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Development of an Economically and Environmentally Sustainable Method for the Oxidation of Rice Bran Wax

Tommy Alfred Hofmann

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Vorsitzender: Prof. Dr. Klaus Köhler

Prüfer der Dissertation:

1. Prof. Dr. Fritz E. Kühn
2. Prof. Dr. Kai-Olaf Hinrichsen

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„*Dem Anwenden muss das Erkennen vorausgehen.*"

(Max Planck)

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Abstract

In today's society waxes play important yet for most people unknown roles. They are used as polishes for shoes, cars and floors, as coating agents for medicine, sweets and chewing gums and as components in cosmetic products like lip sticks. Depending on the intended use different requirements have to be met by the wax and also different sources of wax origin are favoured. For food, cosmetic and pharmaceutical applications the price of the wax is of low importance but it needs to be biocompatible and most important without any doubt non-hazardous to humans. For polishes and other industrial applications such standards and social requirements are less prone making price and physical and chemical properties more important.

For many of the latter applications Montan Wax (MW) is used as a cheap yet hard wax derived from lignite. In its raw form it is a dark, hard substance mainly consisting of long chained aliphatic esters. Processed by bleaching with chromosulfuric acid it becomes a white, still hard substance with long chained aliphatic acids as its main component. The bleaching serves several purposes. By degrading undesired organic compounds, it bleaches the colour and erases any unpleasant odour of the wax, furthermore aliphatic acids are set free by splitting esters and further acids are formed by oxidation of the alkyl parts of the esters.

Already used alternatives to this fossil resource are for example carnauba wax, bees wax and rice bran wax (RBW). Especially interesting is RBW due to being a side-product of the food industry, namely the production of white rice and rice oil. Thus, RBW is not only rather inexpensive but it could also be produced in amounts necessary to replace MW without competing against food crops or natural habitats. Untreated RBW shows many similar properties to raw MW, like high hardness, a high melting point of app. 80 °C and consisting of long chained aliphatic esters. Yet RBW has the advantages of being only slightly yellow coloured and only slightly smelling like rice. In order to gain similar properties to bleached MW RBW only has to be split and oxidized without the need to degrade unwanted organic compounds. In principle the same process utilizing chromosulfuric acid could be applied upon RBW to achieve these results. Yet there are some obstacles in the oxidation of RBW. First of all, RBW is not composed exactly the same as MW and is less easily oxidized by chromosulfuric acid as MW (possibly due to its higher ester content and therefore higher hydrophobicity). Secondly, if RBW was processed unaltered to some recent patents of oxidizing MW, this process would be highly inefficient regarding atom stoichiometry. It would be a waste of resources and generate unnecessary high amounts of waste products. Furthermore, the use of Cr(VI) compounds is restricted by REACH and should in general be replaced by environmentally more friendly processes.

The purpose of this work was therefore to develop an environmentally friendlier process for the oxidation of RBW. To reach this intention raw RBW was analysed and a model substrate developed. Literature-known procedures were evaluated and adapted on small scale experiments (1 g) with the model substrate and RBW, finally developing a method with which 1 kg of oxidized RBW could easily be produced in the research laboratory. Always keeping in mind the intended implementation to industrial scales, the developed process is not only

environmentally friendlier as the compared chromosulfuric acid process, but also economically more favourable, lowering the costs of chemical reagents to far less than one third of the chromosulfuric acid process. The process is free of organic solvent or transition metals and is designed as a one-pot-synthesis with high yield per reaction volume.

Kurzzusammenfassung

In unserer heutigen Gesellschaft erfüllen Wachse wichtige, jedoch für Laien oftmals unbekannte Aufgaben in Industrie und Haushalt. Verwendung finden sie in Polituren für Schuhe, Autos und Böden, als Überzugsmaterial von Kaugummis, Süßigkeiten und Medikamenten sowie als Bestandteile von Kosmetika wie etwa Lippenstiften. Je nach Einsatzgebiet werden unterschiedliche Anforderungen an Wachse gestellt und unterschiedliche Rohstoffquellen bevorzugt. In der Lebensmittel-, Kosmetik- und Pharmazeutischen Industrie spielt der Preis des Wachses eine untergeordnete Rolle, während die Unschädlichkeit über jeden Zweifel erhaben sein muss. Für Polituren und andere industrielle Anwendungen sind derartige Anforderungen deutlich nachrangiger und die Eigenschaften physikalischer und chemischer Natur, sowie der Preis des Rohstoffs werden entscheidender.

Oftmals wird Montanwachs (MW) für solche industriellen Anwendungen verwendet, da es ein günstiges Wachs darstellt. MW wird aus Braunkohle als hartes, dunkles Wachs gewonnen, welches zum Großteil aus langkettigen, aliphatischen Estern besteht. Ein Bleichprozess mit Chromschwefelsäure dient dem Abbau unerwünschter organischer Begleitstoffe, wodurch das Wachs heller wird und den leichten, unangenehmen Geruch verliert. Weiterhin werden die Ester gespalten und die Alkylketten oxidiert, sodass gebleichtes MW zum größten Teil aus langkettigen Säuren besteht.

Alternativen zu diesem fossilen Rohstoff, welche bereits teilweise genutzt werden, sind unter anderem Carnaubawachs, Bienenwachs und Reiskleie-/ Reisschalenwachs (RBW). Besonders hervorzuheben ist unter diesen das RBW, da es als Nebenprodukt der Lebensmittelindustrie bei der Produktion von weißem Reis bzw. Reisöl anfällt. Dadurch ist RBW nicht nur vergleichsweise günstig gegenüber anderen erneuerbaren Wachsen, sondern könnte auch in ausreichenden Mengen zum Ersatz von MW hergestellt werden, ohne dabei zusätzliche landwirtschaftliche Flächen zu benötigen. In vielen Eigenschaften gleichen sich unbehandeltes RBW und MW. Beide sind harte Wachse, mit hohen Schmelzpunkten von etwa 80 °C und sie bestehen hauptsächlich aus langkettigen Estern. RBW hat jedoch die Vorteile einer hellen Farbe und eines lediglich dezenten Eigengeruchs nach Reis. Um gebleichtem MW zu gleichen, müssen daher lediglich die Ester gespalten und die Alkylgruppen oxidiert werden. Ein Abbau störender organischer Nebenbestandteile ist nicht erforderlich. Im Prinzip kann der Chromschwefelsäure nutzende Prozess für MW auch auf RBW angewandt werden, jedoch gibt es einige Argumente dagegen. Zum Einen ist RBW schlechter durch Chromschwefelsäure oxidierbar als MW (wahrscheinlich aufgrund eines größeren Estergehalts und dadurch größerer Hydrophobie). Zum Anderen wäre dieser Prozess bei gleicher Ausführung wie in jüngsten Patenten äußerst ineffizient. Es würden Ressourcen verschwendet und unnötiger Abfall produziert. Weiterhin sind Cr(VI) Chemikalien und deren Anwendung durch REACH beschränkt, und sollten wenn möglich durch umweltfreundlichere Verfahren ersetzt werden.

Das Ziel dieser Arbeit war daher die Entwicklung eines umweltfreundlich(er)en Prozesses zur Oxidation von RBW. Um dies zu erreichen wurde RBW untersucht und ein Modellsubstrat entwickelt. Literaturbekannte Vorgehensweisen wurden im Hinblick auf potentielle

Anwendbarkeit beurteilt und mithilfe von Experimenten im kleinen Maßstab (1 g) angepasst. Auf diese Weise wurde eine Methode entwickelt, mit welcher 1 kg RBW im Labor erfolgreich oxidiert wurde. Im Hinblick auf eine industrielle Umsetzung konnte der neue Prozess nicht nur umweltfreundlicher, sondern auch deutlich kostengünstiger gestaltet werden, sodass die Chemikalienkosten abseits des Wachses auf weniger als ein Drittel des alten Prozesses sanken. Der Prozess ist frei von organischen Lösungsmitteln und Übergangsmetallen und kann als Eintopfreaktion bei hoher Volumenausbeute durchgeführt werden.

List of Abbreviations

AA-TEMPO	4-Acetamido-TEMPO
ABNO	9-Azabicyclo[3.3.1]nonane N-oxyl
Ac	Acyl
acac	Acetylacetonate
Aliquat 336	$(C_n)_3MeNCl$ where C_n is a mixture of octyl and decyl chains
AN	Acid Number, measured in mg(KOH)/g(substance)
app.	Approximately
AZADO	2-azaadamantane-N-oxyl
Bu	Butyl
^{t}Bu	*tert*-Butyl
BW	Bees Wax
°C	Degrees Celsius
CA, $H_3(CA)$	Citric acid
Conc.	Concentration
CW	Carnauba Wax
C_nOH	$H-(CH_2)_n-OH$ (primary aliphatic alcohol)
$C_n=O$	$H-(CH_2)_{n-1}-CHO$ (aliphatic aldehyde)
C_nO_2H	$H-(CH_2)_{n-1}-CO_2H$ (aliphatic acid)
$C_nMe_3N^+$	$(H-(CH_2)_n)Me_3N^+$, Alkyltrimethylammonium
DDQ	2,3-Dichloro-5,6-dicyanobenzoquinone
ΔH_f^0	Standard formation enthalpy
δ	Chemical shift (delta)
DMSO	Dimethylsulfoxid
e.g.	exempli gratia, for example
eq.	Equivalent(s)
Et	Ethyl
FID	Flame Ionisation Detection
g	Gram, 0.001 kg
GC	Gas Chromatography
h	Hour(s)
Hex	Hexyl
HPLC	High Performance Liquid Chromatography
Hz	Hertz, 1/s

I	Integral
i.e.	id est = that is
J	Joule
J	Coupling constant
k	Kilo (* 1000)
KA	Keto-alcohol oil, mixture of cyclohexanol and cyclohexanone
K_{OW}	Octanol/water partition coefficient
L	Litre
m	Mili (1 / 1000)
M	Mega (* 1000000)
M(R)	Molecular weight of a reagent R in g/mol
Me	Methyl
MeCN	Acetonitril
MeO-TEMPO	4-Methoxy-TEMPO
min	Minute(s)
mol	Base unit for amount of substance, 6.022 $*10^{23}$ particles in one mol
MS	Mass Spectrometry
MSTFA	N-Methyl-N-(trimethylsilyl)trifluoroacetamide
MTO	Methyltrioxorhenium, $MeReO_3$
MW	Montan Wax
NMR	Nuclear Magnetic Resonance
OH-TEMPO	4-Hydroxy-TEMPO
Oxo-TEMPO	4-Oxo-TEMPO
PFP	Pentafluorophenol
pH	Negative common logarithm of the activity of protons ($c(H^+) = 10^{-pH}$)
pK_a	Negative logarithm of the acid dissociation constant $K_a=\frac{[A^-][H^+]}{[HA][H_2O]}$, HA being the acid, A^- the deprotonated anion of the acid
ppm	Parts per million
PTA	Phase transfer agent
RBO	Rice Bran Oil
RBW	Rice Bran Wax
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SDS	Sodium dodecyl sulfate
S	Selectivity

SV	Saponification value, measured in mg(KOH)/g(substance)
t	Ton(nes), 1000 kg
T	Temperature
TATTP	(Tris(tetraalkylammonium)tetrakis(oxodiperoxotungsto)phosphate), $[R_4N]_3[PO_4(WO(O_2)_2)_4]$
Bu_4-TATTP	$[Bu_4N]_3[PO_4(WO(O_2)_2)_4]$
Hex_4-TATTP	$[Hex_4N]_3[PO_4(WO(O_2)_2)_4]$
C_n-TATTP	$[C_nMe_3N]_3[PO_4(WO(O_2)_2)_4]$
TBHP	*tert*-Butylhydroperoxide
TCCA	Trichloroisocycanuric acid
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy
TFBQ	Tetrafluorobenzoquinone
TNT	Trinitrotoluene, 2-Methyl-1,3,5-trinitrobenzene
wt.	Weight
X	Conversion
Y	Yield

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1. Introduction

Waxes and their derivatives play an important role in today's everyday life. They are used in all kinds of applications. Everyday products like candles, shampoos, soaps, lip sticks, hair styling products, polishes for cars and floors may contain waxes. The food industry uses waxes to coat citrus fruits, chewing gums or gummy bears, slowing the product's decay, protecting it from drying and avoiding agglomeration. In the ingredient list waxes may be declared as "wax", "cera" (which is Latin for wax) or with their food additive number (also called "E number").[1,2]

Furthermore, they are used in plastics, paints, polishing applications and also in road building and agricultural plant protection. Most applications rely on several properties of the wax, e.g. sharp melting points, water repealing attitudes yet being able to disperse hydrophilic and hydrophobic substances (when molten). There is no unique definition for waxes. But in general a substance that may be called wax is solid at room temperature, has a rather sharp melting point and shows low viscosity when completely melted.[1,3,4]

Most people will know Bees Wax being used for candles and probably also Carnauba Wax for polishing cars. Rather less known are probably Montan Wax (MW), Sun Flower Wax or Rice Bran Wax (RBW). MW is a rather cheap wax with specific characteristics and wide industrial applications. It is derived by extraction of lignite and may also be referred to as Lignite Wax. In 2008 approximately 25 000 tons of MW were produced, of which a great share was afterwards processed by oxidation with chromosulfuric acid. MW has a high melting point (between 75 to 85°C) and a dark to black colour in its crude form. By deresining, bleaching and oxidation MW gains a white to yellow colour and high acid number (AN) of approximately 80-150 mg(KOH)/g(wax). It can afterwards be processed to other wax types with different attitudes by saponification or esterification.[1,5,6]

Currently the world's demand of MW can be satisfied but it is questionable how long it will be profitable to mine and extract lignite. In 1998 *American Lignite Products Co.* already stopped its exploitation of a lignite mine due to changes in environmental protecting laws. The biggest producer *Romonta* (app. 80 % of the world's crude Montan Wax, ca. 19 000 tons per year) is facing similar problems. According to news *Romonta* is facing challenges due to the German government opposing lignite mining for environmental reasons.[4,7-9]

The prices for MW are rising, partially because of the general aspect of inflation, but probably also due to higher requirements to protect the environment and less accessible deposits and therefore higher costs in production. Besides that, a landslip in 2014 interrupted *Romonta*'s usual process cycle. Several million cubic metres of earth slid into the opencast pit, dragging along heavy machinery. In order to keep up production *Romonta* bought lignite from another mine in Saxony with lower wax content. It took *Romonta* over a year to recover and repair the machinery and to take up the former production routine.[5,8,9]

Regarding its own opencast pit *Romonta* calculated that their lignite resources will be sufficient at least until the year 2030. After that other lignite resources would have to be found or existing lignite with lower wax content would have to be used to produce MW, both resulting in higher prices. Therefore renewable alternatives with consistent production amount would be highly favourable.[3,9]

An already available and in some applications used alternative is Carnauba Wax (CW). This wax is produced by the carnauba palms in tropical regions to protect the plant from dehydration. The leaves of these palms are covered with a thin layer of wax thereby prohibiting high evaporation of water. The leaves are harvested two or three times a year, dried and afterwards the wax is flailed of the leaves. The leaves are locally used to cover up roofs, the fruits and other parts of the palms may be used as animal feed or even for human consumption. The palm is able to grow in various regions, but only produces the wax in significant amounts where the plant is forced to do so in order to survive (i.e. where dry seasons occur).[1]

The annual production of CW is approximately 20 000 to 25 000 tons, comparable with the amount of MW. Currently most carnauba palms are growing wild, without specialized plantation. A cultivation of these palms would stay in direct competition to the growth of food crops, or would result in the destruction of rain forest or other non-cultivated area. Besides that, the palms only produce a minor fraction of their potential wax during their first 8 to 20 years, so that it would not be possible to satisfy the markets in a short amount of time.[1,10-12]

An alternative renewable wax, which does not compete with food crops but can be gained from a by-product of an excessively cultivated food crop is Rice Bran Wax (RBW). It is extracted from the bran of rice, which accrues with the production of white rice. The potential annual production of RBW is beyond the cumulated annual production of MW and CW. An obstacle of using RBW for some applications for which currently MW is used, is the low AN of RBW and some thereby resulting characteristics, e.g. no stable emulsion with water.[13-15]

To gain similar properties as bleached MW, RBW may be processed with chromosulfuric acid. In general, chromosulfuric acid is a mixture of chrome(VI) reagents with sulfuric acid in varying contents. Besides the general environmental concerns of using Cr(VI) components there are two major handicaps using this process (on an industrial scale). On the one hand every industrial process that uses chrome(VI) reagents has to be allowed by REACH and may only be allowed if there are no other environmentally more favourable alternatives. To the best of my knowledge, there are only two companies that process MW with chromosulfuric acid in Germany. These are *Völpker Spezialprodukte GmbH* and *Clariant*. Both companies have already been using this process for several years before REACH was enacted. On the other hand, the oxidation of RBW with chromosulfuric acid is not as efficient as for crude MW. This is probably due to the higher ester content with lower amounts of free fatty alcohols and free fatty acids in RBW. Although *Clariant* has worked on improving this method to apply it on RBW, the new methods are still using Cr(VI) reagents and are not very efficient regarding stoichiometry. An alternative process would therefore be highly favourable for economic and ecological reasons.[16-18]

1.1. Scope of work

The aim of this work was the investigation and either invention or adaption of a process that may oxidize RBW in such a manner that the oxidized wax would meet the criteria to (partially) replace oxidized MW.

