS-3-HEPTEENI	0,00	0,01	0,8743
134	DIME-SYKLOPENTEENI	0,00	0,02	0,8563
139	TRANS-2-HEPTEENI	0,02	0,21	0,8743
144	CIS-2-HEPTEENI	0,01	0,11	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,04	0,8563
154	3-ME-SYKLOHEKSEENI	0,00	0,02	0,8563
155	4-ME-SYKLOHEKSEENI	0,00	0,01	0,8563
172	ET-SYKLOPENTEENI	0,00	0,01	0,8563
185	1-ME-SYKLOHEKSEENI	0,00	0,05	0,8563
166	C7H12-DIEENI	0,00	0,03	0,8563
	C7-KETONI	0,00	0,06	1,0000
	C7H14O	0,00	0,01	1,0000
	1-OKTEENI	0,06	0,92	0,8743
207	C8H16-NAFTEENI	0,00	0,02	0,8743
221	C8H16-OLEFIINI	0,00	0,07	0,8743
216	TRANS-2-OKTEENI	0,05	0,75	0,8743
222	CIS-2-OKTEENI	0,02	0,38	0,8743
	SYKLO-OKTEENI	0,01	0,22	0,8586
223	C8H14-SYKLO-OLEFIINI	0,00	0,06	0,8586
218	C8H14-DIEENI	0,02	0,27	0,8586
	C8H12-OLEFIININEN NAFTEENI	0,00	0,01	0,8429
250	ETYYLIBENTSEENI	0,00	0,05	0,8272
257	META-KSYLEENI	0,01	0,15	0,8272
258	PARA-KSYLEENI	0,01	0,10	0,8272
	BENTSALDEHYDI, C7H6O	0,00	0,01	1,0000
	HEPTANAALI	0,01	0,09	1,0000
276	ORTO-KSYLEENI	0,01	0,10	0,8272
281	1-NONEENI	0,01	0,24	0,8743

283	4-NONEENI	0,00	0,01	0,8743
284	C9H18-OLEFIINI	0,00	0,01	0,8743
	TRANS-2-NONEENI	0,00	0,08	0,8743
	CIS-2-NONEENI	0,00	0,04	0,8743
292	C9H16-DIEENI	0,01	0,18	0,8603
288	C9H16-SYKLO-OLEFIINI	0,01	0,25	0,8603
	C9H14-OLEFIININEN NAFTEENI	0,00	0,04	0,8464
306	PROPYYLISYKLOHEKSAANI	0,00	0,03	0,8743
	vety	90,32	25,17	
	typpi	0,90	3,47	
	hiilidioksidi	0,34	2,09	
	hiilimonoksidi	0,82	3,17	
	YHTEENSÄ	100,00	100,00	
	LUKUKESKIM. MOLEKYYLIPAINO =	7,23		
	ORG. mol-%	7,63		

Näyte sisältää jälkiä seuraavista komponenteista:

FORMALDEHYDI
2-PROPANOLI

Table 22. The components and their relative amounts of the second gas sample of experiment 8.

Näyte:	Koe 8, kaasu 2h
Analys.pvm:	6.3.2009
Tekijä:	TKZ
Menetelmä:	NM428/NM291
Oili-koodi:	1299244

NRO	KOMPONENTTI	mol-%	p-%	F
1	METAANI	0,70	1,03	1,0000
2	ETEENI	0,60	1,53	0,8743
3	ETAANI	0,96	2,64	0,9371
4	PROPEENI	0,37	1,40	0,8743
5	PROPAANI	0,43	1,74	0,9162
10	I-BUTAANI	0,00	0,01	0,9057
12	I+1-BUTEENI	0,26	1,33	0,8743
13	1,3-BUTADIEENI	0,00	0,01	0,8429
14	N-BUTAANI	0,51	2,68	0,9057
16	TRANS-2-BUTEENI	0,06	0,30	0,8743
19	CIS-2-BUTEENI	0,04	0,20	0,8743
22	3-ME-1-BUTEENI	0,00	0,02	0,8743
25	I-PENTAANI	0,00	0,01	0,8994
28	1-PENTEENI	0,20	1,25	0,8743
31	2-ME-1-BUTEENI	0,01	0,06	0,8743
32	N-PENTAANI	0,52	3,39	0,8994
34	TRANS-2-PENTEENI	0,06	0,36	0,8743
36	CIS-2-PENTEENI	0,02	0,16	0,8743
39	2-ME-2-BUTEENI	0,02	0,16	0,8743

48	SYKLOPENTAANI	0,01	0,07	0,8743
53	2-ME-PENTAANI	0,00	0,01	0,8952
58	3-ME-PENTAANI	0,00	0,02	0,8952
63	N-HEKSAANI	0,54	4,23	0,8952
66	TRANS-2-HEKSEENI	0,05	0,42	0,8743
71	CIS-2-HEKSEENI	0,03	0,20	0,8743
77	ME-SYKLOPENTAANI	0,01	0,10	0,8743
91	HEKSADIEENI	0,00	0,01	0,8533
93	BENTSEENI	0,02	0,15	0,8114
104	SYKLOHEKSAANI	0,01	0,04	0,8743
115	2,3-DIME-PENTAANI	0,00	0,01	0,8922
116	1,1-DIME-SYKLOPENTAANI	0,00	0,02	0,8743
119	3-ME-HEKSAANI	0,00	0,03	0,8922
120	C7H14-OLEFIINI	0,00	0,01	0,8743
124	CIS-1,3-DIME-SYKLOPENTAANI	0,00	0,03	0,8743
123	3-ET-PENTAANI	0,00	0,02	0,8922
135	N-HEPTAANI	0,50	4,55	0,8922
137	2-ME-2-HEKSEENI	0,00	0,01	0,8743
146	1-CIS-2-DIME-SYKLOPENTAANI	0,00	0,02	0,8743
147	ME-SYKLOHEKSAANI	0,02	0,17	0,8743
152	ET-SYKLOPENTAANI	0,01	0,05	0,8743
174	TOLUEENI	0,02	0,19	0,8204
182	2,3-DIME-HEKSAANI	0,00	0,01	0,8900
188	2-ME-HEPTAANI	0,00	0,02	0,8900
194	3-ME-HEPTAANI	0,00	0,04	0,8900
217?	CIS-1,3-DIME-SYKLOHEKSAANI	0,00	0,01	0,8747
214	N-OKTAANI	0,27	2,83	0,8900
231	C8H14-BISYKLONAFTEENI	0,00	0,03	0,8586
238	C8-NAFTEENI	0,00	0,04	0,8743
235	N-PROPYYLI-SYKLOPENTAANI	0,00	0,01	0,8747
236	ET-SYKLOHEKSAANI	0,00	0,04	0,8747
291	C3-SYKLOHEKSAANI	0,00	0,01	0,8743
315	C9-NAFTEENI	0,00	0,02	0,8743
272	3-ET-HEPTAANI	0,00	0,01	0,8882
273	3-ME-OKTAANI	0,00	0,02	0,8882
280	C9H18-NAFTEENI	0,00	0,01	0,8743
287	N-NONAANI	0,08	0,89	0,8882
	AKROLEIINI	0,10	0,53	1,0000
	ASETALDEHYDI	0,04	0,16	1,0000
24	ASETONI	0,10	0,53	1,0000
	PROPANAALI	0,41	2,15	1,0000
	FURAANI,C4H4O	0,00	0,01	1,0000
45	SYKLOPENTEENI	0,29	1,78	0,8491
40	TRANS-1,3-PENTADIEENI	0,00	0,01	0,8491
43	CIS-1,3-PENTADIEENI	0,00	0,01	0,8491
	ETIKKAHAPPO	0,23	1,25	1,0000
56	2-BUTANONI	0,00	0,02	1,0000
	C5-KETONI	0,00	0,04	1,0000
	2-ME-BUTANAALI	0,00	0,01	1,0000
	C5H8O	0,00	0,01	1,0000
	C5H8O3	0,00	0,01	1,0000
	PROPIONIHAPPO	0,01	0,07	1,0000

	C4-HAPPO	0,00	0,03	1,0000
61	1-HEKSEENI	0,21	1,62	0,8743
64	TRANS-3-HEKSEENI+CIS-3-HEKSEENI	0,00	0,04	0,8743
67	2-ME-2-PENTEENI	0,00	0,01	0,8743
47	3-ME-1-PENTEENI	0,00	0,01	0,8743
68	3-ME-SYKLOPENTEENI	0,01	0,04	0,8533
70	4-ME-SYKLOPENTEENI	0,00	0,01	0,8533
69	CIS-3-ME-2-PENTEENI	0,00	0,01	0,8743
72	TRANS-3-ME-2-PENTEENI	0,00	0,02	0,8743
94	1-ME-SYKLOPENTEENI	0,02	0,16	0,8533
118	SYKLOHEKSEENI	0,07	0,57	0,8533
96	3-ME-1-HEKSEENI	0,00	0,01	0,8952
112	4-ME-1-HEKSEENI	0,00	0,01	0,8952
113	CIS-4-ME-2-HEKSEENI	0,00	0,01	0,8952
95	C6H10-DIEENI	0,00	0,01	0,8533
107	C6H8-SYKLODIEENI	0,00	0,01	0,8324
	C6H8O	0,00	0,01	1,0000
	C6H12O	0,00	0,01	1,0000
	C2-FURAANI, C6H8O	0,01	0,06	1,0000
	SYKLOPENTANONI	0,00	0,02	1,0000
	C6H10O	0,00	0,03	1,0000
	C6-KETONI	0,00	0,02	1,0000
	HEKSANAALI	0,00	0,04	1,0000
	SYKLOHEKSANONI, C6H10O	0,00	0,03	1,0000
	SYKLOHEPTEENI	0,01	0,10	0,8563
127	1-HEPTEENI	0,29	2,58	0,8743
133	TRANS-3-HEPTEENI	0,01	0,09	0,8743
134	DIME-SYKLOPENTEENI	0,01	0,06	0,8563
139	TRANS-2-HEPTEENI	0,10	0,89	0,8743
144	CIS-2-HEPTEENI	0,05	0,43	0,8743
136	CIS-3-HEPTEENI	0,00	0,01	0,8743
145	1-ET-SYKLOPENTEENI	0,00	0,04	0,8563
154	3-ME-SYKLOHEKSEENI	0,01	0,05	0,8563
155	4-ME-SYKLOHEKSEENI	0,00	0,03	0,8563
172	ET-SYKLOPENTEENI	0,00	0,04	0,8563
185	1-ME-SYKLOHEKSEENI	0,02	0,20	0,8563
166	C7H12-DIEENI	0,01	0,05	0,8563
	C7H12-OLEFIININEN NAFTEENI	0,00	0,01	0,8563
	C7H14O	0,00	0,01	1,0000
	1-OKTEENI	0,11	1,11	0,8743
207	C8H16-NAFTEENI	0,00	0,05	0,8743
209	DIME-HEKSADIEENI	0,00	0,02	0,8952
221	C8H16-OLEFIINI	0,02	0,16	0,8743
216	TRANS-2-OKTEENI	0,06	0,61	0,8743
222	CIS-2-OKTEENI	0,03	0,29	0,8743
	SYKLO-OKTEENI	0,02	0,18	0,8586
223	C8H14-SYKLO-OLEFIINI	0,02	0,15	0,8586
218	C8H14-DIEENI	0,00	0,02	0,8586
	C8H10-OLEFIININEN NAFTEENI	0,00	0,04	0,8272
	C8H12-OLEFIININEN NAFTEENI	0,00	0,02	0,8429
250	ETYYLIBENTSEENI	0,00	0,03	0,8272