As the main component of RBW are long-chained esters, and the main component of oxidized MW are long-chained acids, the main focus of this work is the successful hydrolyses of esters and subsequent oxidation of the generated alcohols (compare figure 1).[1,19,20]

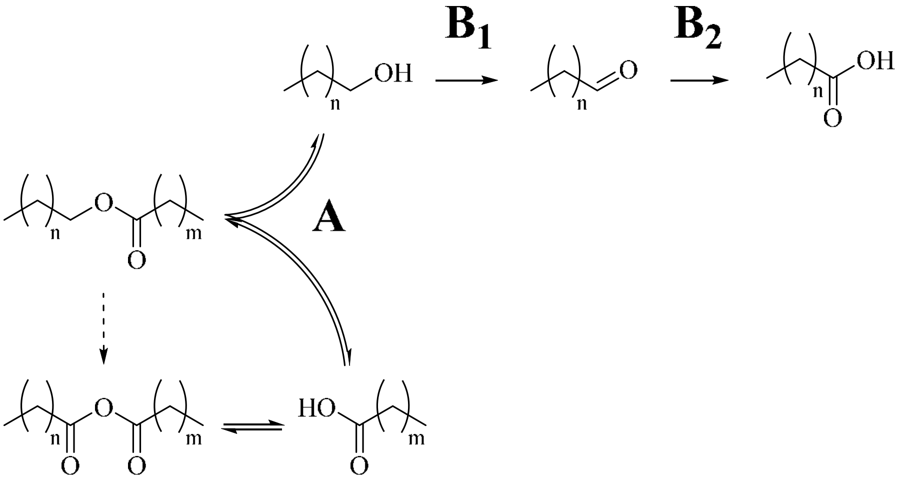


Figure 1: General approach for the oxidation of esters via cleavage (A) and oxidation ($B_{1,2}$).

The final aim of this process might be the conversion of several thousand tons of RBW per year in order to replace MW in as many applications as possible. Thus the reactions to be used need to be not only ecologically more favourable but also economically competitive to the old process. Many reactions to convert chemicals successfully in the lab scale are therefore to be rejected and only such reactions are of interest that may have the potential to be up-scaled easily and competitively.

The potential candidates for such a process shall be sought in literature and tested in the lab-scale (<< 10 g) with a model substrate that represents the most important chemical features of RBW. Reactions which successfully convert the model substrate shall afterwards be tested in the lab-scale with RBW provided by *Kahl GmbH & Co. KG*. Subsequently optimization of the reaction conditions and scale-up in the lab (>>100 g) are intended. In the event of a favourable outcome, judged in cooperation with *Kahl GmbH & Co. KG*, a further scale-up to the industrial scale is intended.

1.2. Montan Wax

The name Montan Wax (MW) is derived from the Latin word montanus meaning mountain. This name is quite fitting, as MW is a wax which is accessible from resources in the earth. More precisely MW is obtained from lignite ores, therefore also called Lignite Wax. The lignite ores which are valuable for wax extraction are special as they have to derive from plants which produced a wax layer upon their leaves, similar to carnauba palms today. Furthermore, the lignite may only have encountered lower pressure and heat than other soft or hard coal ores. The following three sides are the only currently known sides where lignite with comparably high MW contents is accessible:

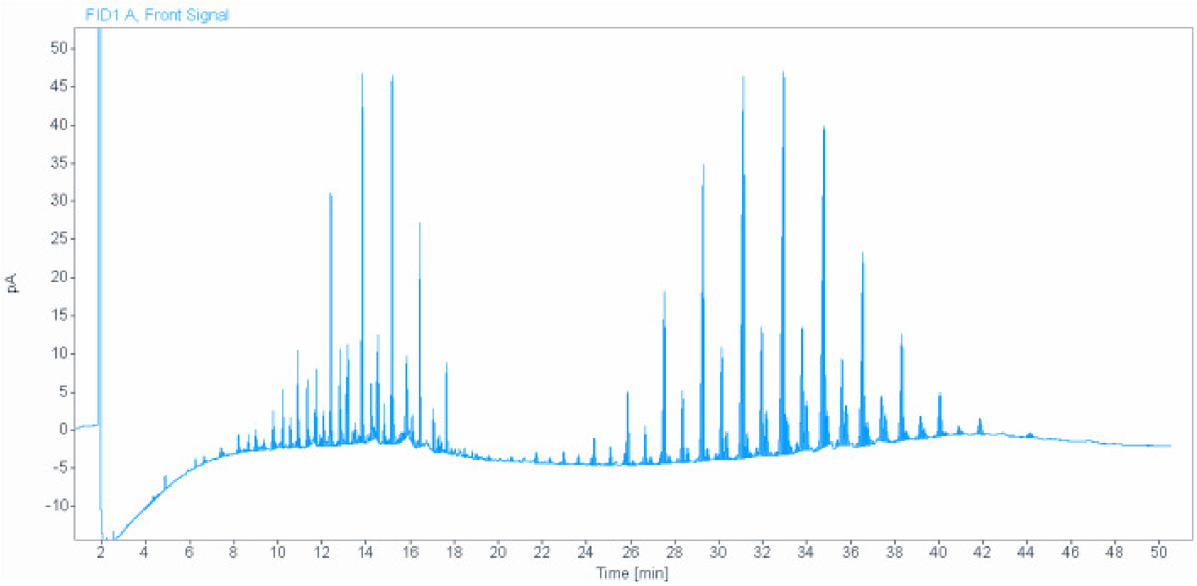
- Amsdorf, Germany, which is exploited by *Romonta*
- Völpke, Germany, exploited by *Völpker Spezialprodukte GmbH*
- Ione, California, USA, until 1998 exploited by *American Lignite Products Co.*[1,4,5]

Other sides where currently no lignite is mined but may be reconsidered if prices rise, include Alexandrija, Ukraine and Baschkiren, Russia. Besides that there are several factories in China that work with wax contents of 2-9%, although the processing of lignite becomes increasingly less profitable with wax contents below 10 %.[5]

The wax is gained by extraction with organic solvents from lignite. Subsequently the wax is dried and depending on its application deresined and bleached. The bleaching has two purposes. One is obviously to lighten up the colour, as crude MW is brown to black and can therefore only be used in applications for which colour is of no major importance. Secondly the "bleaching" also breaks down the esters in MW and oxidises them to two acids. The resulting wax is called "S-Wachs" or "Säure-Wachs" in German, meaning "acid wax".[1,7]

There are several successful ways of bleaching MW. The only knowingly used one today is the bleaching with chromosulfuric acid (the mixture of sulfuric acid with Cr(VI), further explained in 1.5.1). Disadvantages of this process are its low atom efficiency and the use of the highly toxic Cr(VI) reagents, which are restricted by REACH (Regulation concerning the Registration, Evaluation, Authorisation and Restriction of CHemicals). Another successful way of processing is the dehydrogenation of esters with alkaline hydroxides, further explained in 1.5.2. As there are no current publications or patents regarding this method one may assume that this method is not used anymore, due to high costs of operation. As patents suggest, other reactions were tried, but apparently none of them met the quality standards or economical requirements given by industry. [1,16,21-25]

A sample of Montan Wax, provided by Kahlwax, was analysed with gas chromatography (chromatogram 1). The proportion of lower boiling "monomers" to higher boiling dimers and possible oligomers is approximately 2:3 (40 % monomers). Further analyses were not conducted, as it was not regarded constructive. Literature suggested a rather a complex mixture of a variety of substance classes, which makes sense due to its extraction from lignite and the possible varieties in processing. The main contents are reported to be wax esters, wax alcohols and wax acids (making up between 60-90 %), resin acids, sterols, hydrocarbons and other minor components making up the rest in varying amounts.[1,3,26]



Chromatogram 1: Raw montan wax.

1.3. Rice Bran Wax

As the name is telling, Rice Bran Wax (RBW) is produced from Rice Bran which is a side-product of white rice in the food industry. Rice is usually processed in the following manner:

Harvested rice is dehusked yielding brown rice, which is edible and high in nutrients but has a rather low shelf life. Most of the brown rice is subsequently milled to remove bran and germ (hereafter only referred to as bran) yielding white rice. In order to gain Rice Bran Oil (RBO), the bran is afterwards extracted with hexane. Current Research is also investigating the possibility to use less harmful solvents for extraction, i.e. supercritical CO_2, or butane. The crude RBO is then refined by dewaxing which is achieved by cooling and separating the liquid (oil) from the precipitating solid fraction (wax). This process is also referred to as winterization. If it is intended to use or sell the wax, the crude wax will usually be refined further, especially removing residual RBO in order to gain a hard and high melting RBW.[20,27-30]

Today approximately 740 Mt (million metric tons) of paddy rice are produced annually. According to literature approximately 8-10 % of this is bran, which results in 59-74 Mt. The oil content of bran is reported to be 10 to 34% (depending on various parameters[a]). In the lowest case this would lead to app. 6 Mt of theoretically available RBO. The wax content thereof is reported to be 2-5 %, again depending on the prior workup and efficiency of dewaxing. In the lowest case this would lead to potential 120 kt of RBW per year, which is much higher than the current production of crude MW.[13,27,30,31]

Regarding the chemistry of RBW there are many reports which show a certain variation, but all agree on the general composition. The main components are long-chained saturated esters accompanied by a minor fraction of free fatty/wax alcohols and free fatty/wax acids.[1,5,14,27,32] For this work RBW was provided by *Kahl GmbH & Co. KG*. Its examination provided the following results:

GC-FID showed that the wax consists of app. 91 % long-chained esters and 9 % shorter, presumably monomeric substances (compare chromatogram 2). With GC-MS three components of these shorter substances were identified as 0.4 % $C_{16}O_2H$ (hexadecanoic / palmitic acid, $C_{15}H_{31}COOH$), 0.6 % $C_{22}O_2H$ (docosanoic / behenic acid, $C_{21}H_{43}COOH$) and 1.4 % $C_{24}O_2H$ (tetracosanoic / lignoceric acid, $C_{23}H_{47}COOH$). The other minor monomeric species of raw RBW were not further investigated.

After hydrolysis of the wax the major monomeric alcohols and acids which comprise the wax esters were determined (chromatogram 3). The main acids are the same three acids that were already identified in the raw wax ($C_{16/22/24}O_2H$). The main alcohols are all even-numbered aliphatic primary alcohols and generally have higher molecular weights than the acids, ranging

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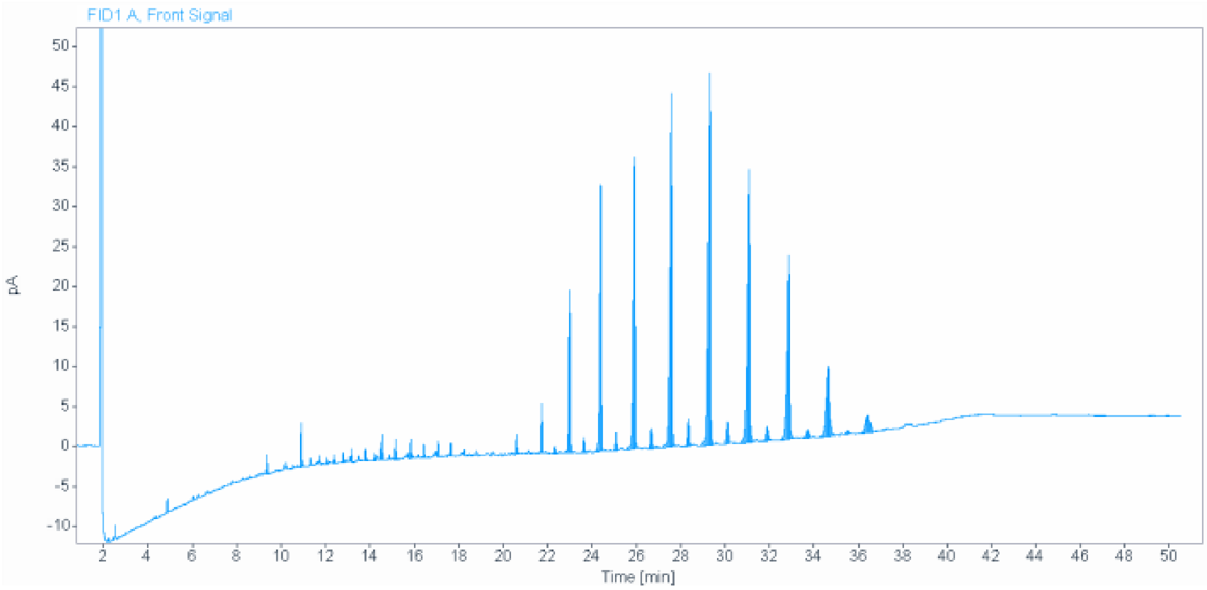
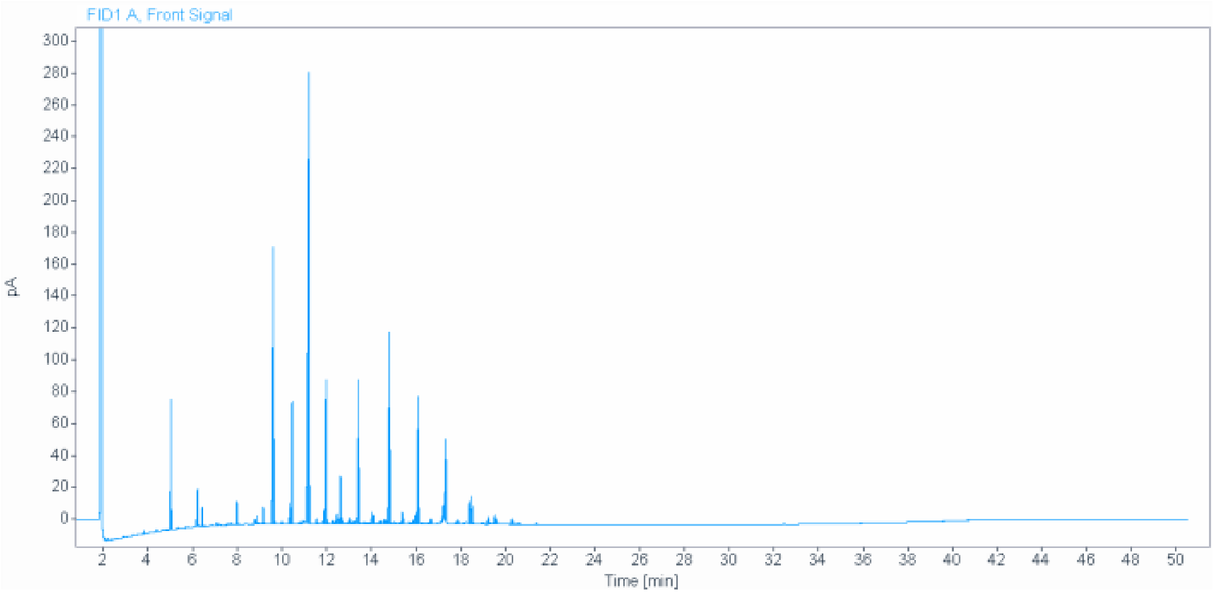
[a] This high variation in oil content may derive from the extraction method, prior workup and the quality of the rice. Prior workup may include parboiling, mainly for preservative reasons, leading to a higher oil content of the bran. Depending on the degree of milling (removing of the bran from the rice) the bran may have some portion of the white rice which lowers its ratio of oil.

from 24 to 36 carbon atoms (table 1). These acids and alcohols combined represent app. 87 % of the area found by GC-FID, leaving out a minority of app. 13 % which were not completely further investigated. Within this minority there are uneven-numbered long-chained alcohols, like $C_{29}OH$ or $C_{31}OH$. There is app. as much C_{29} compounds as refer to 5 % of $C_{30}OH$, and as much C_{31} compounds as refer to 7 % of $C_{30}OH$ ($C_{29}OH$ having app. 0.8 % of the total integral; these numbers of course depend on the batch of RBW).

With these results it was possible to estimate an approximate medium molecular weight for this RBW (or rather for its 87 % identified components). For the hydrolysed RBW the medium molecular weight was M(split RBW) = 773 g/mol, and thus 755 g/mol if all monomers formed dimers (esters).



Chromatogram 2:RBW as provided by Kahl GmbH & Co. KG.



Chromatogram 3: Alkaline split RBW.

Table 1: Composition of the major components of hydrolysed Rice Bran Wax (compare chromatogram 3 regarding the app. retention times). (The total area I_{Total} *refers to the area calculated automatically by the program, therefore including all major and minor substances besides the solvent. The area ratios are not revised regarding the trimethylsilylation.)*

Component	**Retention time [min]**	**Area ratio [I/I$_{Total}$]**	**Molar contribution (of listed substances)**
		Acid	
$C_{16}O_2H$	5.0	4.3 %	7.5 %
$C_{22}O_2H$	9.6	10.3 %	13.8 %
$C_{24}O_2H$	11.2	22.0 %	27.3 %
$C_{26}O_2H$	12.6	1.7 %	1.9 %
		Alcohol	
$C_{24}OH$	10.5	3.7 %	4.5 %
$C_{26}OH$	12.0	4.8 %	5.6 %
$C_{28}OH$	13.4	7.0 %	7.6 %
$C_{30}OH$	14.8	13.1 %	13.3 %
$C_{32}OH$	16.1	9.6 %	9.2 %
$C_{34}OH$	17.3	7.0 %	6.3 %
$C_{36}OH$	18.4	2.6 %	2.2 %
$C_{38}OH$	19.5	0.9 %	0.8 %
Sum		86.8 %	100.0 %

1.4. Principles of Ester Cleavage

The first step of any intended reaction to this process is the cleavage of the ester components to an acyl/acid and an alcohol/alkyl compound. In the easiest case acid and alcohol are both free and not ligated to any other substance. In chemical laboratories the most common ways to split esters are acid and alkaline induced splitting in aqueous media. The mechanism and the driving force of these splitting reactions differ immensely.[33,34]

In the case of alkaline splitting the ester is attacked by a hydroxyl-anion and the resulting products are a free alcohol and an organic salt (see figure 2 and 3). The formation of the organic salt is energetically favourable and often takes place quantitatively. Therefore, no free acid is available to react with any alcohol to an ester, and as long as the concentration of hydroxyl-anions is high enough the splitting of remaining esters proceeds.[33,34]

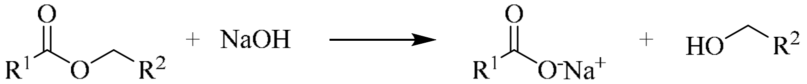


Figure 2: Chemical equation of alkaline splitting with sodium hydroxide.

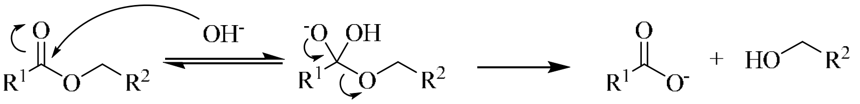


Figure 3: Mechanism of the alkaline splitting.[33,34]

In case of acidic splitting the ester is attacked by a proton and subsequently by a water molecule. The resulting products are a free alcohol and a free acid (compare figure 4 and 5). There is only a minimal amount of acid needed to catalyse this process, but it is under the control of chemical equilibrium and therefore the back reaction will also take place. If either the acid or the alcohol can be removed from the equilibrium further ester will be split shifting the reaction to equilibrium (in agreement with *Le Chatelier*'s principle). Depending on the substrate this may be done by distillation (for volatile alkyl or acyl parts). In the present case, the ideal way would be to remove free alcohol by oxidizing it to a free acid, and executing the splitting and oxidation until the desired amount of oxidation is reached.[33-35]

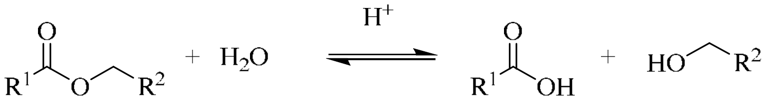


Figure 4: Chemical equation of the acid catalysed splitting.

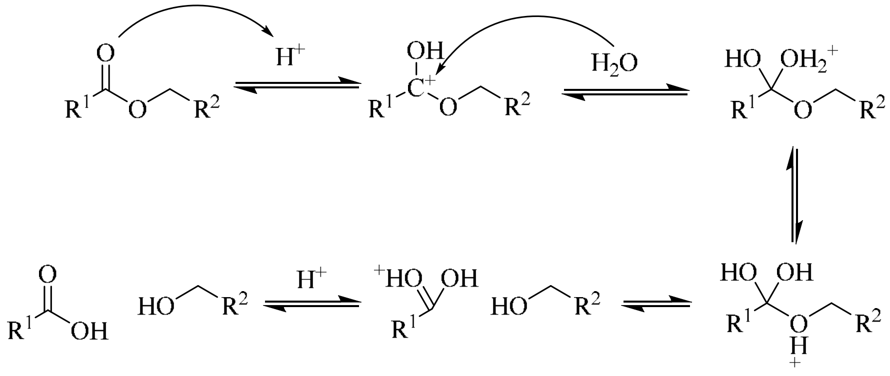


Figure 5: Mechanism of the acid catalysed splitting.[33,34]

1.5. Established Wax/Ester Oxidizing Systems

1.5.1. Cr(VI)/H_2SO_4

The apparently only currently used method for oxidation of MW seems to be the processing with chromosulfuric acid (sulfuric acid combined with Cr(VI)). The highly acidic conditions are responsible for the splitting of the wax esters, succeeded by a very fast oxidation of the freed alcohols by chrome(VI). Due to its fast and rather clean (at least at low temperatures) alcohol oxidation, the last step is also often used in other alcohol oxidation reactions (when the substrate has no other sensitive groups). It is quite difficult to tell the exact process conditions as there are many patents with various conditions and no company will give away their manufacturing secrets.[1,15,21-23,36-38]

Comparing several patents regarding this process an exemplary (lab-scale) process would consist of the following steps:
100 g of the corresponding wax are emulsified with 500 g of 50 wt.% H_2SO_4 at 120 °C. Subsequently 330 g of 60 wt.% $Na_2Cr_2O_7$ solution are slowly added over a time period of two hours and the mixture is stirred for another 3-5 hours. Usually this procedure is done two or three times, resulting in a wax with an AN of more than 100[b]. The second and third stage are often executed with twice the amount of wax but the same amount of the other reagents (the first stage mainly seems to be responsible for oxidizing colouring impurities, whereas the second and third stage are supposed to split and oxidize the esters to acids). Overall this sums up to approximately 375-500 g H_2SO_4 (100 wt.%), 300-400 g $Na_2Cr_2O_7$ and 570-760 g H_2O per 100 g of wax, processing time taking up 10-21 hours,[c] not including the time for filling the tanks, heating, washing the wax, etc.[15,36,39,40]

A rather recently published patent is using this method to oxidize RBW as well. In this patent RBW is oxidized with the help of various “oxidation promoters”, especially named are nonafluoro-butanesulfonic acid, heptadecafluoro-butanesulfonic acid, $AlCl_3$ and $HCl_{(aq.)}$ (35 wt.%). 500 g molten RBW are added to 4.96 L of chromosulfuric acid (100 g CrO_3/L, no further specification) at 70 °C, heated to 110 °C and stirred for 12 hours. Compared to the oxidation of 60 g RBW without oxidation promoters (AN of 72), higher ANs were gained. For the experiments several quality types of RBW were used, which makes the comparison difficult. Additionally, only a few SVs and chromatograms of the products are given. In general, the ANs were between 93 and 121, with one exceptional reaction gaining an AN of 172. However, the substrate for this experiment was crude RBW with an SV of 110, whereas the other substrates had SVs of 81 to 88. This high SV cannot be explained by the given chain length distribution for the crude RBW, which suggests a similar composition as the RBW utilized for this work (for comparison: the later described model substrate C_{16}-O_2C_{18} would have an SV of 110). The

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[b] To ease the reading fluency the unit “mg(KOH)/g(wax)” is omitted.

[c] Considering 2 or 3 stages in previously described manner.

high SV and also the high AN could however be explained by the high oil content of 31 % and other impurities in this wax.[17]

To get an impression of the molecular efficiency of these methods, it may be valid to calculate a theoretical (electron) efficiency for these reactions. To ease calculations it may be assumed that the raw wax consisted of 100 % esters and the final product would consist of 100 % acids, with no other reactions being performed besides cleaving and oxidizing.[d] Further assuming the oxidation resulted in an AN of 150, this would mean that 2.7 mmol of acid were in 1 g of oxidized wax. The medium molecular weight of the carboxylic acids was about 374 g/mol, the corresponding esters having a medium molecular weight of app. 716 g/mol, resulting in 0.14 mol esters in 100 g of raw wax.[e]

The lowest amounts of oxidant are used in the second and third oxidation step to oxidize MW (app. 198 g $Na_2Cr_2O_7$ per 200 g wax, equal to 1.5 mol of Cr(VI)). Taking into account, that the oxidation of an ester into two acids is a 4 electron reaction and the reduction of Cr(VI) to Cr(III) is a 3 electron reaction one may calculate a theoretical efficiency for this reaction (see equation 1).

$$Y = \frac{n_{e^-}(Ox)}{n_{e^-}(Red)} = \frac{0.28\,mol * 4\,e^-}{1.5\,mol * 3\,e^-} = \frac{1.1\,mol(e^-)}{4.5\,mol(e^-)} = 24.6\,\%$$

Equation 1: Theoretical electron efficiency for the ester oxidation with chromosulfuric acid.

So 25% would be the electron efficiency if the process would be concluded at the given assumptions; one oxidation step, from an AN of 0 to 150 with no side-reactions. Of course one may not forget, that the chromosulfuric acid bleaches the crude MW from a dark brown appearance to a yellow or white appearance and not only oxidizes the esters. For the oxidation of RBW the bleaching is not that necessary, as the wax is only slightly coloured and the main purpose of the process is the generation of acids from esters. So for this purpose this process (even with oxidation promotors added) does not seem to be anywhere near satisfying to the present challenge.

1.5.2. Dehydrogenation with Alkaline Hydroxides

As stated before the oxidation with chromosulfuric acid is not the only possible (once industrially established) way to oxidize MW. In the late 80’s the German company *BASF* developed another method and patented it. The process consisted of mixing molten wax with app. two molar equivalents of molten alkaline hydroxides, preferable an eutectic of potassium and sodium hydroxides. This mixture was then either stirred or passed through a screw mixer

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[d] This is not the case as the process also bleaches the wax of coloured lignite artefacts and side reactions happen, including the shortening of alkyl-chains.