257	META-KSYLEENI	0,00	0,04	0,8272
258	PARA-KSYLEENI	0,00	0,02	0,8272
	BENTSALDEHYDI, C7H6O	0,00	0,01	1,0000
	HEPTANAALI	0,00	0,02	1,0000
274	STYREENI	0,00	0,01	0,8114
276	ORTO-KSYLEENI	0,00	0,02	0,8272
281	1-NONEENI	0,02	0,24	0,8743
283	4-NONEENI	0,00	0,01	0,8743
284	C9H18-OLEFIINI	0,00	0,04	0,8743
	TRANS-2-NONEENI	0,01	0,10	0,8743
	CIS-2-NONEENI	0,00	0,05	0,8743
292	C9H16-DIEENI	0,00	0,02	0,8603
288	C9H16-SYKLO-OLEFIINI	0,01	0,06	0,8603
	C9H14-OLEFIININEN NAFTEENI	0,00	0,01	0,8464
306	PROPYYLISYKLOHEKSAANI	0,00	0,02	0,8743
	vety	79,67	14,61	
	typpi	0,02	0,04	
	hiilidioksidi	4,11	16,44	
	hiilimonoksidi	7,43	18,93	
	YHTEENSÄ	100,00	100,00	

LUKUKESKIM.
MOLEKYYLIPAINO = 10,99

ORG. mol-% 8,78

The pressure curves of thermal degradation experiments as functions of time and temperature

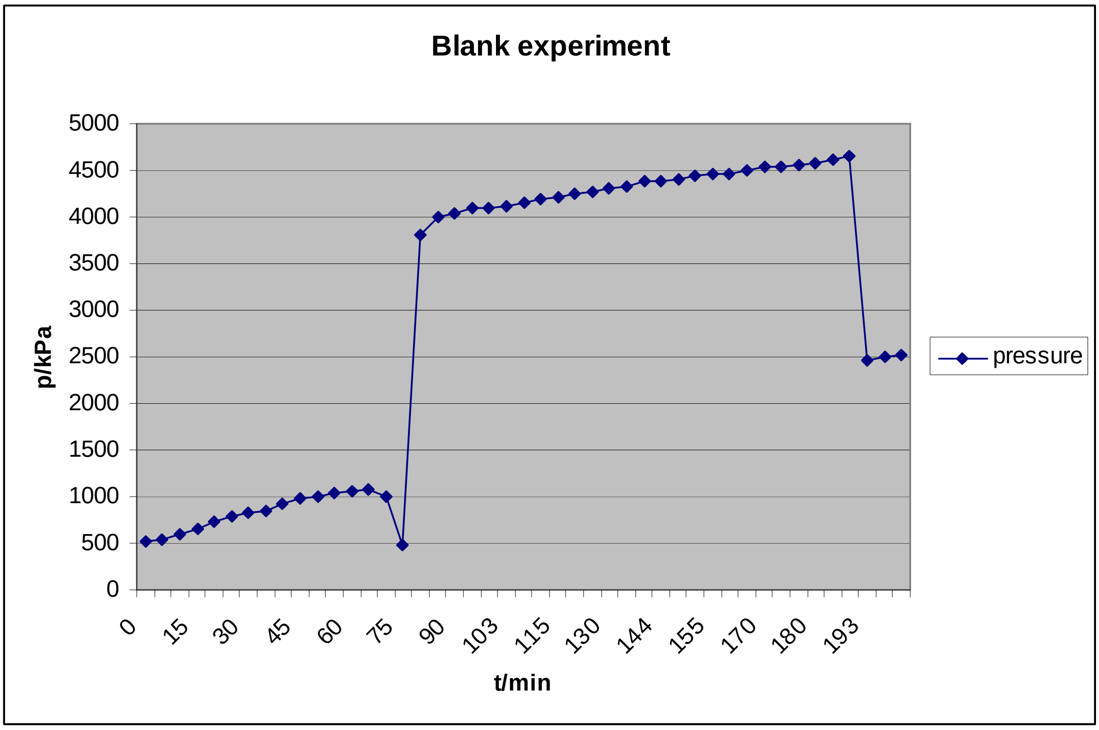

Figure 2. Pressure curve of blank experiment as a function of time which was carried out with alkali refined rapeseed oil in 340°C and in 40 bar with nitrogen gas.

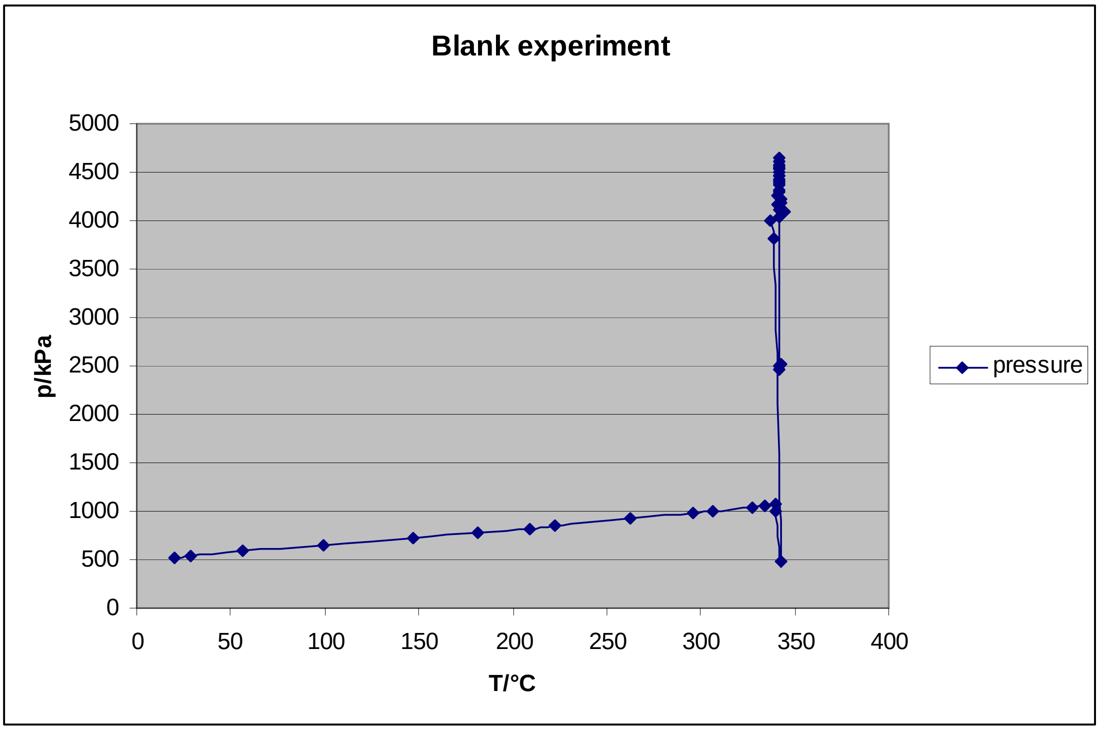

Figure 3. Pressure curve of blank experiment as a function of temperature.

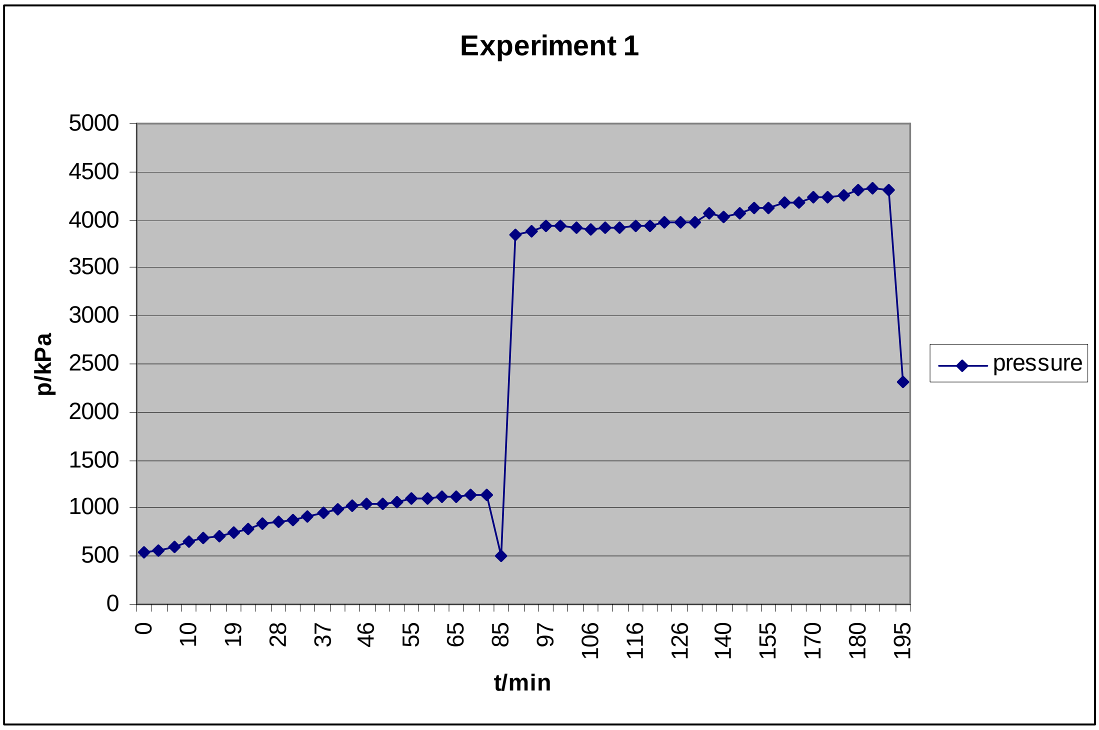

Figure 4. Pressure curve of experiment 1 as a function of time which was carried out with alkali refined rapeseed oil in 340°C and in 40 bar with hydrogen gas.

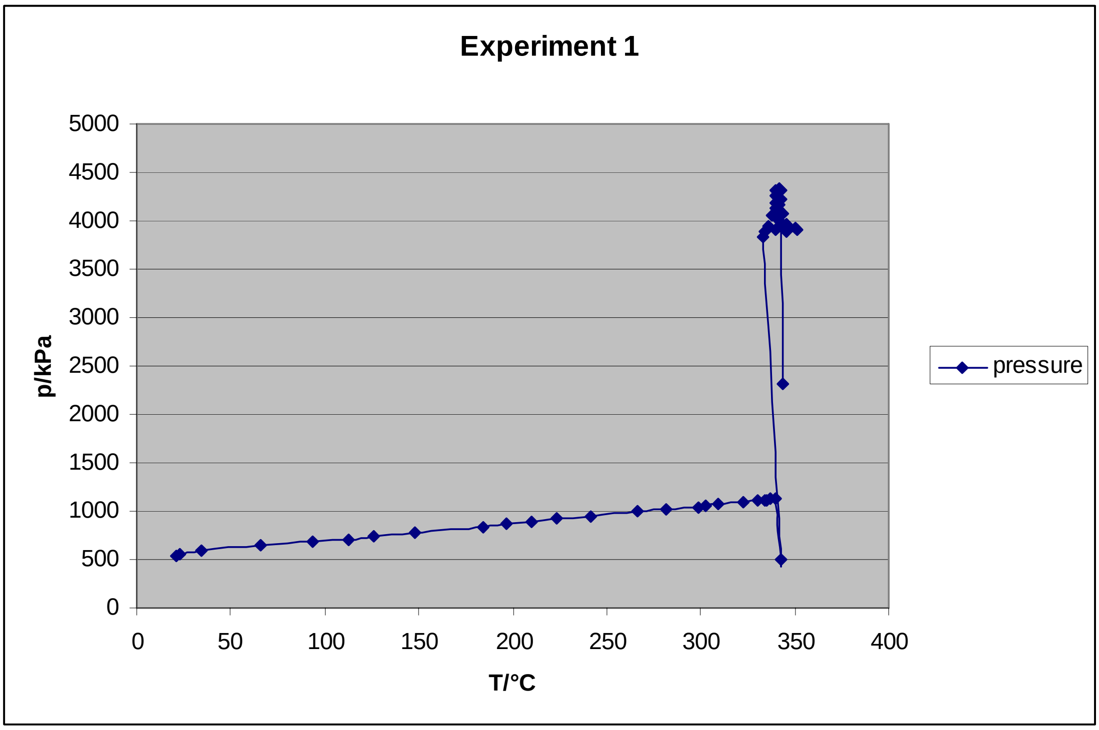

Figure 5. Pressure curve of experiment 1 as a function of temperature.

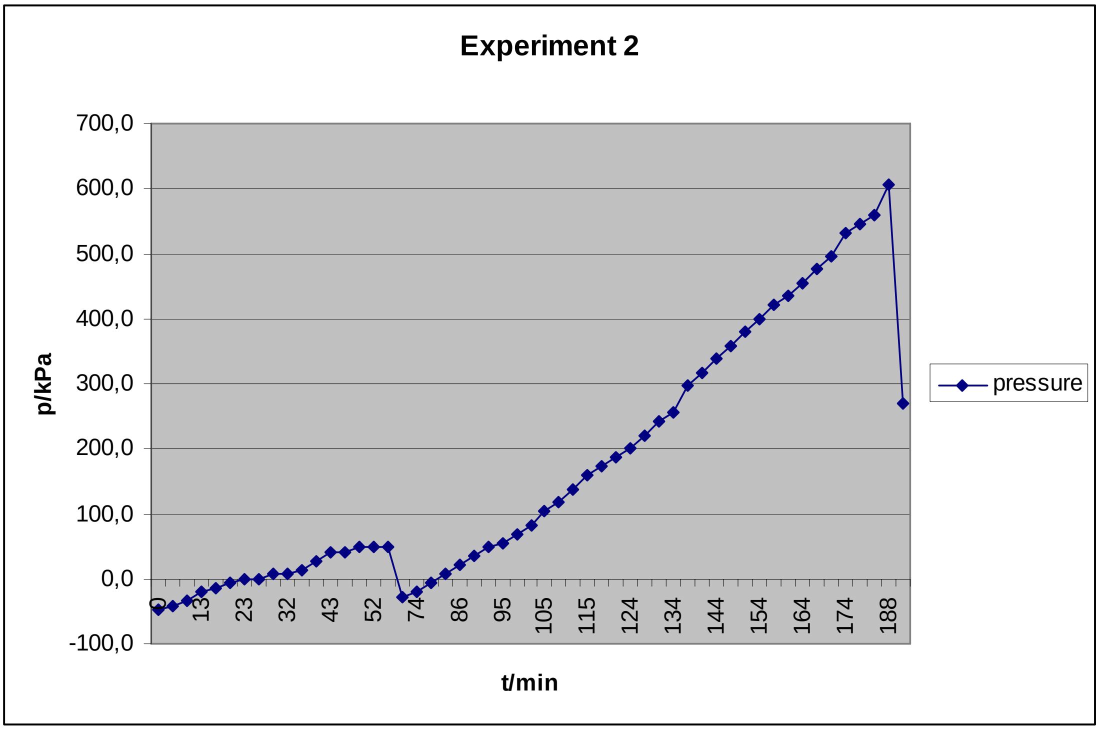

Figure 6. Pressure curve of experiment 2 as a function of time which was carried out with alkali refined rapeseed oil in 340°C and in atmospheric pressure in air.

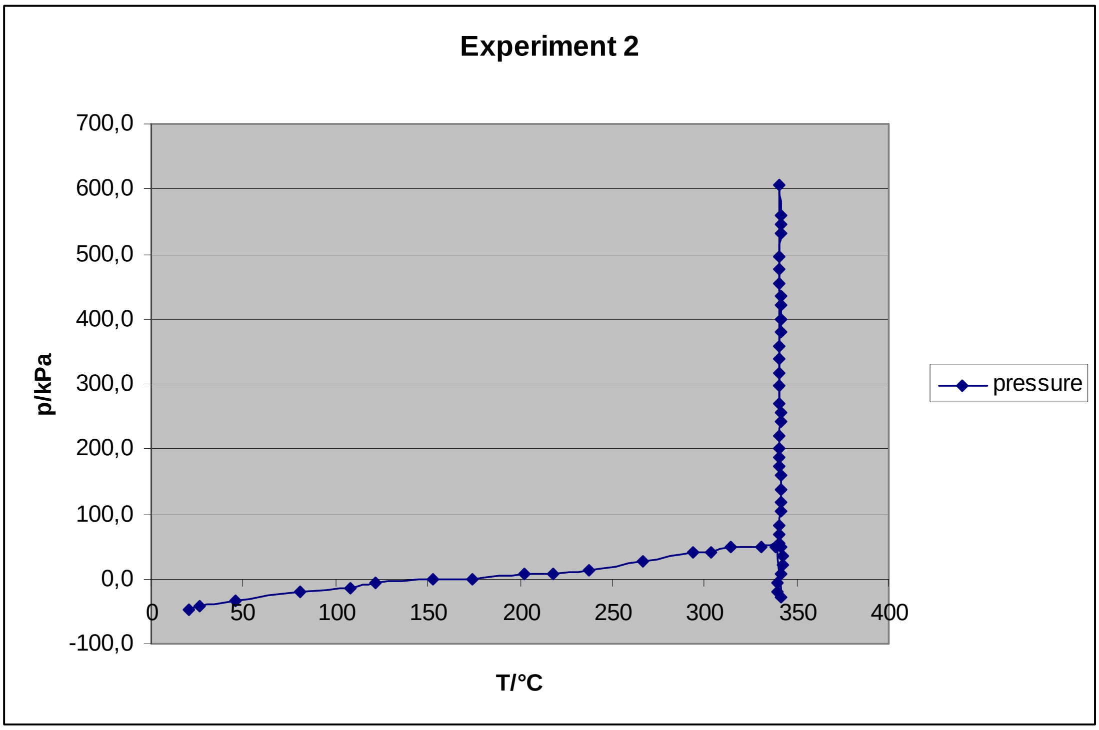

Figure 7. Pressure curve of experiment 2 as a function of temperature.