[e] 374 g/mol for the acid + 360 g/mol for the alcohol – 18 g/mol for water of condensation.

at temperatures of 250-350 °C, thereby splitting the esters and dehydrogenizing the alcohols to fatty acid salts. Mixing with water and acidifying with inorganic acids would yield the oxidized wax. For purification the wax was distilled at 220-280 °C under high vacuum of app. 0.1 mbar.[1,24]

Disadvantages of this process are the high temperatures and high vacuum. Not only do both conditions require high amounts of energy but also expensive equipment to handle such conditions. Probably this led to a low profitability, as the chromosulfuric acid process is still used and has not been replaced.[1]

1.5.3. Alkaline Splitting followed by Cr(VI)/H_2SO_4

A rather recently published patent is combining the prior described methods to oxidize RBW. In the patent the successful splitting of 500 g RBW with 35 g NaOH in 300 mL H_2O in an autoclave at 220 °C and pressure of app. 12 bar over 6 hours is described. Thereafter, the reaction mixture is cooled to 80 °C and acidified with 49.7 g $H_2SO_{4(conc.)}$. The split wax is worked-up by several steps, including cooling, melting and washing with water. The oxidation following is very similar to the second oxidation stage of MW. The molten split wax is added to 4.96 L of chromosulfuric acid (100 g CrO_3/L, no further specification) at 90 °C and stirred at 110 °C for 12 hours. The gained AN are reported to range from 136 to 168, the highest value being gained with crude RBW with 31 % oil content (compare 1.5.1). Although RBW was split prior to the oxidation not all alcohols seem to be oxidized, but rather have reformed esters (for the first example an AN of 144 is reported with an SV of 193, for other examples chain length distributions are given, showing remaining or newly formed esters). Quite interesting are the fact that Cr(VI) is still used in high excess (similar to the 2nd or 3rd stage of the MW oxidation) and the statement that “a pressureless saponification is possible only with a considerable excess of KOH or NaOH and […] additional solvent use (xylene)” (compare chapters 2.4 and 2.5).[18]

1.5.4. Carbon Monoxide Insertion

The *Tennessee-Eastman-Process* was not developed to oxidize waxes but for the production of acetic anhydride, a basic chemical used in various reactions, that is produced on a low mega-ton scale. This process uses methyl acetate, one of the smallest possible esters, and carbon monoxide as feedstock. The catalytic components are rhodium or iridium salts and iodide compounds. The process conditions include > 150 °C and carbon monoxide pressures of 30-60 bar. Variations of this process or maybe rather the processes of which the *Tennessee-Eastman-Process* was derived from, include the *Monsanto process* and the *Cativa process*, which both transform methanol into acetic acid.[41,42]

Via formation of methyl iodide, the alkyl chain may react with a $[RhI_2(CO)_2]^-$ complex, inserting a carbon monoxide moiety into the metal-organic bond (compare figure 6). High carbon monoxide pressures shift the equilibrium to release acetyl iodide, which may react with another molecule of methyl acetate, forming new methyl iodide and acetic anhydride.[41,42]

In theory this chain-elongation with introduction of a carboxylic acid group would be perfect for the oxidation of ester waxes (direct conversion of the esters, no chain shortening). However, due to the high temperatures and high carbon monoxide pressures this reaction is rather demanding to material and safety aspects. Thus this process seems rather unfavourable, unless new catalysts were unveiled that are able to handle this reaction at less demanding conditions.

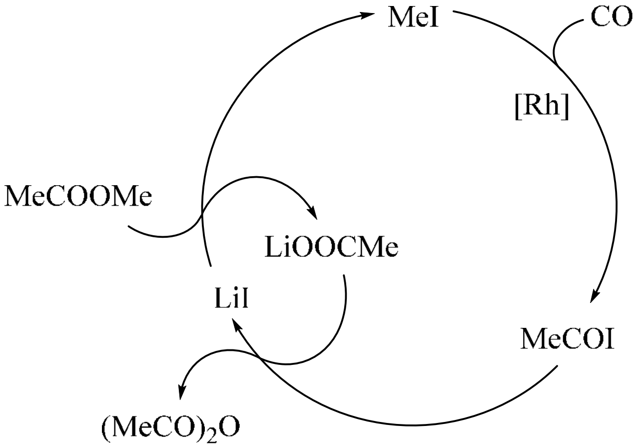

Figure 6: Schematic reaction of methyl acetate to acetic anhydride.[42]

1.6. Alcohol Oxidizing Systems

As the aim of this thesis is to find an easy, robust, sustainable and economically favourable ester/alcohol oxidation system, the first evaluation was done by comparing and evaluating different oxidants, as these have a significant influence on the reaction conditions and overall costs of the process. Reactions and reagents that are only reasonable in laboratory scale or for the production of expensive fine chemicals are not mentioned in the following (e.g. *Swern* oxidation).[43]

In table 2 the most reasonable oxidants for the large-scale oxidation of RBW are listed, i.e. oxidants that were repeatedly used for the oxidation of alcohols. They are assorted by their approximate costs per mol of active oxygen, on the assumption of large scale uses or direct on-side-production. Approximate pricing was taken from large scale import/export data to/from India. These prices do not depict the prices that one will actually pay, but for comparison these are better than prices from distributors that sell smaller samples for which packaging, transport and administration are accountable for a great share of the price.[f] Interestingly, for oxidants this "economic number" is in strong correlation to the oxygen content. The only "mix-up" being the chromates compared to permanganate, probably due to their comparably easy production.[44,45]

Table 2: Economic comparison of several large scale available oxidation reagents. H_2O, OH^- and H^+ as side products were neglected for all reactions . Costs for 1 kg of reagent with given concentration (compare table 57).*

Oxidants	Oxygen equivalent [wt.%(O)]	Reduction products	App. Costs [€/kg]*	App. Costs [€/kmol(O)]
O_2 / air	100 / 21	-	-	-
H_2O_2 (50 wt.%)	47.1	-	0.35	23.6
$NaClO_2$ (80 %)	35.4	NaCl	1.27	72.0
$Na_2Cr_2O_7$	18.3	Na^+, Cr^{3+}	0.95	87.5
CrO_3	24.0	Cr^{3+}	1.74	122.2
$KMnO_4$	25.3	K^+, Mn^{2+}	2.04	135.7
TBHP (70 wt.%)	17.8	^{t}BuOH	1.54	197.9

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[f] In order to ensure reliability and accuracy of each chemical's price, data were compared with suppliers and other sources. For comparability between chemicals the prices of one source are always depicted.

1.6.1. O_2 as oxidant

As oxygen is obtainable everywhere, there has been significant research on oxidation reactions to utilize this reagent. Besides many rather academically interesting catalysts and reactions there are several applications which make use of oxygen in industry. Apart from simple oxidation of fuel in motors or power stations, major processes include the production of the following base chemicals:

- Sulfuric acid from sulfur (Contact Process, vanadium catalysts)[46]
- Nitric acid from ammonia (Ostwald Process, platinum and rhodium catalysts)[35,46,47]
- Formaldehyde from methanol (silver or metal oxide catalysts)[12]
- Benzoic acid from toluene (cobalt or manganese catalysts)[48]
- Adipic acid from cyclohexanol (with nitric acid)[49]

In addition to the production of adipic acid, nitric acid is also sometimes used to synthesize organic acids from their corresponding alcohols. This aspect made the use of HNO_3 quite interesting as it is a strong acid that can split esters and with its oxidizing properties, it could as well be the key reagent for the intended task. HNO_3 is one of the most abundant and versatile used chemicals, some of its main uses being the production of fertilizers and explosives. For oxidizing reactions, it often depends on the point of view, whether HNO_3 is described as oxidant or catalyst. HNO_3 is usually not applied in catalytic amounts to reactions but rather in excess, therefore the word "catalyst" seems misleading. Then again, HNO_3 is reduced during the performed oxidation to various nitrous oxides, most of which can be recycled easily to HNO_3, creating a catalytic cycle.[12,35,46,50-52]

The mechanisms of HNO_3-based oxidations are not perfectly understood, as nitrogen can form various species with oxygen and organic molecules, most of which are not stable enough for thorough analyses. In case of alcohol oxidations, the usually first expected mechanism that comes to mind is the formation of nitric esters, which should lead to aldehydes and subsequently oxidize the aldehydes through their hemi-acetal form to the corresponding acids (figure 7). Literature objects this mechanism and it states that some ester of nitrous acid must be a key intermediate (compare figure 8). For the follow-up reaction(s) there are several possibilities stated yet none seems to be certified and it is possible that several reaction mechanisms may work, depending on the reaction conditions. *Ross et al.* found evidence for the attack of an N(III) species, but they could not rule out the attack of a proton. Irrespective of the exact mechanism the greatest part of the reduced "nitrogen containing" compounds are easily reoxidized to the priorly used oxidant by molecular oxygen (compare figure 9). Due to the unsolved mechanism(s) and influencing parameters (T, pH, catalysts, substrate) reactions with nitric acid or derivatives thereof are often not highly selective and therefore not often used in academia where the costs of chemicals are not of highest importance. For large scale applications in industry this differs immensely and for any new process the costs of operation are usually among the most important criteria (others being restricting laws and safety arguments).[51,53]

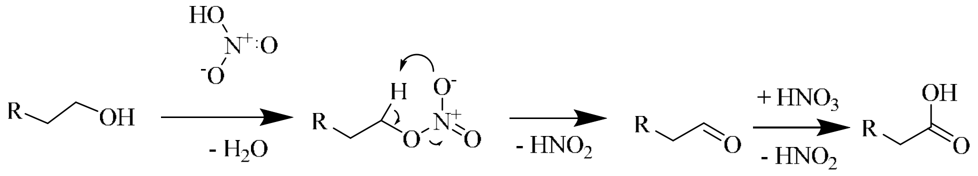


Figure 7: Theoretically possible, yet by literature objected reaction mechanism for the oxidation of alcohols with nitric acid.

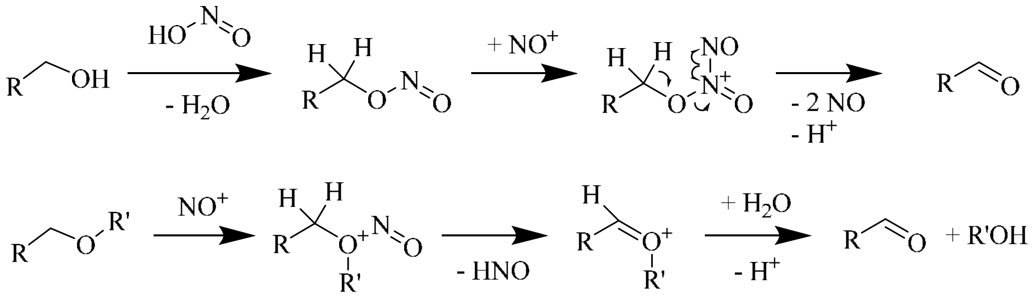


Figure 8: By Ross et al. proposed reaction mechanism for the oxidation of alcohols and for the oxidative splitting of ethers with nitrous oxides.[51]

$$3\,NO \xrightarrow{+\,1.5\,O_2} 3\,NO_2 \xrightarrow{+\,H_2O} 2\,HNO_3 + NO$$

Figure 9: Simplified reaction of NO to NO_2 to nitric acid.[46]

One large scale application utilizing the advantages of nitric acid is the production of adipic acid (hexanedioic acid, annual production app. 2.5 Mt). The raw materials for this process are usually cyclohexanol, cyclohexanone or a mixture of these, which may be referred to as KA oil (keto-alcohol oil). The oxidation thereof with nitric acid is usually run in a two temperature profile, first at 50-60 °C and then at increased temperature. In the first stage the actual conversion of KA oil to adipic acid takes place. The second stage then mainly reduces the amount of side products through oxidation, whereas any aliphatic acid usually is not decomposed at these conditions. Due to its importance this process has been focused by academia and industry. As can be seen in figure 10, there is more than one possible reaction route leading from KA oil to the desired product and to undesired side-products. In order to support the intended reactions, vanadium and copper salts are utilized as catalysts.[49,54]

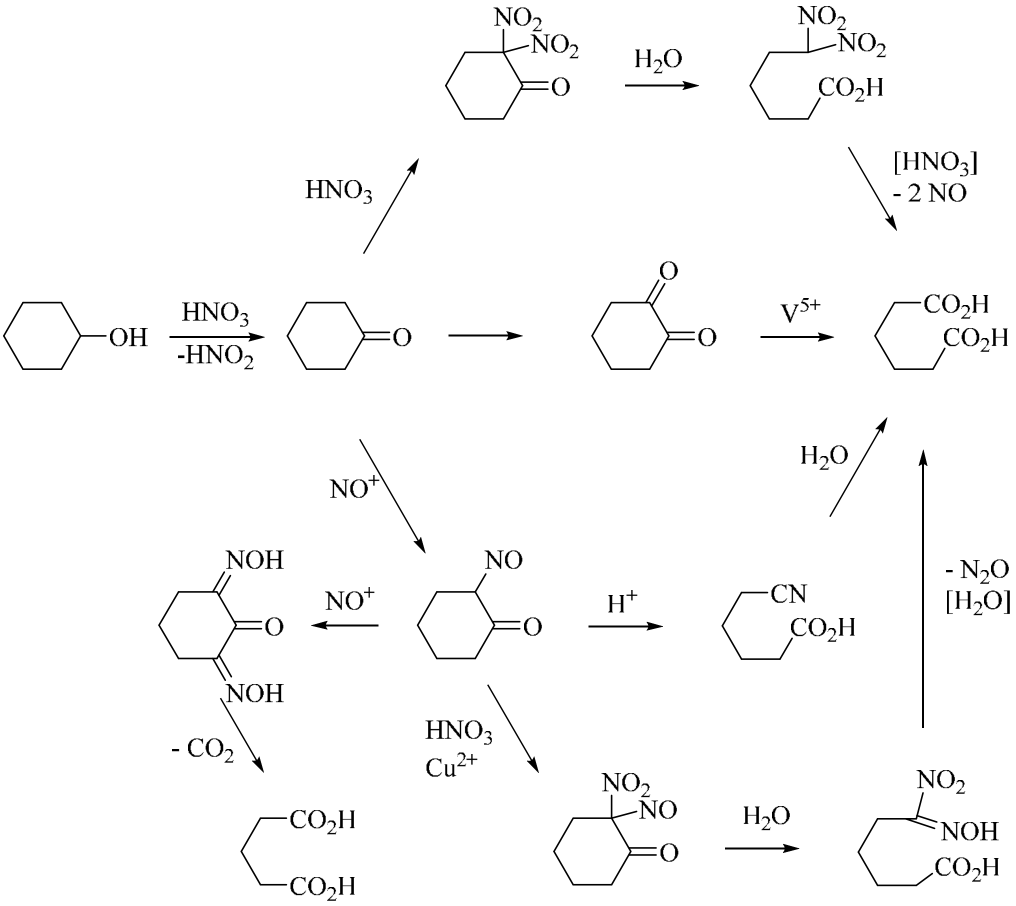


Figure 10: Possible reaction paths from cyclo-hexanol to adipic acid.[49]

Besides the use of HNO_3 in the production of adipic acid it may be mentioned that also the salts of nitric and nitrous acid are investigated for oxidation applications. Depending on the set-up and conditions the salts are either used as quantitative oxidants or as catalysts to activate oxygen as the final oxidant. Iron, manganese, copper, cobalt and other transition metal nitrates seem to be very interesting for such investigations. Regarding these investigations no general guide line can be drawn and it would not serve the scope of this work to go into more detail on these reactions.[55-59]

1.6.2. H_2O_2 as oxidant

Hydrogen peroxide is nearly as good as oxygen regarding availability and environmental friendliness. Its only waste product is water, and there are several possibilities to easily dispose of excessive oxidant by catalytic means, resulting in oxygen and water as the only degradation products. H_2O_2 is used in various applications ranging from cosmetics, disinfection, propellants and various synthetic applications. The latter include syntheses of epoxides, peroxides, aldehydes and carboxylic acids.[35,46]