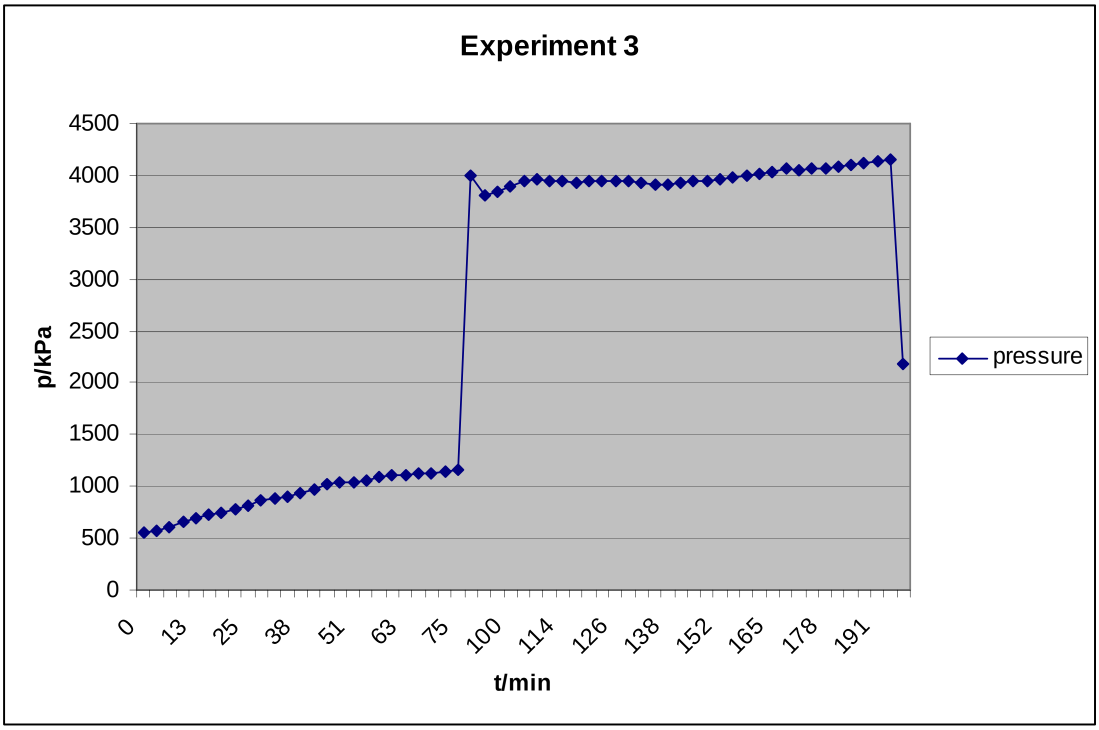

Figure 8. Pressure curve of experiment 3 as a function of time which was carried out with RBD palm oil in 340°C and in 40 bar with hydrogen gas.

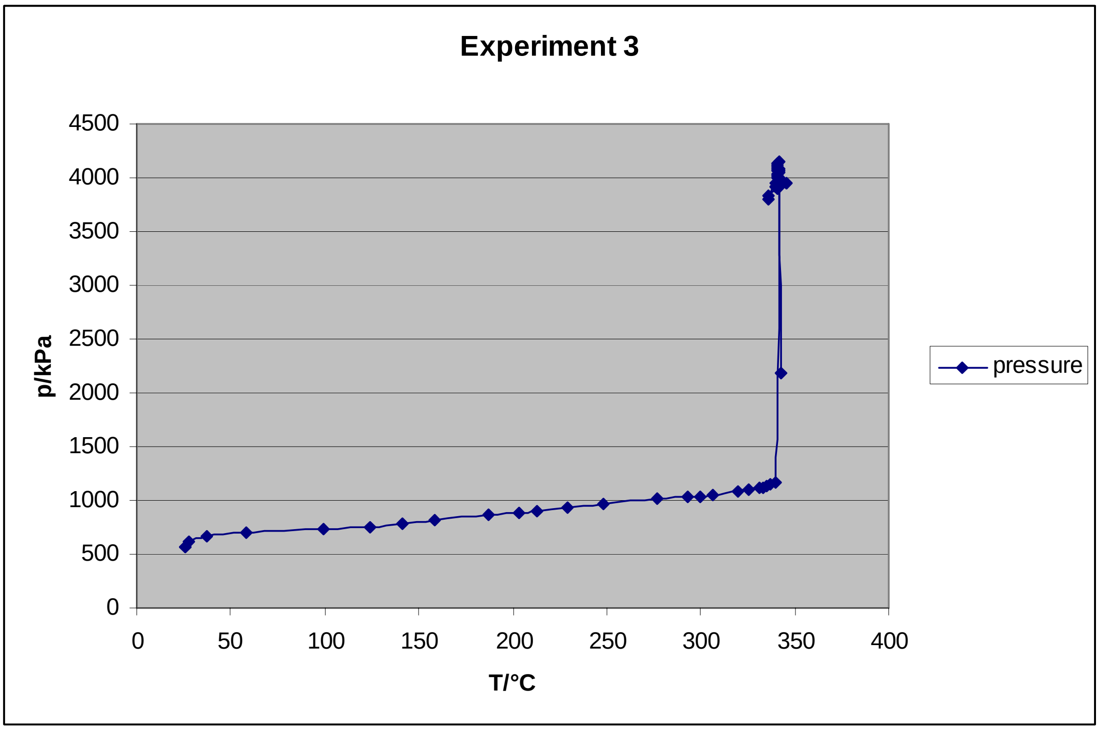

Figure 9. Pressure curve of experiment 3 as a function of time.

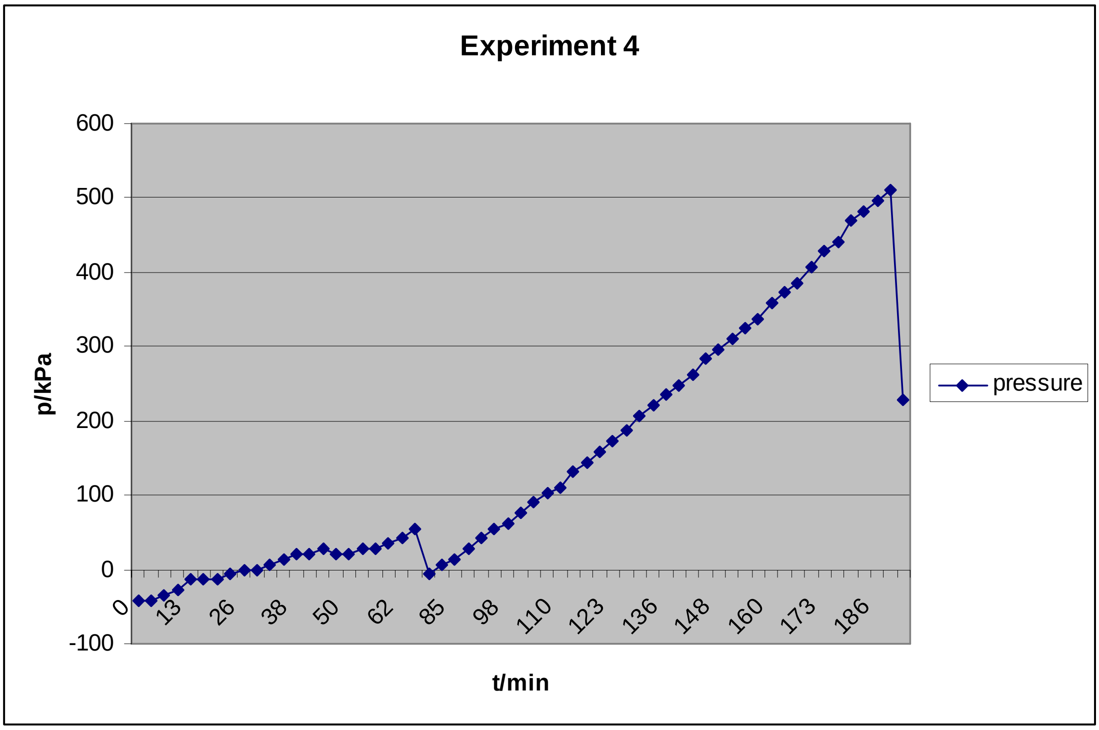

Figure 10. Pressure curve of experiment 4 as function of time which was carried out with RBD palm oil in 340°C and in atmospheric pressure in air.

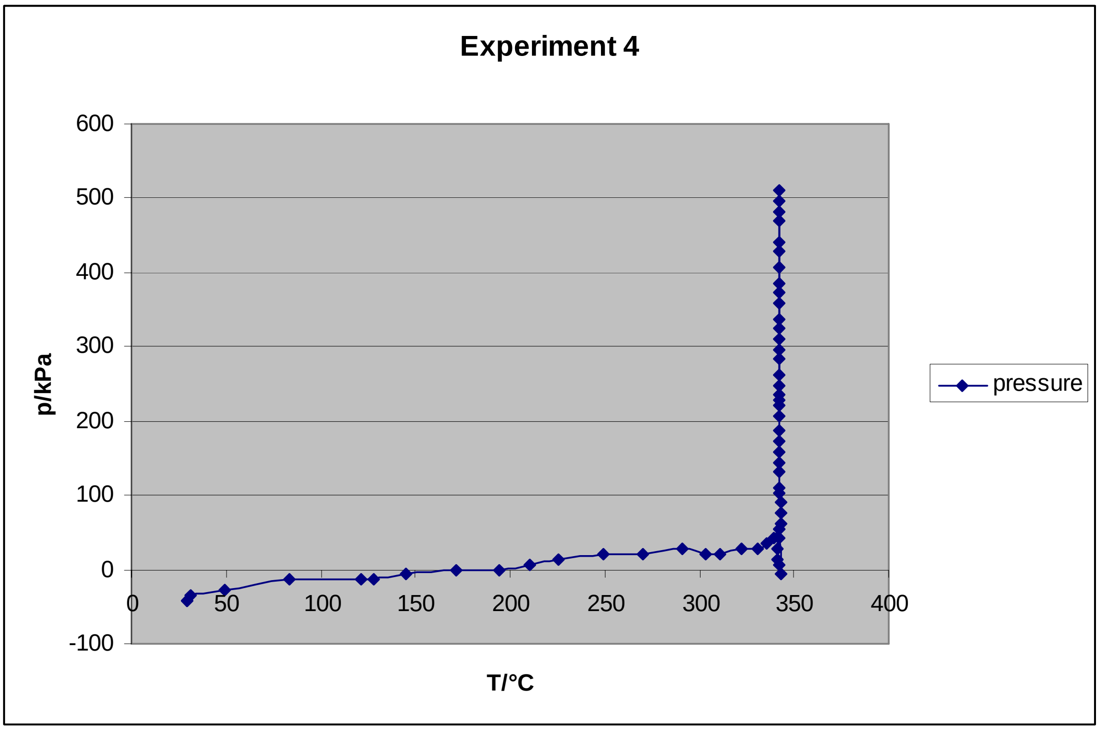

Figure 11. Pressure curve of experiment 4 as a function of temperature.