While reviewing literature, the impression arose that a great part of H_2O_2 research was focussed on epoxidation and that rather few (successful) investigations regarding the oxidation of primary alcohols were conducted. Reasons therefore are not obvious, but one may argue that other cheap reagents are available that perform such oxidations without catalysts and that H_2O_2 exhibits properties which are rather unfavourable for some applications. Like other peroxides, it is easily activated and can react violently if catalytic contaminations are present. Even if it does not react violently, H_2O_2 may decompose with contaminations and thus lose oxidation capability. Other oxidation agents like (di-)chromates, chlorites or permanganates can be considered more stable and are more easily storable. The potential risk of violent reactions also influences the actual oxygen per weight factor; 100 % H_2O_2 provides app. 47 wt.% oxygen usable for oxidations, but it is extremely dangerous to handle, as smallest contaminations may cause explosions. Thus hydrogen peroxide is usually traded as 35-50 wt.% solutions in water, resulting in usable oxygen contents of 16.5-23.5 wt.%. Thereby, H_2O_2 loses the advantage of having a very high oxygen content for oxidations (compare table 2). Still, "diluted" H_2O_2 is highly reactive and causes severe burns upon contact with skin. (Furthermore, the oxidants containing transition metals (Cr, Mn) have the advantage of exhibiting distinctive colours, so that any spilt chemical is easily detected, whereas spilt hydrogen peroxide cannot be differentiated from water by its visual appearance.) Whether any of these reasons are responsible for the allegedly less frequent use of H_2O_2 to oxidize (primary) alcohols is not certain, but would seem logical.[60-63]

Due to the objective of oxidizing RBW this chapter will only deal with those applications and investigations that are known for their ability to oxidize alcohols to their corresponding carboxylic acids. The probably most known and applied systems for this purpose are on the basis of methyltrioxorhenium (MTO), molybdates (MoO_x) and tungstates (WO_x). Earlier investigations with shorter primary alcohols already showed some superiority of tungstate derivatives compared to MTO. Besides that, prices for raw materials of the catalysts make tungsten or molybdenum based catalysts more attractive. Whereas molybdenum and tungsten cost app. 16 €/kg, respectively 27 €/kg, rhenium metal currently costs more than 2000 €/kg (compare table 58).[64-70]

Tungstates and derivatives thereof have been investigated intensely by many research groups and one may divide the research with "rather simple" salts into two fields. These are oxidation reactions utilizing sodium tungstate as precatalyst, which forms peroxotungstates with hydrogen peroxide, and there are methods utilizing hetero poly acids (e.g. $H_3PW_{12}O_{40}$) which are usually reacted with some nitrogen containing cation (ammonium, pyrolidine, etc.) in hydrogen peroxide to rather complex structures (e.g. $[Bu_4N]_3[PO_4(WO(O_2)_2)_4]$, Bu_4-TATTP). Newer research is also investigating the formation of water-soluble tungstates without nitrogen containing cations for such reactions.[68,71-84]

The reactions performed by these catalysts are quite diverging, having the similarity to introduce at least one oxygen atom to a functional group. Amines can be oxidized to N-oxides (one way of synthesizing TEMPO, compare chapter 1.6.3), alkenes may be epoxidized, oxidized to vicinal diols or ketones or split to gain two carboxylic acids (very interesting for adipic acid), and alcohols can be oxidized to aldehydes/ketones or carboxylic acids. A great advantage of many of these reactions is the absence of additional organic solvents. Many of these reactions simply use diluted hydrogen peroxide and the liquid substrate as a biphasic system, only utilizing additional organic solvents, when the substrate is a solid.[68,71-73,76-81]

In general, these reactions are executed under acidic conditions, which serves the purpose of stabilizing the peroxide and also improves the performance of the catalyst. *Noyori et al.* proposed a mechanism which explains the pH dependency of "simple" tungstate based catalysts. As depicted in figure 11 there are several tungsten species possible, whose ratio and resulting properties depend on the pH. Whereas the di-ionic species is highly unlikely to enter the organic phase, the mono-ionic species may enter the organic phase with the help of lipophilic cations like quaternary ammonium ions (compare figure 12). The neutral species should also be able to enter the organic phase but due its pK_a value of 0.1 this species is rather unlikely to exist under "usual" reaction conditions for alcohol oxidations, as low pH values may lead to undesired esterification of the substrates. Regarding the oxidation of alcohols to aldehydes, there is evidence that the tungstate is oxidizing the alcohol to its corresponding aldehyde, whereas the aldehyde may be oxidized by H_2O_2 without involvement of the metal centre.[76]

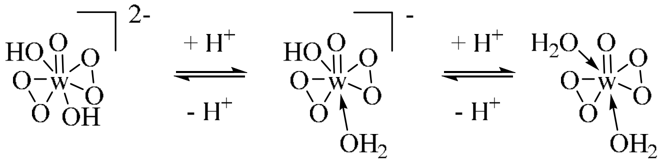


Figure 11: Possible species of the W(VI)-diperoxo compound.[76]

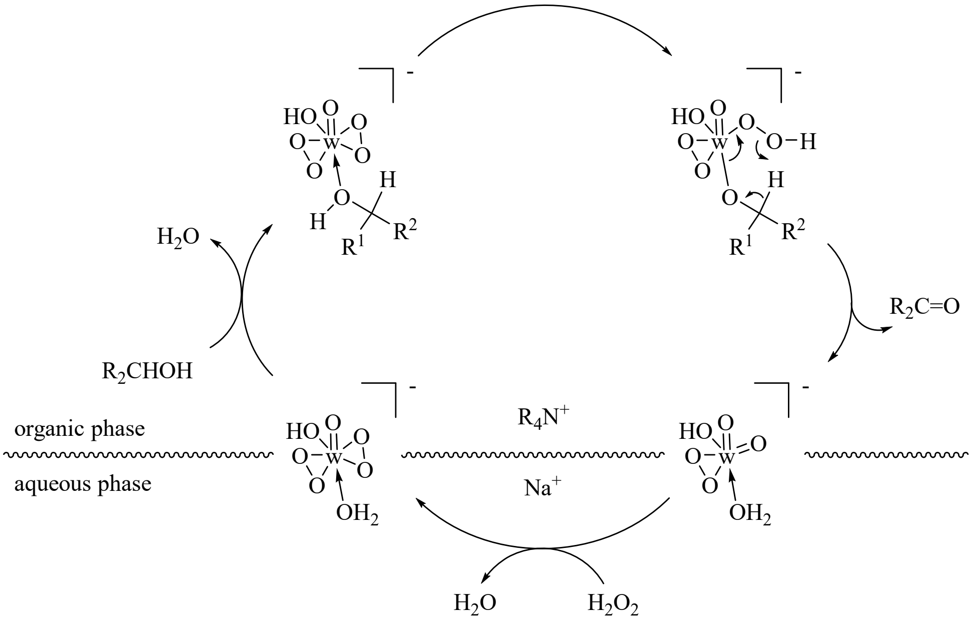


Figure 12: Proposed mechanism for the oxidation of alcohols with tungstates in a biphasic system.[76]

1.6.3. $NaClO_2$ as oxidant

After O_2 and H_2O_2 the next cheapest oxidant for which alcohol oxidizing methods are known is $NaClO_2$. Being a solid it is easily transportable, yet due to its high solubility in water also applicable as concentrated solutions. It is easily storable and will not decompose as easily as hydrogen peroxide (storage was monitored over several years without significant loss of active oxygen). Its applications include disinfection and bleaching, e.g. in swimming pools and textile bleaching. In academic research it is known for its ability to oxidize aldehydes to carboxylic acids very fast and efficiently, known as *Pinnick* or *Lindgren* oxidation. In these reactions the side product sodium hypochlorite is scavenged to avoid side reactions. For scavenging sulphamic acid or resorcinol were originally used by *Lindgren et al.*, whereas *Pinnick et al.* used the 2-methylene-2-butene.[35,85-87]

Besides reactions with double bonds or aromatic systems, *Anelli et al.* experienced that hypochlorite is a valid oxidant to work in combination with oxoammonium salts for the oxidation of alcohols to aldehydes or carboxylic acids. Shortly after that *Torii et al.* developed a method utilizing oxoammonium salts and sodium bromite to oxidize alcohols either to aldehydes or to carboxylic acids, depending on solvents. This idea was picked up by *Zhao et al.* when they investigated the possibility to oxidize alcohols with the cheaper and readily available sodium chlorite instead of bromite. They experienced an induction period and were able to circumvent it by addition of catalytic amounts of sodium hypochlorite. A mechanism was proposed for the oxidation, which involved the addition of the alcohol to the nitrogen atom of the oxoammonium salt and subsequent disintegration to the aldehyde and the N-hydroxyl derivative (figure 13). Further research was done regarding the mechanism of oxidation and so far this mechanism is still considered valid at alkaline conditions. However, under more acidic conditions the mechanism seems to be slightly different and is supposed to involve a hydride transfer (another theory suggests a one electron transfer followed by abstraction of a proton). These mechanisms are supported by the tendency that primary alcohols are faster oxidized than secondary alcohols under basic conditions, and vice versa under acidic conditions. The primary alcohol being sterically less hindered and hence being oxidized when no hydride transfer is involved, for which secondary alcohols are better stabilized. The proposed mechanism under acidic conditions is further supported by the ability of oxoammonium salts to split benzyl alkyl ethers.[88-91]

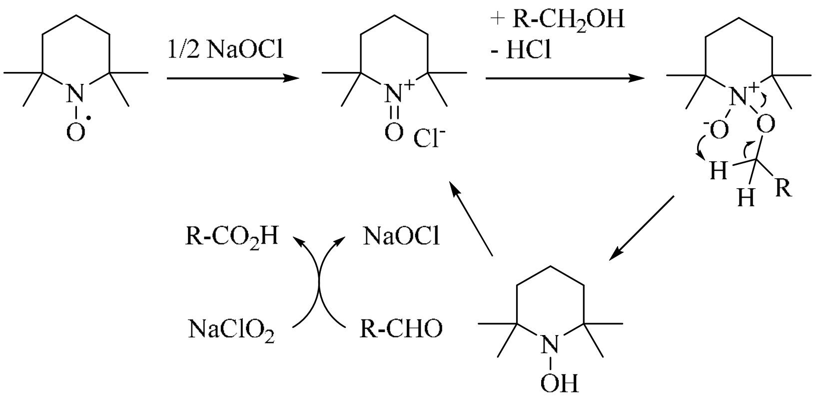


Figure 13: Proposed mechanism for the oxidation of alcohols to acids under neutral or slightly basic conditions.[90]

1.7. Criteria for possible processes

To compare and evaluate reactions/processes with completely different reagents and mechanisms, comparable criteria have to be established. Due to the industrial background of this project economic issues are considered of high importance. This includes the pure costs of reagents, solvents and catalysts, and also the time needed to accomplish the oxidation. After all, several patents and also processes have been invented to circumvent the use of Cr(VI), yet apparently none is efficient enough to have replaced this process thoroughly. Furthermore, environmental aspects of the components have to be taken into account. At the time the chromosulfuric acid process was established, considerations regarding environmental or health issues were much lower than today. Besides these features the nature of the wax should not be forgotten. Rice Bran Wax is melting at approximately 80°C, slightly varying with its exact composition. Its solubility in organic solvents is rather low at room temperature, and only increases at higher temperatures. For environmental reasons and possible economic advantages, it was decided to develop a process which is able to operate with molten wax and without the need of organic solvents. This is supposed to simplify the work-up of the product, as no removal of organic solvents is needed. When water soluble reagents are used simple washing with water should be sufficient to purify the product. Furthermore, the possible yield per volume is expected to be higher, as no volume is incorporated by solvent.[1,92-101]

The best possible system would split the ester of RBW in an acidic medium with simultaneous catalytic oxidation of the freed alcohols utilizing oxygen as oxidant. Such a system would have the advantage of theoretically no running costs for chemicals, as the acid for splitting and the catalyst for oxidation would not be consumed by the desired reactions. Both could be reused if recycling was possible and economically favourable. Yet also other systems that employ other oxidants or even employ a non-catalytic splitting of the esters may be a great step ahead, yet not the very best.

The development of completely new oxidation catalysts for the oxidation of esters or waxes was considered. However, due to the limited time and the aim to develop an industrially accepted and sustainable method, it was considered wiser to employ known and accepted reactions and adapt one of these to the given challenge. Robust systems using industrially available and affordable reagents are to be favoured.

A short summary of the criteria set for the oxidation of RBW can be seen in table 3. Additionally, there is a short assignment whether the reason for this criterion is rather of economic or ecologic origin. Often these go hand in hand, as lower energy consumptions not only lead to lower prices, but also cause less emissions and are therefore environmentally favourable.

Table 3: Set criteria for the oxidation of RBW.

	Main reason		
	Economy	**Environment**	**Remarks**
Operation temperature > 80 °C	X		T_M(RBW)
Operation temperature < 160 °C	X	X	
No organic solvents, only H_2O	(X)	X	
H_2O soluble reagents	X		Easy work-up
Atmospheric / low pressure	(X)		Safety, handling
Low toxicity / risk potential of reagents		X	Safety
High selectivity to desired products	X	(X)	
High efficiency of overall process	X	(X)	
Use of established & affordable reagents	X		
Short process duration	X		

1.8. Analyses

Suitable Model Substrates

As already depicted in chapter 1.3 RBW is not a uniform chemical compound but a mixture of diverse linear long-chained saturated esters and a minor fraction of free fatty acids and alcohols. The composition may change depending on climate, geological factors, the region the rice was grown and other influences. Due to the expectation of a high number of trials prior to satisfying results, no assurance which side products might occur and the complexity of RBW, it was decided to first develop a suitable analysis method with a model substrate, which would diminish misinterpretation and help identifying side-products. As RBW's main components are aliphatic esters without double bonds or any other reported functional groups, it was decided to use a derivative thereof. By that only one alkyl and one acyl part would interact in the reactions and it should be possible to understand the occurrence of not intended side-reactions.[1,13,14,19,20,27-29,102]

From previous research it is known that the use of two equally long carbon chains for alkyl and acyl part should be omitted. Side reactions with the alkyl chain might otherwise be misinterpreted as successful oxidation (if the side-products were not found). Using an alcohol with a shorter carbon chain and thus differing residence time in chromatographic analyses has therefore the advantage of easy detection of side reactions not only by detecting the corresponding by-products, but also by using the acyl part as an internal standard for quantification of the alkyl-part and its products. As the alkyl and acyl parts of RBW are mainly even-numbered chains, and uneven-numbered long-chained alcohols and acids are much more expensive than their even-numbered analogues, it was decided to use an alcohol that is two methylene ($-CH_2-$) units shorter than the carboxylic acid. Thereby, shorter intermediates or side products of the alcohol are unlikely to be overlapping with the carboxylic acid (as the acid is considered to be chemically more stable at oxidizing conditions, whereas for the alcohol chain shortening may be expected depending on the reaction conditions). Any products that are detected with the length of the acyl part or one methylene group less could clearly be identified to be deriving from the acyl part.[64]

Commercially no model substrates were found with reasonable pricing for screening reactions. The ester was therefore synthesized from a commercially available alcohol and acid. Comparing prices showed, that C_{16} and C_{18} alcohols and acids were reasonable in price, whereas for longer chains the prices increased immensely (compare table 4). Therefore, it was decided to synthesize hexadecyl octadecanoate (C_{16}-O_2C_{18}, figure 14) as the model substrate for RBW.

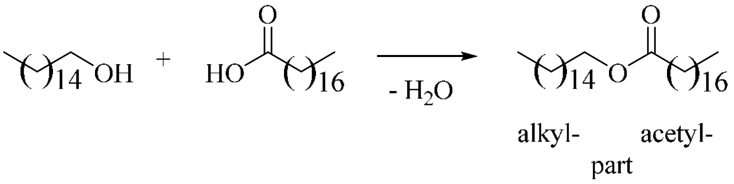


Figure 14: Synthesis scheme for the model substrate hexadecyl octadecanoate.