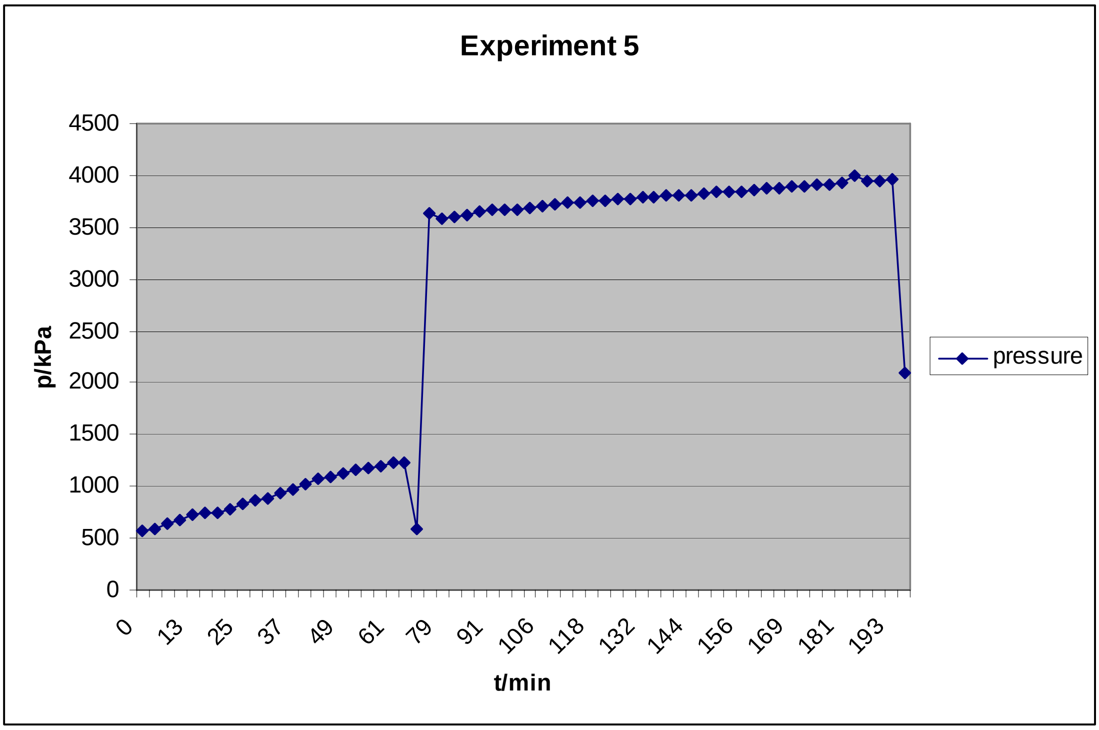

Figure 12. Pressure curve of experiment 5 as a function of time which was carried out with a mixture of crude palm oil and animal fat in ratio 1:1 in 340°C and in 40 bar with hydrogen gas.

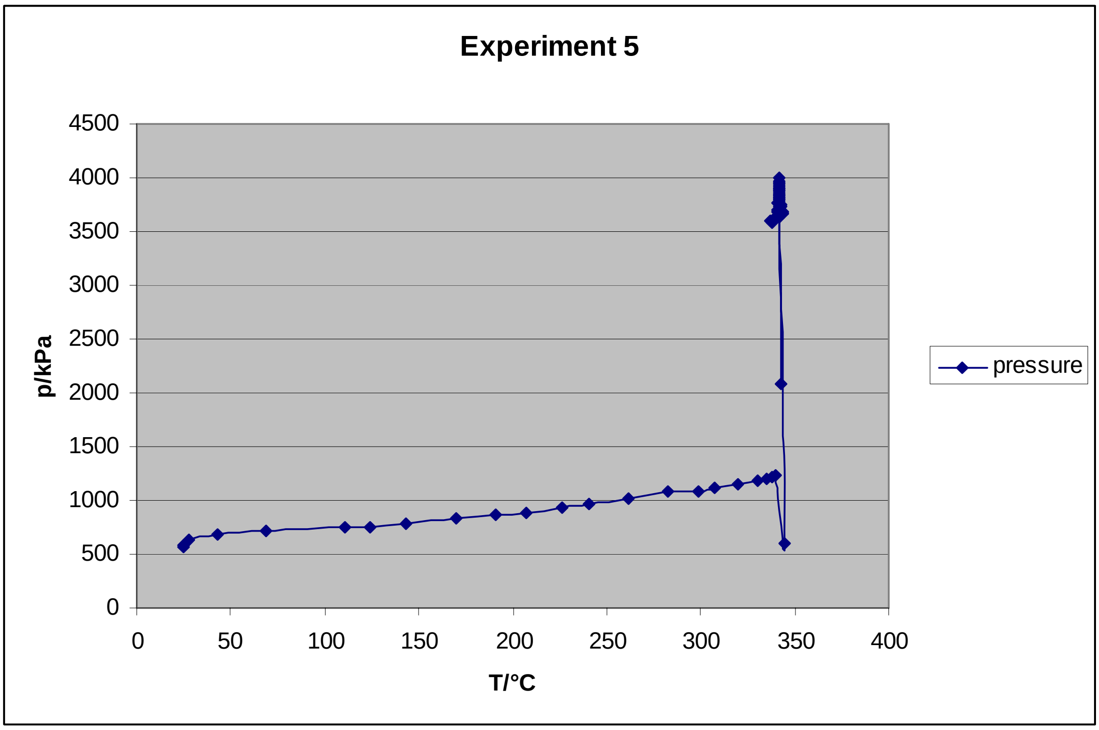

Figure 13. Pressure curve of experiment 5 as a function of temperature.

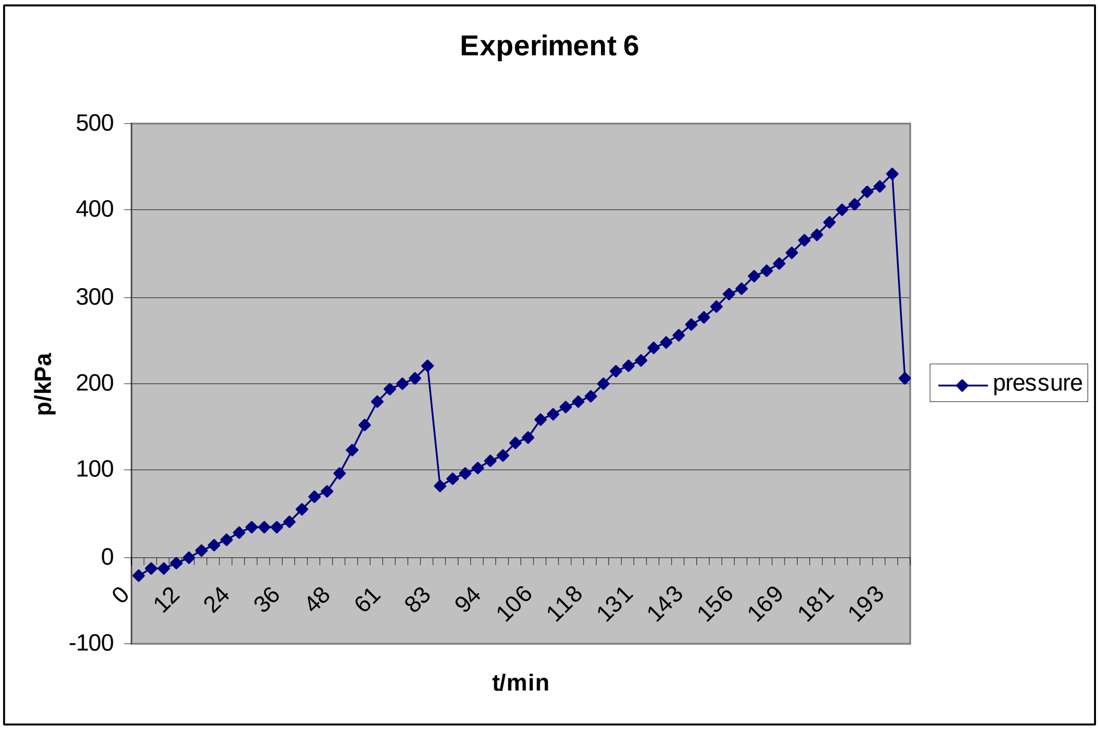

Figure 14. Pressure curve of experiment 6 as a function of time which was carried out with a mixture of crude palm oil and animal fat in ratio 1:1 in 340°C and in atmospheric pressure in air.

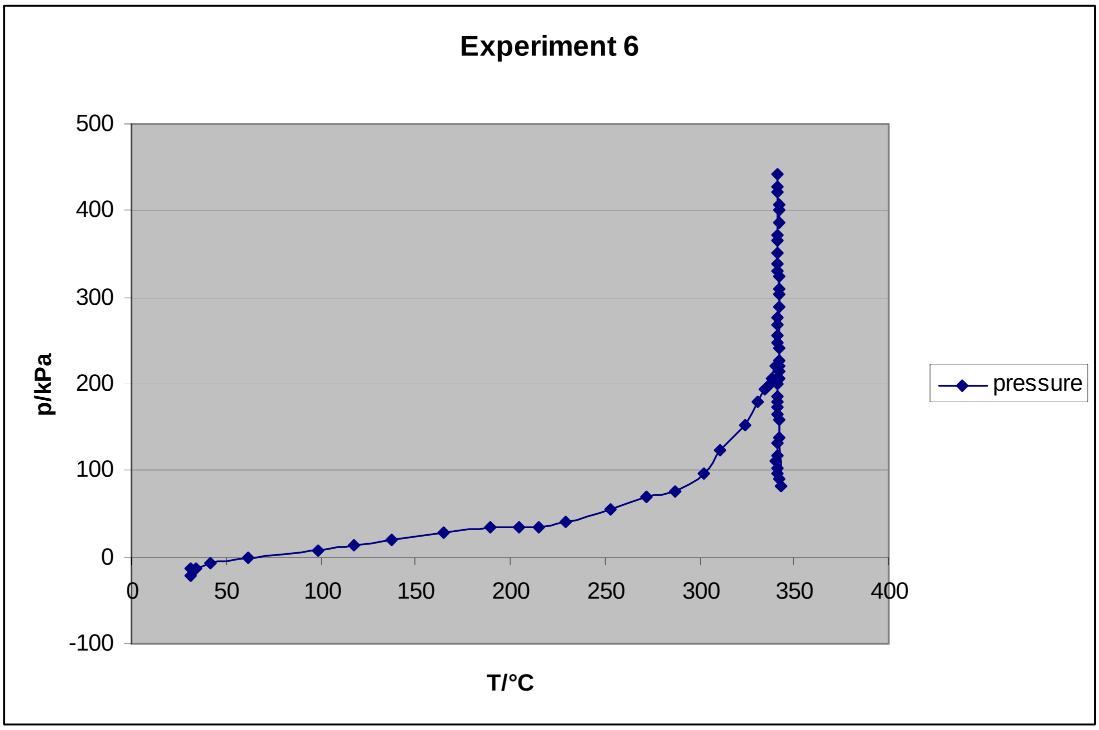

Figure 15. Pressure curve of experiment 6 as a function of temperature.

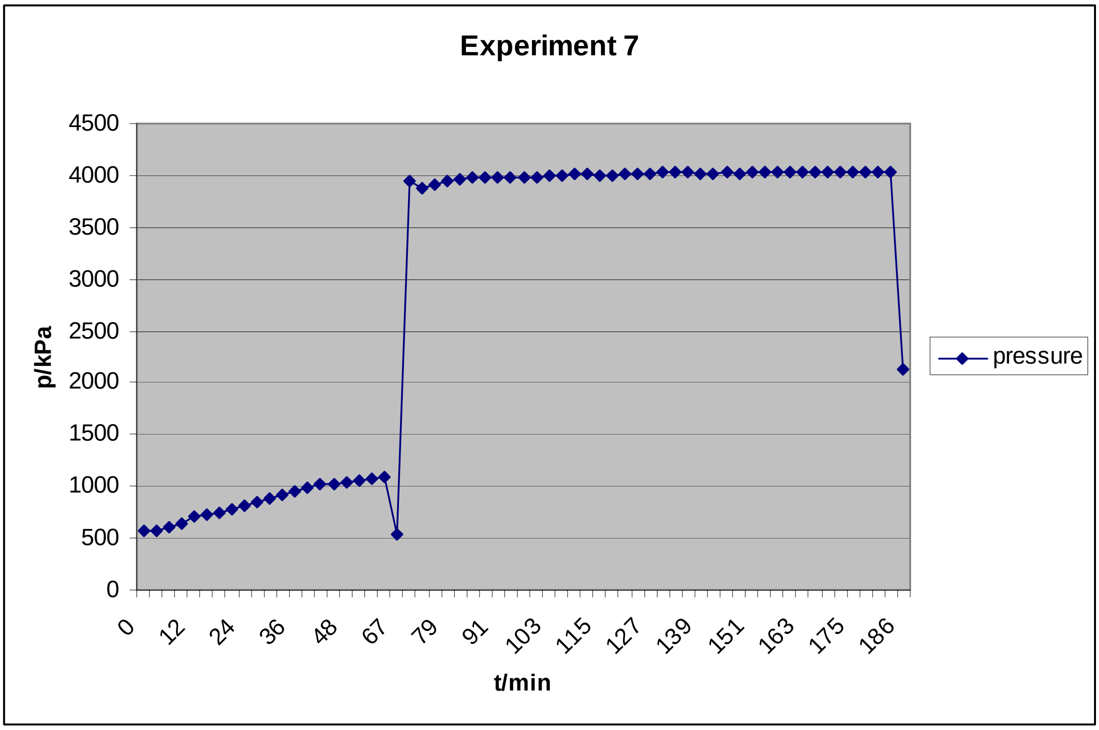

Figure 16. Pressure curve of experiment 7 as a function of time which was carried out with RBD palm oil in 325°C and in 40 bar with hydrogen gas.

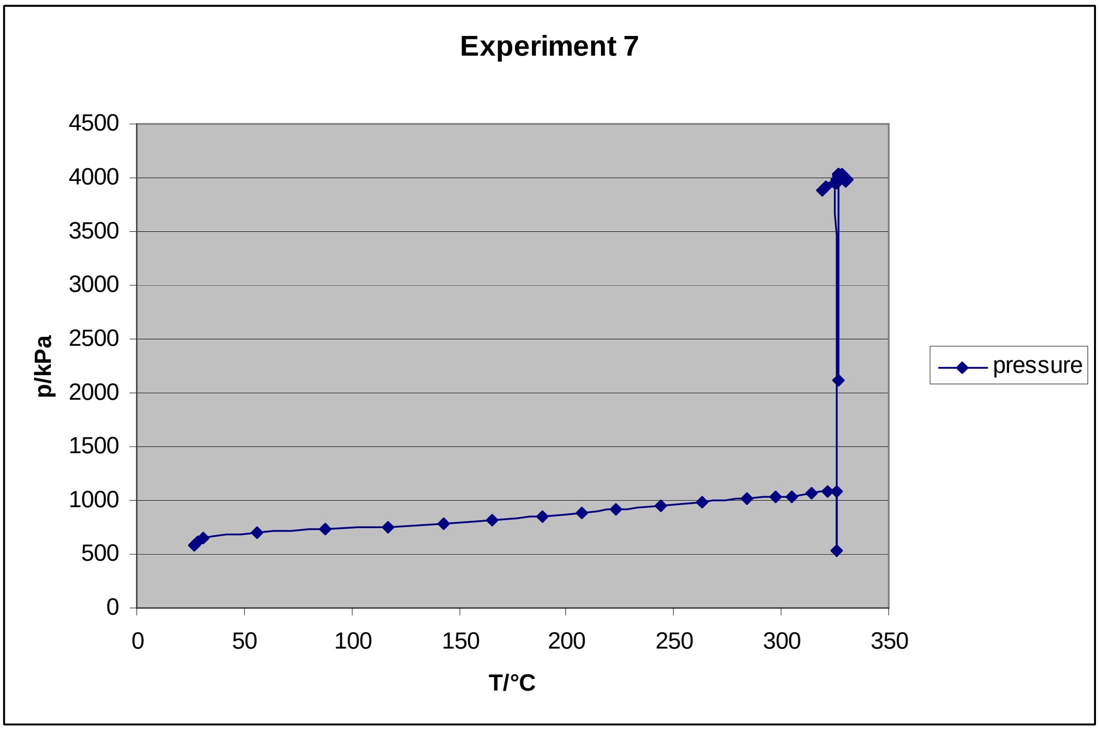

Figure 17. Pressure curve of experiment 7 as a function of temperature.

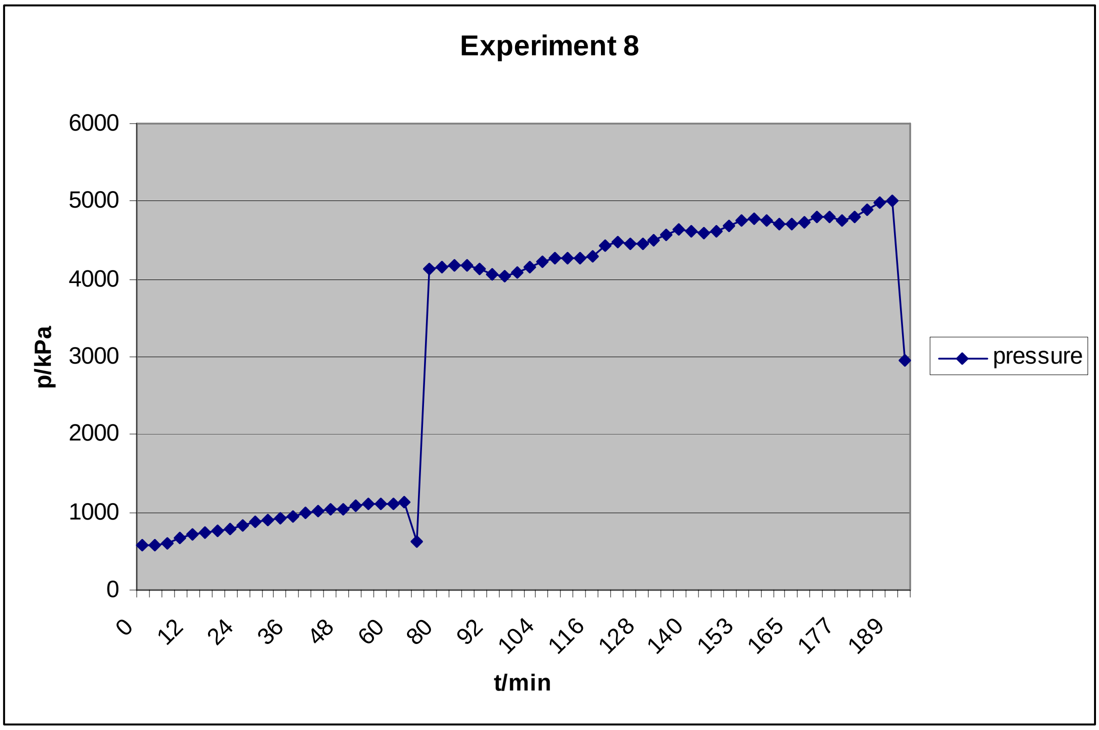

Figure 18. Pressure curve of experiment 8 as a function of time which was carried out with RBD palm oil in 340°C and in 40 bar with hydrogen, but the amount of the test charge was only half of the amount used in other experiments.

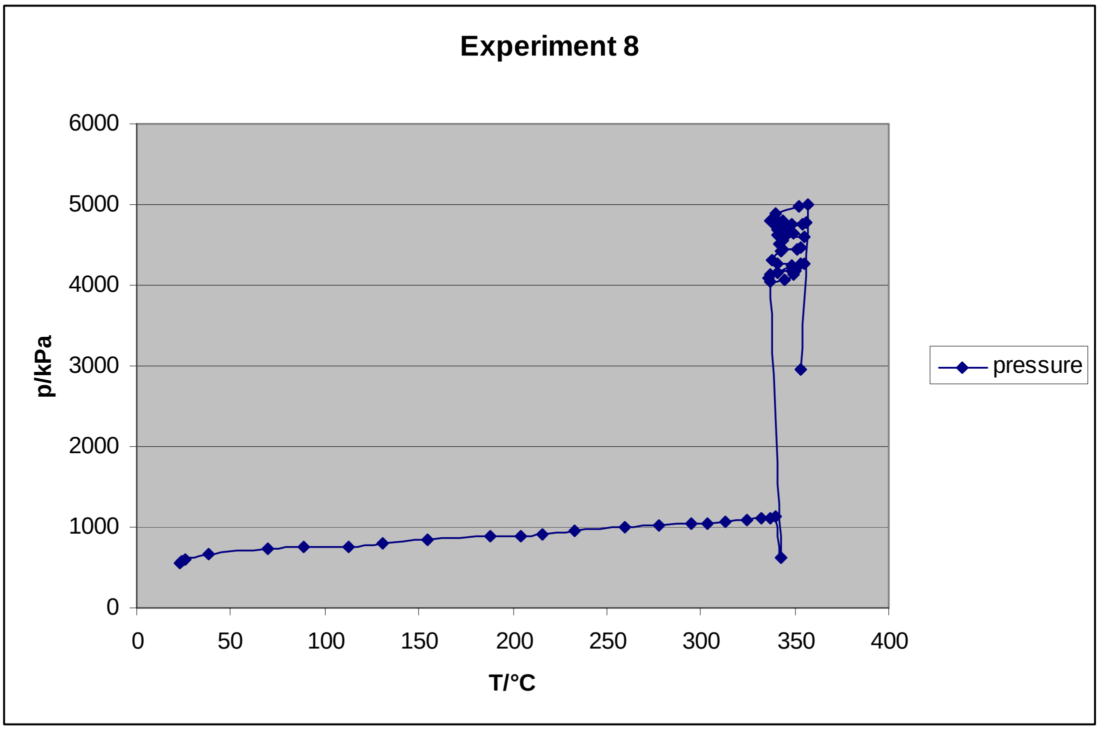

Figure 19. Pressure curve of experiment 8 as a function of temperature.