Table 4: Prices for different alcohols and acids (for comparison, prices were all taken from Sigma-Aldrich).[103]

Component	Purity	Price [€/kg]
	Acid	
$C_{16}O_2H$	98 %	34
$C_{18}O_2H$	97 %	29
$C_{20}O_2H$	99 %	8 000
$C_{22}O_2H$	99 %	18 620
	Alcohol	
$C_{16}OH$	99 %	64
$C_{18}OH$	95 %	50
$C_{20}OH$	90 %	679
$C_{22}OH$	97 %	375

Analysis of the Model Substrate, RBW and Products

Standard analysis for waxes comprise the measurement of the acid number (AN) and a gas chromatogram. For quick, reliable and meaningful analyses evaluations of AN are not suitable. The measured sample may not contain any (inorganic) acid or base from the reaction as these would directly inflict the titration (either increasing or decreasing the AN). Nor may it contain any solvent as it is necessary to know the exact amount of each sample, remaining solvent would therefore artificially decrease the AN.[1]

After comparison and first trials with HPLC-MS, GC-FID and GC-MS, it was decided, that GC analyses were the methods of choice (the applied methods are depicted in chapter 0). With HPLC-MS it was not possible to reliably detect the long-chained alcohols, whereas all substrates and expected products (of the model substrate and also of RBW) were detectable with GC-FID and all monomeric substances were verifiable with GC-MS. The exact composition of the esters was not determined by GC-MS; for the model substrate there was no additional information to be gained, as only one synthetic ester was used, whereas for RBW a mix of different esters was expected for each signal in the chromatogram and no additional value would be gained by that information. The only drawback of GC would be that non-volatile compounds could not be detected, and therefore no information about remaining metal salts in the wax could be gathered.

After a method had been developed and first oxidation experiments had been analysed the performance of the column changed (for a description of the method, see 0 experimental section). Acids and esters were still detected within close time frames but a close time frame for the alcohols was not given anymore. It might have been that some residue salts in the first samples reached the column and remained there, or that the layer of the column was attacked by some compound. The alcohols could only be seen as very flat integrals over time periods of several minutes. As the esters and acids were not affected, it was suspected that some sort of acidic compound on the inner surface of the column had been produced and would bind the alcohols temporarily (similar to ester bonds). Protection of the alcohol group should therefore solve the problem. In order to do that several silylating agents were tested, before it was decided to add MSTFA (N-Methyl-N-(trimethylsilyl)trifluoroacetamide) to each sample before the GC analysis. This agent reacts very fast and efficiently at room temperature, whereas other reagents are reported to need elevated temperatures for complete conversion. The reference times and calibration to each compound had to be adapted accordingly.

The application of an internal or external standard was considered for analyses, as it usually increases the reliability of any analysis method. However, for the herein used substrates and methods the utilization of an "additional" standard was not beneficial. The application of an external standard was neglected due to the intended two-phase reaction and therefore inhomogeneous sample drawing during a running reaction and an elongated work-up time that would have slowed down the project beyond reasonable gain in information. As possible internal standard n-dodecane was considered as it does not have functional groups which are often labile to oxidizing conditions. However, even the alkane was attacked under certain conditions. Disproportioned results (calculated selectivities of over 100 %) showed that the alkane was not fit as standard. Furthermore, the model substrate C_{16}-O_2C_{18} (as well as RBW) already comes with its own "internal standard". When the ester is split the acyl part is converted into an acid, which is much more resistant to any occurring side reactions than the free alcohols (besides re-esterification). It was assumed that the acid derived from the ester would undergo only minor side reactions which would not affect the results to a significant degree.

1.9. Evaluation of the results

For evaluation one has to distinguish between the model substrate and the real wax. In case of the model substrate the conversion was monitored by the formation of stearic acid ($C_{18}O_2H$) in comparison to the substrate C_{16}-O_2C_{18}. For oxidation reactions palmitic acid ($C_{16}O_2H$) was considered the desired product and its yield Y($C_{16}O_2H$) was calculated by its molecular ratio in comparison to $C_{18}O_2H$ (or its integral ratio in comparison with all other detected integrals for alcohol oxidation reactions). When chain shortening was encountered and shorter acids were formed, this was also taken into consideration, however the documentation of every attained product was not considered to be appropriate.

In case of the RBW there are 9 major ester peaks in the raw product. The split wax consists of 3 major acids and 7 major alcohols. Progress of splitting/conversion of the raw wax was monitored by the ratio of monomers versus dimers. Progress of oxidation for the split wax was monitored by the oxidation of $C_{30}OH$ to $C_{30}O_2H$ as this was the most abundant alcohol with a medium alcohol chain length, and only a minor amount of the corresponding acid ($C_{30}O_2H$) was detected in the split wax.

At this point it has to be mentioned, that with the conducted GC analysis any alcohol C_nOH has a very similar retention time as the acid $C_{n-1}O_2H$. Thanks to nature, RBW mainly consists of even-numbered alcohols and acids (compare table 1), so that the conflict with $C_{29}O_2H$ interfering with $C_{30}OH$ and $C_{31}OH$ interfering with $C_{30}O_2H$ is rather low as long as no chain-shortening is occurring (as described in 1.3 there are app. 5 % as much C_{29} and 7 % as much C_{31} as C_{30} compounds in RBW). The distinction of these species becomes more difficult the greater the difference in concentration of the species is and the distinction can only be done with an elongated GC method and manual evaluation of each chromatogram. As the information benefit is rather low (for experiments conducted with RBW) the use of this method was omitted and it was decided to accept the possible but small and consistent error of mixing up $C_{29}O_2H$ with $C_{30}OH$, and $C_{31}OH$ with $C_{30}O_2H$.

Under the assumption of no chain shortening, which can be evaluated with the model substrates, the biggest possible mistake would happen in the case of 0 % real oxidation and a mix up of $C_{31}OH$ with $C_{30}O_2H$. In this case app. 7 % wrong oxidation would be calculated. As it is intended to first investigate with the model substrates and later deal with RBW when high yields of oxidation, excessing 80 and 90 % can be met, this mistake will have rather low impact, and will be outdone by the other possible mistake, mistaking $C_{29}O_2H$ for $C_{30}OH$. The biggest mistake in that scenario happens, when 100 % conversion is reached. In this case mistaking $C_{29}O_2H$ for $C_{30}OH$ results in a “miscalculated” oxidation of 95 %. As can be seen in diagram 1 the “real” oxidation of experiments with low conversion will be below the “calculated” oxidation, but for high conversions the “real” oxidation will exceed the “calculated” oxidation.

Comparing this possible error with the possible errors of a standard method for waxes can be estimated by calculating the theoretical ANs in regard to achieved oxidation. If one assumes a saponification value (SV) of 70 mg(KOH)/g(wax) and further assumes that the wax consists of esters to 100 %, this would mean 1.25 mmol ester would be contained in 1 g wax and these esters would have a medium molecular weight of 800 g/mol. If split without oxidation, there would be 2.5 mmol monomers (alcohols and acids) with a medium molecular weight of 409 g/mol. Due to the gain of weight to 1.023 g the AN would not be 70 but 68.5. Similarly, if the wax was split and oxidized to 100 %, 2.5 mmol acids with a medium molecular weight of 416 g/mol would be the result, the weight of the sample would have increased to 1.04 g, thereby resulting in an AN of 135. If the wax was split and partially oxidized without side-reactions one cannot calculate an exact AN, but values which reflect the upper and lower limit of possible ANs. On the lower end, a "permanent" AN, i.e. if all freed alcohols would re-esterificate with free acids, the wax will not have an AN below this value. On the upper end, one may calculate a "temporary" AN, being calculated from the permanent AN plus the AN resulting from acids freed from simple ester hydrolyses. In diagram 2 temporary and permanent AN are depicted for the oxidation for a pure ester wax with SV of 70 mg(KOH)/g(wax). As one can see, the determination of AN alone is no perfect indicator for the success of the oxidation. In theory it will only exceed the accuracy of the prior presented method for very high oxidation values. Furthermore, the determination of an AN requires extensive work-up, as any contamination (water, acids, bases, salts, etc.) falsifies the result. In the simplest case the contamination adds up to the weight of the wax, thereby lowering the AN, but remaining (inorganic) acids and bases also directly influence the titration, increasing or lowering the AN.

Following these "chemical" evaluations and due to the intended industrial upscaling, the costs of promising methods were regularly observed and (re-) calculated. For this purpose prices were compared throughout different (laboratory) suppliers and commodity markets. Self-explanatory, prices of small scale suppliers do not meet the prices of commodity markets as services like packaging, shipment, customer service are responsible for a greater share of the final costs. However, they are able to give a first impression which chemical might be the cheapest in bulk (if two or more chemicals are able to do the same job). In order to have reliable comparison for the costs of different chemicals, one retailer or other source of information was sought that would provide reliable information for a wide spectrum of chemicals. In the end two sources turned out to be suitable for this purpose. For bulk chemicals *Zauba Technologies & Data Services Private Limited*, for "speciality" chemicals *Sigma-Aldrich Chemie GmbH* provided free pricing data via their websites. Regarding bulk chemicals, prices were attained from shipments of the years 2014 to 2016, given in Indian rupees (INR). Conversion into Euro was done with an assumed exchange rate of 75 INR/Euro, as the most extreme exchange rates from 2014 to 2016 were 86.5 INR/Euro (27.01.2014) and 66.0 INR/Euro (13.04.2015). Thus and for several other reasons, these prices may not be taken as definite but only for comparison of different reactions regarding their possible chemical costs. For instance, the purity or concentration was not always specified. In these instances, the purity was assumed to be 95 % for the calculation of molecular chemical prices. To assure general reliability, several prices were compared with other sources of information and the order of magnitude was always met by the specified source (e.g. the price for Rhenium was found to be 467 € in 2014, whereas other sources reported prices of 972 € in 2017 and 466 € in 2018, compare table 58).[44,104]

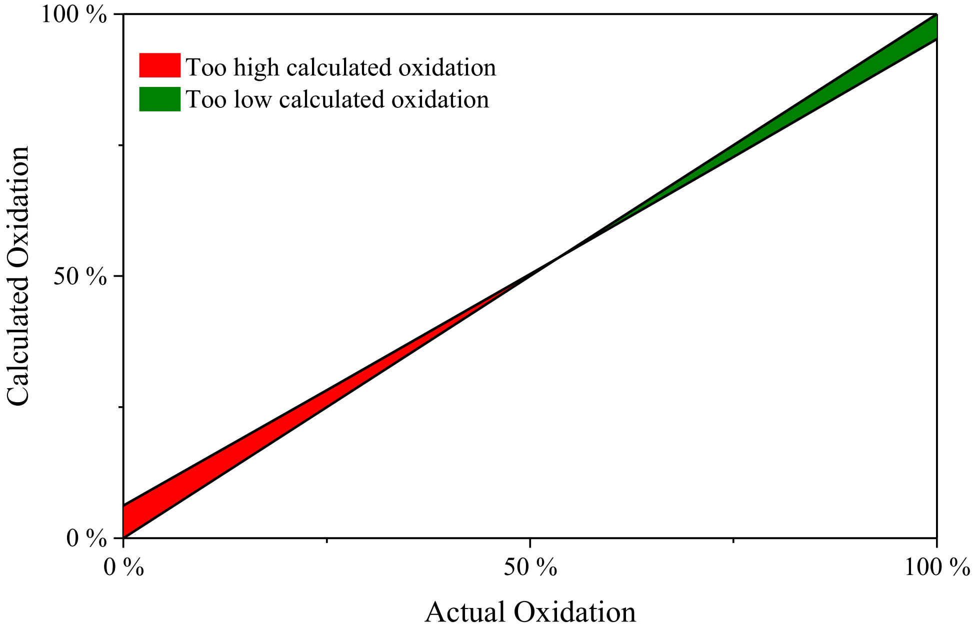


Diagram 1: Showing the actual C_{30}-oxidation of the provided RBW in comparison with the "wrongly" calculated one.

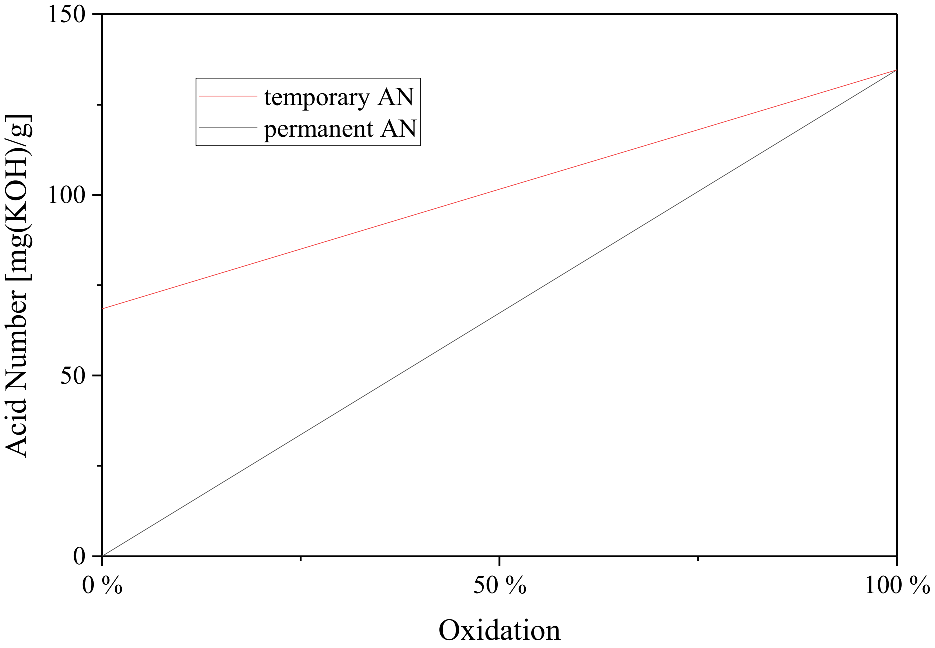


Diagram 2: Exemplary permanent and temporary AN for a pure ester wax with a SV of 70 mg(KOH)/g(wax).