The example calculation of the gas amounts of experiment 8

The calculation is based on the use of equation of a classical ideal gas. Table 23 shows all the changing parameters that are needed in the calculations. Absolute pressure and temperature are retrieved from the measurement data. Experiment 8 was carried out with RBD palm oil and the density of the oil in state 1 has been determined on the basis of a laboratory analysis like for other two oils used in the experiments. The liquid densities in states 2 to 5 have not been determined in such high temperatures in a laboratory. This is why an Aspen simulation to determine the density was carried out in temperatures from 20 to 340ºC to a flow stream of a vegetable oil resembling the composition and characteristics of RBD palm oil. Based on this information density was presented as a function of temperature. In the calculations subindexes from 1 to 5 are used to distinguish separate states.

Table 23. Absolute pressure, absolute temperature and density at every state required to calculate the gas amounts of experiment 8.

	Absolute pressure p [Pa]	**Absolute temperature T [K]**	**Temperature T [ºC]**	**Density ρ [kg/m^3]**
State 1	666 325	296,15	23	908,56
State 2	1 232 325	613,15	340	820,77
State 3	729 325	616,15	343	819,95
State 4	4 225 325	610,15	337	833,07
State 5	5 107 325	630,15	357	827,89

There are also constants in the calculations and these are as follows:

- the volume of the reactor vessel $V_{vessel} = 0{,}001$ m^3
- the mass of the test charge (oil) $m_{oil} = 0{,}225$ kg
- the universal gas constant $R = 8{,}3145$ J/mol K.

In other experiments the mass of the test charge m_{oil} is 0,450 kg. Experiment 8 was carried out with half of the normal test charge aiming to examine the impact of the amount of the oil to gas formation and composition. Absolute pressures, absolute temperatures and densities of other experiments are presented in table 24.

Table 24. Absolute pressures, absolute temperatures and densities of blank experiment and experiments 1 to 7.

	Absolute pressure *p* [Pa]	**Absolute temperature *T* [K]**	**Temperature *T* [ºC]**	**Density *ρ* [kg/m^3]**
Blank experiment				
State 1	618 325	293,15	20	917,60
State 2	1 177 325	613,15	340	820,77
State 3	584 325	616,15	343	819,95
State 4	3 908 325	612,15	339	832,54
State 5	4 749 325	615,15	342	831,77
Experiment 1				
State 1	639 325	294,15	21	916,92
State 2	1 232 325	613,15	340	820,77
State 3	598 325	616,15	343	819,95
State 4	3 935 325	606,15	333	834,10
State 5	4 411 325	616,15	343	831,51
Experiment 2				
State 1	53 025	293,15	20	917,60
State 2	149 625	612,15	339	821,04
State 3	73 725	615,15	342	820,23
State 4	708 125	614,15	341	820,50
Experiment 3				
State 1	660 325	299,15	26	906,60
State 2	1 260 325	613,15	340	820,77
State 3	855 429	613,15	340	820,77
State 4	4 101 325	615,15	342	831,77
State 5	4 252 325	615,15	342	831,77
Experiment 4				
State 1	60 325	302,15	29	904,64
State 2	156 325	615,15	342	820,23
State 3	94 325	616,15	343	819,95
State 4	611 325	615,15	342	820,23
Experiment 5				
State 1	673 325	298,15	25	907,60
State 2	1 335 325	613,15	340	826,06
State 3	694 325	618,15	345	824,68
State 4	3 728 325	615,15	342	837,13
State 5	4 066 325	615,15	342	837,13
Experiment 6				
State 1	80 325	304,15	31	903,52
State 2	322 325	613,15	340	826,06
State 3	184 325	616,15	343	825,23
State 4	542 325	614,15	341	825,78
Experiment 7				
State 1	660 325	299,15	26	906,60
State 2	1 184 325	599,15	326	824,59
State 3	632 325	599,15	326	824,59
State 4	4 052 325	598,15	325	836,17
State 5	4 142 325	600,15	327	835,66

To find out the volume of the gas in state 1, the volume of the oil has to be calculated. This is done with equation 1:

$$V_{oil,1} = \frac{m_{oil}}{\rho_1}, \tag{1}$$

where $V_{oil,1}$ is the volume of the oil in state 1
m_{oil} is the mass of the oil put in the reactor vessel
ρ_1 is the density of the oil in state 1.

Both of the parameters are known, so the volume of the oil in the beginning can be calculated:

$$V_{oil,1} = \frac{0{,}225kg}{908{,}56kg/m^3} = 0{,}000248m^3$$

Now the volume of the gas inside the reactor can be calculated:

$$V_1 = V_{vessel} - V_{oil,1}, \tag{2}$$

where V_1 is the volume of the gas in state 1
V_{vessel} is the volume of the reactor vessel.

The volume of the gas in state 1 of experiment 8 is as follows:

$$V_1 = 0{,}001m^3 - 0{,}000248m^3 = 0{,}000752m^3$$

All the initial data is known and the number of moles in state 1 can be calculated with equation 4 which is deduced from the equation of a classical ideal gas:

$$n_1 = \frac{p_1 V_1}{RT_1}, \tag{3}$$

where n_1 is the number of gas moles in state 1
p_1 is the absolute pressure in state 1
T_1 is the absolute temperature in state 1.

The number of gas moles in state 1 is as follows:

$$n_1 = \frac{666325 Pa \cdot 0{,}000752 m^3}{8{,}3145 J/mol \cdot K \cdot 296{,}15 K} = 0{,}20345 mol$$

The calculations of the volume of the oil $V_{oil,2}$, the volume of the gas V_2 and the number of gas moles n_2 in state 2 are identical to state 1 and can be calculated with equations 1, 2 and 3 as follows:

$$V_{oil,2} = \frac{m_{oil}}{\rho_2} = \frac{0{,}225 kg}{820{,}77 kg/m^3} = 0{,}000274 m^3$$

$$V_2 = V_{vessel} - V_{oil,2} = 0{,}001 m^3 - 0{,}000274 m^3 = 0{,}000726 m^3$$

$$n_2 = \frac{p_2 V_2}{RT_2} = \frac{1232325 Pa \cdot 0{,}000726 m^3}{8{,}3145 J/mol \cdot K \cdot 613{,}15 K} = 0{,}17550 mol$$

In state 3 the volume of the oil cannot be calculated with equation 1 because a liquid sample has been taken and flushing of the sampling pipe has been carried out. These decrease the mass of the oil in the reactor vessel and have to be taken into account. This is done in equation 4 by subtracting the mass of the liquid sample and the mass of the oil needed to flush the sampling pipe from the original mass of the oil:

$$V_{oil,3} = \frac{m_{oil} - m_{sample,l} - m_{flush}}{\rho_3}, \tag{4}$$

where $V_{oil,3}$ is the volume of the oil in state 3
m_{oil} is the mass of the oil put in the reactor vessel

$m_{sample,l}$ is the mass of a taken liquid sample

m_{flush} is the mass of the oil needed to flush the sampling pipe.

The required masses are gained from the measurement data, and they are as follows:

- $m_{sample,l} = 0{,}0373$ kg
- $m_{flush} = 0{,}0081$ kg.

The corresponding masses of other experiments are presented in table 25.

Table 25. The masses of liquid samples and flushing oils of blank experiment and experiments 1 to 7.

	Mass of a liquid sample m_{liquid} [kg]	**Mass of a flushing oil m_{flush} [kg]**
Blank experiment	0,0377	0,0057
Experiment 1	0,0386	0,0105
Experiment 2	0,0393	0,004
Experiment 3	0,0358	0,0052
Experiment 4	0,0381	0,0054
Experiment 5	0,0369	0,005
Experiment 6	0,0398	0,0047
Experiment 7	0,0373	0,0077

Now the volume of the oil can be calculated:

$$V_{oil,3} = \frac{0{,}225kg - 0{,}0373kg - 0{,}0081kg}{819{,}95kg/m^3} = 0{,}000219m^3$$

Now equation 2 can be used to calculate the volume of the gas in state 3:

$$V_3 = V_{vessel} - V_{oil,3} = 0{,}001m^3 - 0{,}000219m^3 = 0{,}000781m^3$$

All parameters are known and the number of gas moles in state 3 can be calculated:

$$n_3 = \frac{p_3V_3}{RT_3} = \frac{729325Pa \cdot 0{,}000781m^3}{8{,}3145J/mol \cdot K \cdot 616{,}15K} = 0{,}11118mol\,.$$

The calculations of the volume of the oil $V_{oil,4}$, the volume of the gas V_4 and the number of gas moles n_4 in state 4 are identical to state 3 and can be calculated with equations 4, 2 and 3. The masses of the sample and flushing have to take into consideration also in state 4 with the help of equation 4:

$$V_{oil,4} = \frac{m_{oil} - m_{sample,l} - m_{flush}}{\rho_4} = \frac{0{,}225kg - 0{,}0373kg - 0{,}0081kg}{833{,}07kg/m^3} = 0{,}000216m^3$$

$$V_4 = V_{vessel} - V_{oil,4} = 0{,}001m^3 - 0{,}000216m^3 = 0{,}000784m^3$$

$$n_4 = \frac{p_4 V_4}{RT_4} = \frac{4225325Pa \cdot 0{,}000784m^3}{8{,}3145J/mol \cdot K \cdot 610{,}15K} = 0{,}65210mol$$

Also the calculations of state 5 follow the two previous states and are as follows:

$$V_{oil,5} = \frac{m_{oil} - m_{sample,l} - m_{flush}}{\rho_5} = \frac{0{,}225kg - 0{,}0373kg - 0{,}0081kg}{827{,}89kg/m^3} = 0{,}000217m^3$$

$$V_5 = V_{vessel} - V_{oil,5} = 0{,}001m^3 - 0{,}000217m^3 = 0{,}000783m^3$$

$$n_5 = \frac{p_5 V_5}{RT_5} = \frac{5107325Pa \cdot 0{,}000783m^3}{8{,}3145J/mol \cdot K \cdot 630{,}15K} = 0{,}76326mol$$

All the volumes of the oil V_{oil} and gas V, and the number of moles n at every state for other experiments are presented in table 26.