2. Results and Discussion

2.1. Benchmark: Cr(VI)/H_2SO_4

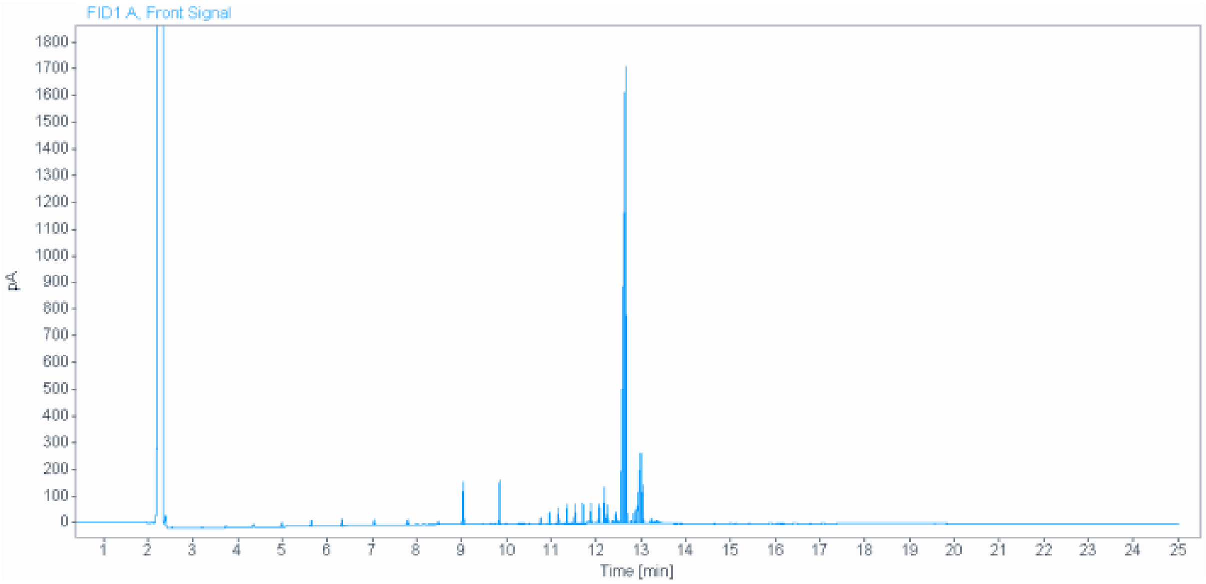
For comparison with other methods and being able to recognize suitable results, benchmark experiments with chromosulfuric acid were performed. The experiments with model substrate and RBW were performed under lab scale conditions adapted from the patents of *Völpker Montanwachs GmbH* and *Kahl GmbH & Co. KG*.[15,36]

For these reactions 0.5 g ester respectively RBW were emulged at 120 °C with 3.0 g of 50 wt.% H_2SO_4 for 30 min. 1.3 g of a sodium dichromate solution (66 wt.%) were subsequently added within 2 hours and the resulting mixture stirred for another 3 hours (table 14).

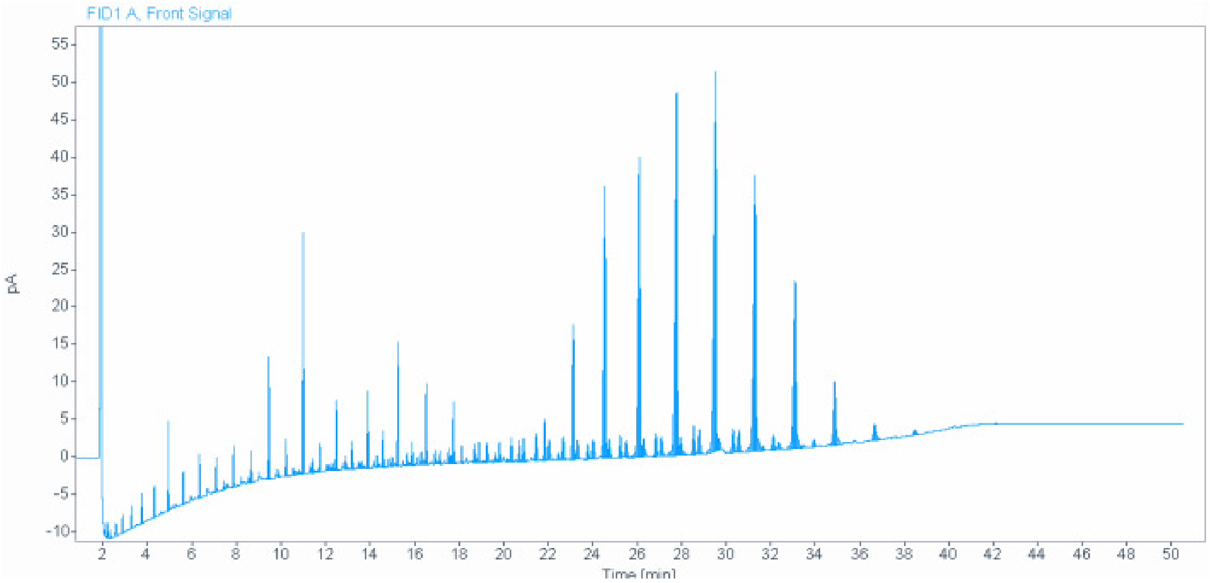
The model substrate was split and oxidized to approximately 7 %, with 69 % of the model ester being unaffected (see chromatogram 4). For the RBW it is more difficult to distinguish, as the longest acids and shorter esters, which have been formed during the reaction, show similar retention times and are therefore difficult to distinguish (compare chromatogram 5). The longest acids in completely oxidized RBW have retention times of approximately 19 minutes and the shortest esters in unoxidized split RBW of approximately 21 minutes (compare chromatogram 1 and 3). Dividing the chromatogram at 20.0 minutes, the ratio of shorter to longer compounds is app. 5:18, leading to the assumption of approximately 21 % split and oxidized esters.

As can be derived from the chromatograms 4 and 5, this method is not very selective. It sets free acids from the carbonyl components of the esters and it gains further acids from the alkyl parts but there is a lot of chain shortening – leaving aside that only 21 % conversion were reached with 6.5 times the amount of Cr(VI) theoretically necessary to oxidize all alcohols present in RBW.

It may be noteworthy, that the very first trials with less pure model substrate (there was still some monomer left) showed a slightly better conversion. This was probably due to these slightly polar contaminations that acted as emulsifier or phase transfer agents (PTAs). This theory would explain as well the higher conversion of RBW. The present monomeric species in RBW would act as PTAs as well and accelerate the reaction in contrast to a “pure” ester substrate. The other explanation for the higher conversion of RBW is its higher molar mass and therefore lower molar amount for the same weight amount compared to the model substrate. Therefore, the same number of molecular reactions would result in higher partial conversion.



Chromatogram 4: Benchmark reaction with C_{16}*-*O_2C_{18}*.*



Chromatogram 5: Benchmark reaction with Rice Bran Wax.

2.2. Acidic Ester Cleavage

As explained in chapter 1.7 the most desirable reaction path for wax oxidation is to split and oxidize the substrate in an acidic medium as a one-pot-synthesis. The first step therefore is the splitting of an ester by an acid.

In the first experiments different acids were tested using 0.2 g C_{16}-O_2C_{18}, app. 0.5 g of acid with 0.5 g of water at 110 °C for 4 hours. The acids used were chosen due to their comparable low price and their rather low tendency to form esters with the freed alcohols. E.g. if acetic acid had been used, formation of hexadecyl acetate would have been expected. This reaction would set free the corresponding acid but the acetate ester would be similarly inert to successive oxidation reactions. The water is supposed to shift the equilibrium to the side of split products. The concentrated acids would rather be expected to dehydrate organic mixtures and therefore shift the equilibrium to the starting material. As can be seen in diagram 3 phosphoric acid does not split any ester, hydrogen chloride splits at least 0.7% of the ester. Better are methanesulfonic acid, H_2SO_4 and HNO_3, all reaching more than 3 % conversion.

As H_2SO_4, HNO_3 and methanesulfonic acid showed already interesting results, these acids were investigated further. When using H_2SO_4 in higher concentration (68 wt.%) more ester was split (app. 9 %), but the proportion of recovered $C_{16}OH$ to $C_{18}O_2H$ decreased. In this experiment only 35 % of the expected $C_{16}OH$ was detected by GC. There was no other species spotted which would explain the loss of product. A possible side reaction would be the formation of hexadecyl hydrogen sulfate which might have been lost during the preparation for the GC.

In the case of methanesulfonic acid an increase of acid content first decreased the splitting when using 75 wt.% concentrated $MeSO_3H$, as less water was available to shift the equilibrium. Further increasing the acid content to 90 or 100 wt.% increased the splitting again, but lowered the yield of $C_{16}OH$ immensely. In the case of 100 wt.% $MeSO_3H$ the highest splitting was observed, however no $C_{16}OH$ at all was recovered. Similar to H_2SO_4 there was no side-product detected and the formation of an ester (hexadecyl mesylate) is suspected.

Splitting the ester with nitric acid showed a direct correlation between the concentration of acid and the conversion (diagram 4): The higher concentrated, the higher the conversion. Similar to the other acids not all $C_{16}OH$ was recovered, with higher acid content the “loss” of $C_{16}OH$ increased. For these experiments often other species were detected. They were identified as C_{16}=O, $C_{16}O_2H$ and shorter analogues.

C_{16}=O and $C_{16}O_2H$ are already the (intermediate) products of the intended follow-up reaction(s). Therefore, nitric acid seemed to be an ideal system to start investigations on oxidizing RBW. Under the right conditions every alcohol that is gained by splitting an ester might be oxidized to its corresponding aldehyde and subsequently to the acid.

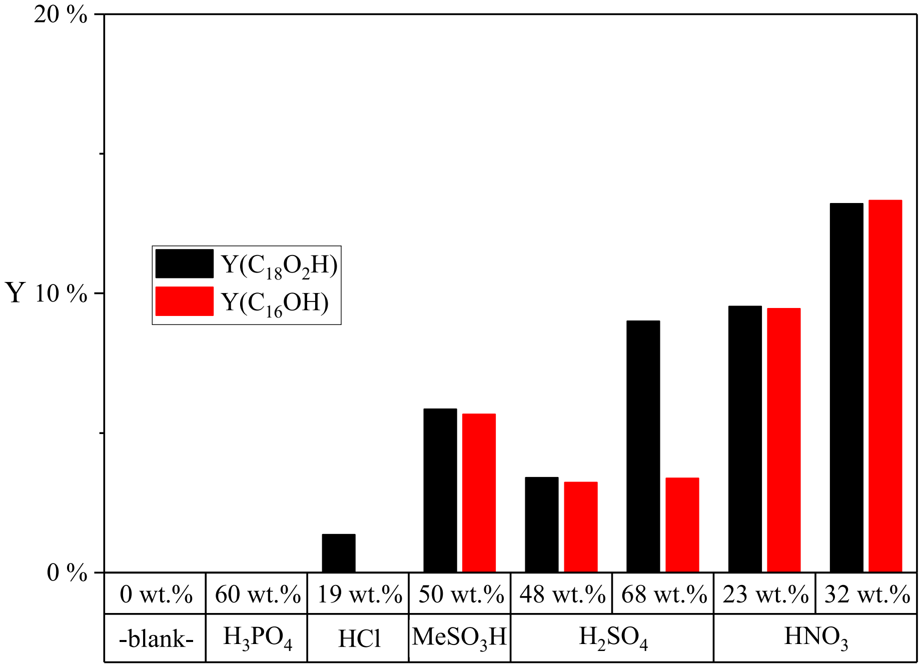


Diagram 3: Splitting C_{16}-O_2C_{18} with different acids. 95 °C, 4 h. Amount of acid was chosen to gain an app. 5 M aqueous phase (compare table 15).

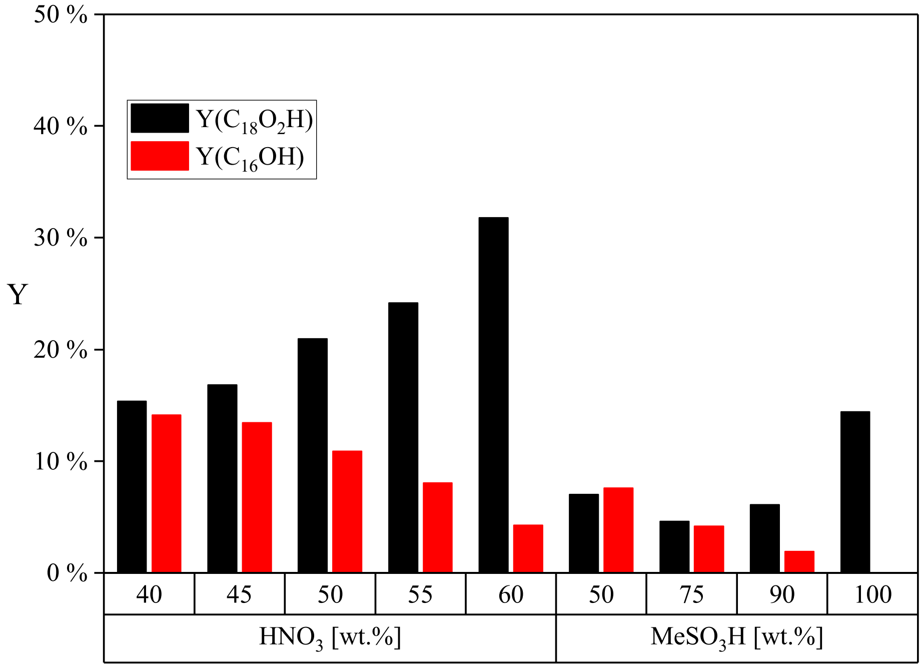


Diagram 4: Splitting C_{16}-O_2C_{18} with HNO_3 and $MeSO_3H$ (compare table 16).

2.3. Oxidation with HNO_3

Without additives

As shown in the previous chapter, nitric acid is able to split esters more effectively than the other investigated acids. In order to start the investigation, the splitting was monitored with different concentrations of nitric acid at various temperatures over a time period of 4 hours. The HNO_3 concentration was increased by 20 wt.% from 20 to 100 wt.%, temperature was monitored between 80 °C (approximate melting point of RBW) and 140 °C (app. 20 °C above the azeotropic boiling point of nitric acid at 1 bar). The conversion was monitored by the formation of $C_{18}O_2H$ in comparison to the substrate C_{16}-O_2C_{18}, as the alkyl part of the ester was freed but thereafter oxidized or degraded in varying amounts. Altogether, the conversion of C_{16}-O_2C_{18} was higher with increased concentration and temperature (see diagram 5). Very interesting are the differences between the results when using nitric acid concentration of 40 to 80 wt.%. When using 80 wt.% HNO_3 the conversion of ester increased nearly linearly with temperature, whereas with 40 wt.% HNO_3 the conversion was only slightly affected by increased temperature.

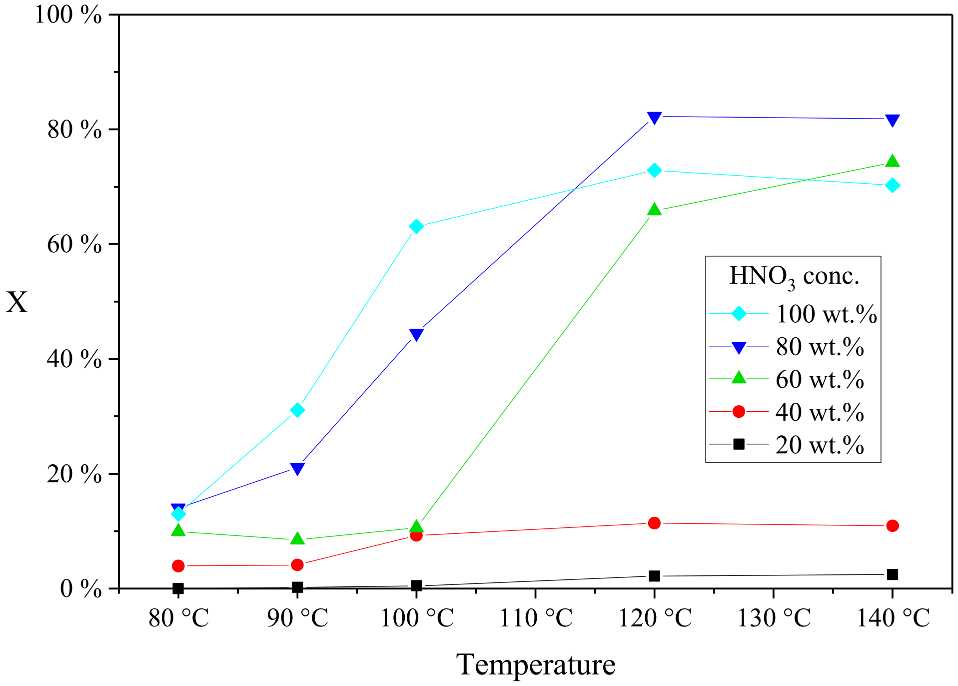


Diagram 5: Conversion of model substrate C_{16}-O_2C_{18} with nitric acid of varying concentration at various temperatures (compare table 17).