Table 26. The volumes of the oil and gas, and the number of moles at every state of blank experiment and experiments 1 to 7.

	Volume of the oil V_{oil} [m^3]	**Volume of the gas V [m^3]**	**Number of gas moles n [mol]**
Blank experiment			
State 1	0,000490	0,000510	0,12927
State 2	0,000548	0,000452	0,10432
State 3	0,000496	0,000504	0,05750
State 4	0,000489	0,000511	0,39287
State 5	0,000489	0,000511	0,47466
Experiment 1			
State 1	0,000491	0,000509	0,13312
State 2	0,000548	0,000452	0,10920
State 3	0,000489	0,000511	0,05969
State 4	0,000481	0,000519	0,06166
State 5	0,000482	0,000518	0,44593
Experiment 2			
State 1	0,000490	0,000510	0,01109
State 2	0,000548	0,000452	0,01329
State 3	0,000496	0,000504	0,00727
State 4	0,000496	0,000504	0,06994
Experiment 3			
State 1	0,000496	0,000504	0,13371
State 2	0,000548	0,000452	0,11168
State 3	0,000498	0,000502	0,08418
State 4	0,000492	0,000508	0,40758
State 5	0,000492	0,000508	0,42258
Experiment 4			
State 1	0,000497	0,000503	0,01207
State 2	0,000549	0,000451	0,01380
State 3	0,000496	0,000504	0,00928
State 4	0,000496	0,000504	0,06029
Experiment 5			
State 1	0,000496	0,000504	0,13694
State 2	0,000545	0,000455	0,11924
State 3	0,000495	0,000505	0,06824
State 4	0,000487	0,000513	0,37359
State 5	0,000487	0,000513	0,40746
Experiment 6			
State 1	0,000498	0,000502	0,01594
State 2	0,000545	0,000455	0,02878
State 3	0,000491	0,000509	0,01830
State 4	0,000491	0,000509	0,05405
Experiment 7			
State 1	0,000496	0,000504	0,13371
State 2	0,000546	0,000454	0,10800
State 3	0,000491	0,000509	0,06459
State 4	0,000484	0,000516	0,42016
State 5	0,000485	0,000515	0,42781

Now the needed information to calculate the number of moles of added hydrogen to the reactor system can be calculated:

$$n_{H2} = n_1 + (n_4 - n_3)\,, \tag{5}$$

where n_{H2} is the total number of hydrogen moles added to the reactor system
n_1 is the number of gas moles in state 1
n_4 is the number of gas moles in state 4
n_3 is the number of gas moles in state 3.

In blank experiment added gas is nitrogen and the calculation proceeds in the same way as in experiments carried out with hydrogen gas. The total number of added air moles in experiments 2, 4 and 6 is simply the number of gas moles in state 1, because the experiments carried out in air do not include gas input after taking liquid and gas samples. Now all the information required is known and the total number of added hydrogen moles in experiment 8 can be calculated:

$$n_{H2} = 0{,}20345mol + (0{,}65219mol - 0{,}11118mol) = 0{,}74437mol$$

The mass of added hydrogen can be calculated when it is universally known that the molar mass of molecular hydrogen is 2,016 g/mol:

$$m_{H2} = n_{H2}M_{H2}\,, \tag{6}$$

where m_{H2} is the mass of added hydrogen to the reactor system
M_{H2} is the molar mass of molecular hydrogen.

Now the mass of hydrogen can be calculated:

$$m_{H2} = 0{,}74437mol \cdot 2{,}016g/mol = 1{,}50065g$$

The molar masses of nitrogen, hydrogen and air are presented in table 27 in order to calculate the masses of added gas into the system in every experiment. The numbers of moles and masses of added gases for other experiments are presented in table 28.

Table 27. The universally known molar masses of nitrogen, hydrogen and air.

Molar mass of molecular nitrogen M_{N2} [g/mol]	**Molar mass of molecular hydrogen M_{H2} [g/mol]**	**Average molar mass of air M_{air} [g/mol]**
28,02	2,016	29,01

Table 28. The numbers of moles and masses of added gases for blank experiment and experiments 1 to 7.

	Added gas *n* [mol]	**Added gas *m* [g]**
Blank experiment	0,46464	13,01923
Experiment 1	0,13508	0,27233
Experiment 2	0,01109	0,32161
Experiment 3	0,45710	0,92152
Experiment 4	0,01207	0,35009
Experiment 5	0,44229	0,89166
Experiment 6	0,01594	0,46252
Experiment 7	0,48928	0,98638

Blank experiment was carried out in a nitrogen sphere, experiments 1, 3, 5, 7 and 8 were carried out in a hydrogen sphere and experiments 2, 4 and 6 were carried out in air. The amount of added gas has to be known in order to determine the mass balance of the experiment. Mass balance of experiment 8 is presented in chapter 5.4. Also the amount of developed gas in the experiments is one changing variable. Referring to figure 20 (on page 71) gas is developed between states 1-2 and 4-5 because temperature is kept constant but pressure is rising. This indicates that decomposition of larger molecules into smaller ones occurs and this contributes to gas formation. The number of moles of developed gas is calculated as follows:

$$n_{dev} = n_5 - n_{H2} + n_{sample,g} , \tag{7}$$

where n_{dev} is the total number of moles of developed gas

$n_{sample,g}$ is the number of gas moles of the first gas sample.

In the case of experiments carried out with air equation (7) is slightly different: the term n_5 is replaced by n_4 because state 4 is the last state in experiments 2, 4 and 6. Equation 8 is deduced from the molar balance of experiment 8. The number of gas moles of the first gas sample $n_{sample,g}$ is determined with the help of the mass of the sample and of an average molar mass of the sample. The mass of the sample is retrieved from the measurement data and the average molar mass is based on the analysis result the first gas sample. The number of gas moles of the sample is 0,04147 mol and n_{H2} is determined above. The total number of developed gas moles can be calculated:

$$n_{dev} = 0{,}76326 mol - 0{,}74437 mol + 0{,}04147 mol = 0{,}06036 mol$$

The development of gas calculation of experiment 1 is exceptional compared to other experiments: the mass of the first gas sample of the experiment was so small that the scale did not measure any mass and the result was 0 g. This occurred because the accuracy of the scale is 0,1 g. This is why in experiment 1 an assumption, that the mass of the first sample was 0,09 g, was made. Otherwise the calculation was similar to other calculations of hydrogen sphere.

The number of developed gas moles can also be calculated in another way. Equations 8 and 9 present gas development in two steps:

$$n_{dev1} = n_2 - n_1 , \tag{8}$$

where n_{dev1} is the number of gas moles that is developed between the states 1 and 2.

$$n_{dev2} = n_5 - n_4 , \tag{9}$$

where n_{dev2} is the number of gas moles that is developed between the states 4 and 5.

The sum of the results of equations 8 and 9 is theoretically the same as n_{dev}:

$$n_{dev1+2} = n_{dev1} + n_{dev2} \tag{10}$$

Equations 8, 9 and 10 give the results below:

$$n_{dev1} = 0{,}17550mol - 0{,}20345mol = -0{,}02795mol$$

$$n_{dev2} = 0{,}76326mol - 0{,}65210mol = 0{,}11116mol$$

$$n_{dev1+2} = -0{,}02795mol + 0{,}11116mol = 0{,}08321mol$$

The result of n_{dev1+2} shows that the number of developed gas moles in experiment 8 is not the same when calculated in two different ways, though theoretically it should be. The numbers of developed gas moles of all experiments are presented in table 28 on page 72 in the text.

Mass balances of thermal degradation experiments

Table 29. Mass balances of blank experiment and experiments 1 to 7.

Blank experiment	**IN [g]**	**OUT [g]**
Liquid oil	450,0	400,0
Added nitrogen (N_2)	13,0	-
Samples		
liquid	-	37,7
gas	-	10,3
sample pipe flushing	-	5,7
Altogether	**463,0**	**453,7**
Experiment 1	**IN [g]**	**OUT [g]**
Liquid oil	450,0	399,0
Added H_2	0,3	-
Samples		
liquid	-	38,6
gas	-	2,2
sample pipe flushing	-	10,5
Altogether	**450,3**	**450,3**
Experiment 2	**IN [g]**	**OUT [g]**
Liquid oil	450,0	405,8
Added air	0,3	-
Samples		
liquid	-	39,3
gas	-	2,5
sample pipe flushing	-	4,0
Altogether	**450,3**	**451,6**
Experiment 3	**IN [g]**	**OUT [g]**
Liquid oil	450,0	407,0
Added H_2	0,9	-
Samples		
liquid	-	35,8
gas	-	2,3
sample pipe flushing	-	5,2
Altogether	**450,9**	**450,3**
Experiment 4	**IN [g]**	**OUT [g]**
Liquid oil	450,0	405,0
Added air	0,4	-
Samples		
liquid	-	38,1
gas	-	2,1
sample pipe flushing	-	5,4
Altogether	**450,4**	**450,6**
Experiment 5	**IN [g]**	**OUT [g]**
Liquid oil	450,0	405,0
Added H_2	0,9	-
Samples		
liquid	-	36,9
gas	-	2,1

sample pipe flushing	-	5,0
Altogether	**450,9**	**449,0**
Experiment 6	**IN [g]**	**OUT [g]**
Liquid oil	450,0	403,0
Added air	0,5	-
Samples		
liquid	-	39,8
gas	-	2,7
sample pipe flushing	-	4,7
Altogether	**450,5**	**450,2**
Experiment 7	**IN [g]**	**OUT [g]**
Liquid oil	450,0	405,0
Added H_2	1,0	-
Samples		
liquid	-	37,3
gas	-	1,2
sample pipe flushing	-	7,7
Altogether	**451,0**	**451,2**