For further investigations 95 °C was set as model temperature for various reasons. This temperature is high enough to liquefy any wax of interest (RBW, MW), only minor amounts of water would evaporate (compared to temperatures above 100 °C) and the temperature supposedly is already high enough to set off reactions with nitric acids at technical concentrations. In diagram 6 the ratio of C_{16} to C_{18} compounds (alcohol, aldehyde and acid) clearly shows the increased degradation of the alkyl part with increasing nitric acid concentration. The ratio of $C_{16}OH$ to $C_{18}O_2H$ decreased continuously with increasing acid concentration, whereas the concentration of $C_{16}O_2H$ did not increase in a similar amount. The corresponding aldehyde was detected in all experiments with 45 wt.% or higher nitric acid content. Remarkably the aldehyde content increased slightly with higher acid concentrations. It is suspected that the oxidation of the alcohol to the corresponding aldehyde is rather facile under these conditions, whereas any subsequent reaction of the aldehyde is hindered in some way. This hypothesis is supported by the next experiment that oxidized $C_{16}OH$ with nitric acid at 95 °C. In diagram 7 the resulting compositions of the reaction products are depicted. With 50 °wt.% nitric acid most alcohol was converted to various esters (mainly with 31 carbon atoms, probably being C_{16}-O_2C_{15}), app. 9 % substrate was still unaffected, 6 % was detected as the aldehyde and 7 % were detected as shorter acids (mainly $C_{15}O_2H$).

As expected, increasing the concentration of nitric acid leads to a decrease of esters in the product and a steady increase of acids. The amount of $C_{16}O_2H$ increased up to app. 19 % in 60 wt.% HNO_3 and then slightly decreased again. The amount of shorter acids rose steadily with increased HNO_3 concentration. Quite remarkable is the rather steady concentration of aldehyde in the product for HNO_3 concentrations from 40 to 70 wt.%. The C_{16}=O content only varied between 4.5 % (70 wt.% HNO_3) and 7.7 % (55 wt.% HNO_3) in this range. It seems that only a certain concentration of aldehyde can be reached before it is converted to other products. As the products that result from the aldehyde are varying with the HNO_3 concentration, the reaction paths therefore seem to be dependent on the acidity of the medium or the concentration of various nitric acid derivatives. If it was possible to promote the reaction path gaining $C_{16}O_2H$ or to introduce a new path by additional chemicals, the challenge of oxidizing esters to the two corresponding acids might be solved.

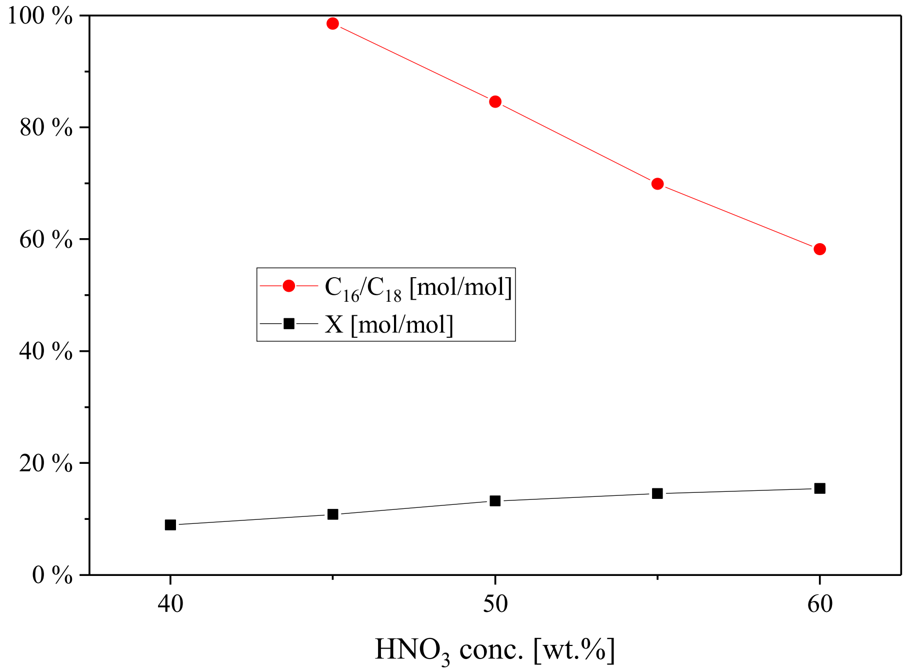


Diagram 6: Conversion X and C_{16}/C_{18} ratio, when converting model substrate C_{16}-O_2C_{18} at 95 °C with varying concentrations of nitric acid (compare table 18).

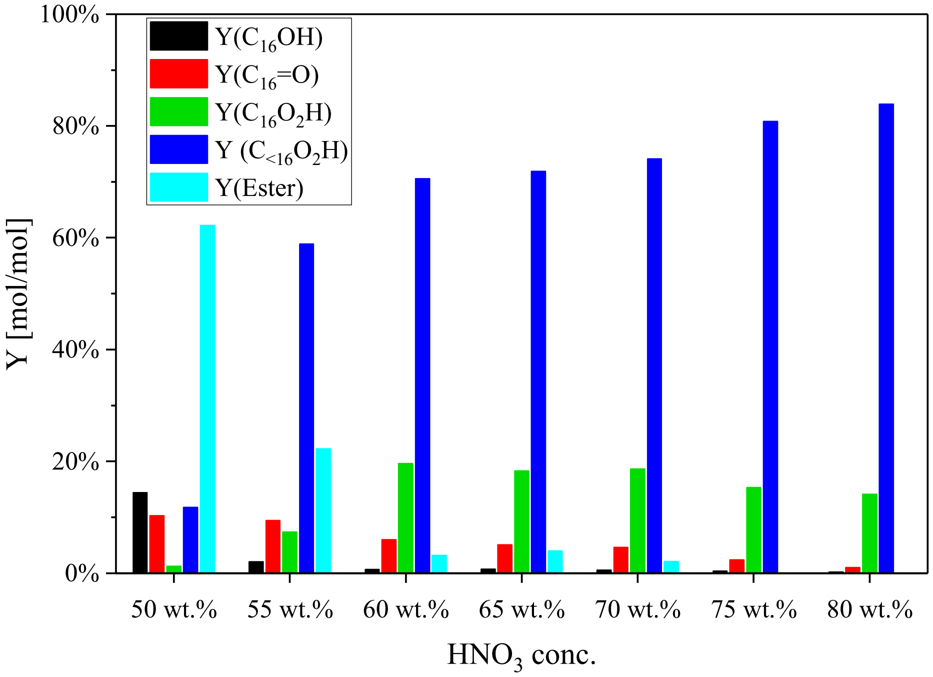


Diagram 7: Product contribution for the oxidation of $C_{16}OH$ at 95 °C with nitric acid in varying concentrations (compare table 19).

Addition of catalytic salts

As *Ross et al.* explained extensively, nitrate and nitric acid itself are probably not the real oxidizing components but rather some sort of "pre-oxidant".[51] Thus it seemed logical to perform experiments with the addition of some nitrite, which could be transformed into nitrous acid. In comparing experiments with synthetic ester and nitric acid it was confirmed that the addition of sodium nitrite accelerated the overall reaction and that more of the alkyl part was detectable than without nitrite (compare figure 15 and 16). With the addition of 4 eq. of $NaNO_2$ the conversion increased from app. 77.5 % to 99 %. At the same time the selectivity of $C_{16}O_2H$ increased from app. 5 % to nearly 21 %. It is quite interesting that there was more $C_{15}O_2H$ built than $C_{16}O_2H$, probably indicating a similar mechanism as with adipic acid, for which the cyclohexanone is first oxidized in alpha-position and then split. Similarly, the aldehyde C_{16}=O could first be oxidized at its alpha-position and then be split to gain $C_{15}O_2H$ and a corresponding C_1 compound (either formic acid or carbon dioxide). In the homologous row of acids their amount steadily decreased from $C_{16}O_2H$ to $C_{12}O_2H$, yet then increased again. This was probably a result of using dodecane as an internal standard in these experiments. Apparently the alkane was also oxidized by nitric/nitrous acid, mainly resulting in acids with 11 or less carbon atoms. Furthermore, other compounds were formed that were detectable via GC-FID (retention time of app. 11.5-14 min in figure 16) but could not be identified by GC-MS.

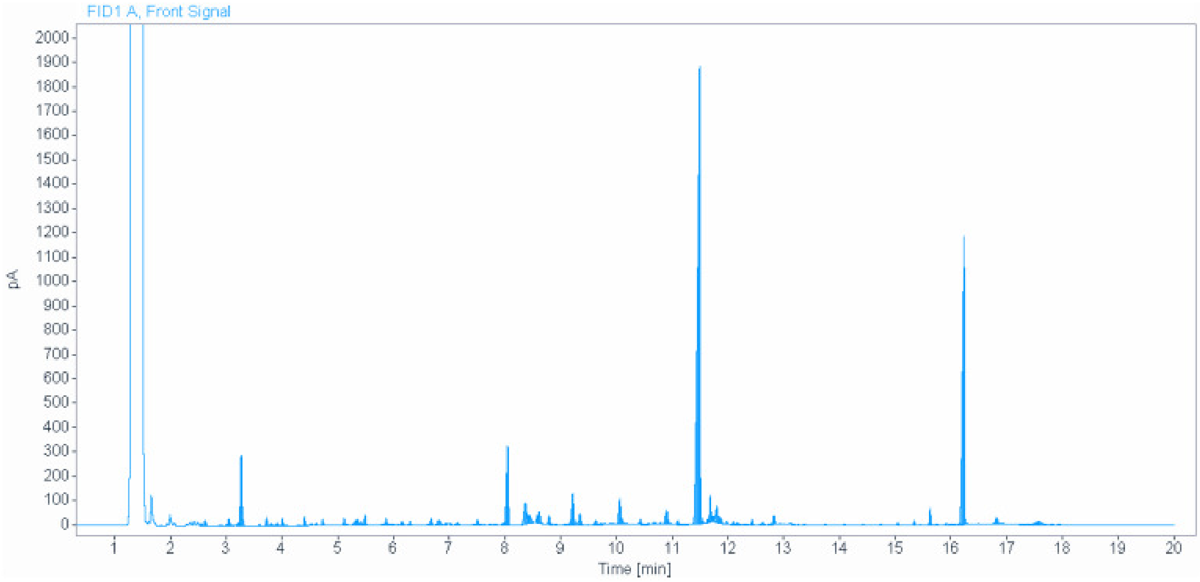


Figure 15: Oxidation of C_{16}-O_2C_{18} with HNO_3 at 120 °C.

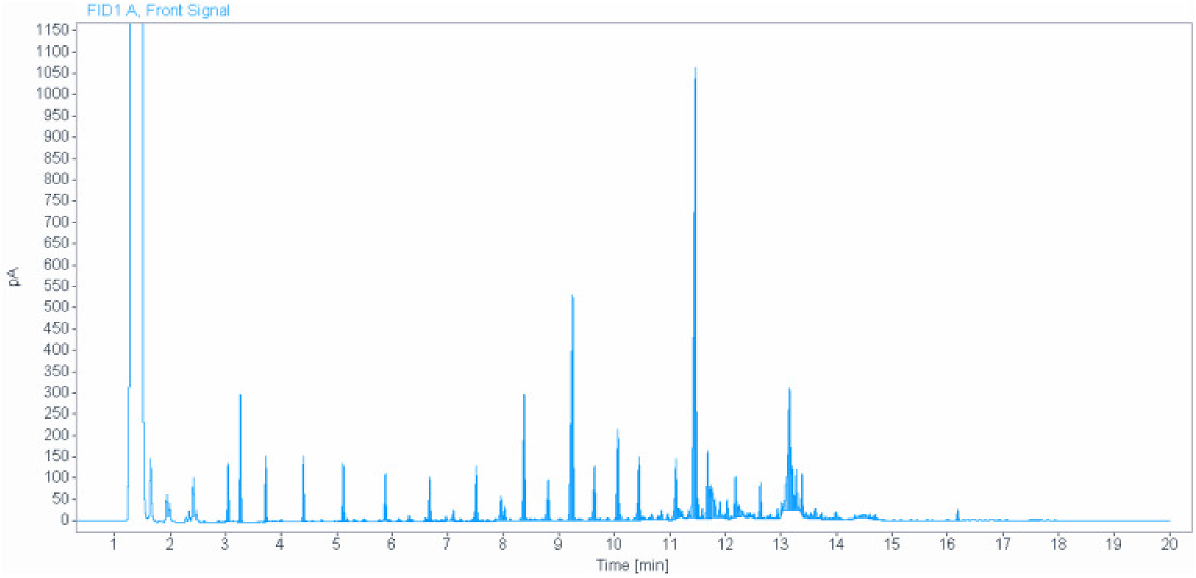


Figure 16: Oxidation of C_{16}-O_2C_{18} with HNO_3 at 120 °C with 4 eq. of $NaNO_2$.

Coming back to the previously mentioned process to produce adipic acid, vanadium and copper compounds are used in this process to catalyse certain reactions. Vanadium is used to split the cyclic diketone into the dicarboxylic acid, while copper is used to convert a nitroso-compound into a nitro-nitroso-compound which is afterwards oxidized to adipic acid (compare figure 10). As hexadecanal may react similar to the ketone, it is likely that similar intermediates are also present in the oxidation of $C_{16}OH$ or C_{16}-O_2C_{18}. Under the assumption of a correct picture of the mechanism, the addition of vanadium would be beneficial for the oxidation of the possible intermediate 2-oxo-hexadecanal. The expected possible benefit for this reaction by copper is however lower for the shown reaction path for adipic acid. Copper supposedly lowers the attack on the second alpha-position in 2-nitroso-cyclohexanone by offering a third reaction path. As there is no second alpha position in hexadecanal or 2-nitroso-hexadecanal, this is no issue in this oxidation. However, a certain acceleration or even increase in selectivity cannot be excluded without experiments as the exact reaction mechanisms are unknown yet.

Experiments with the model substrate and $VO(acac)_2$ as catalytic additive revealed interesting results (compare diagram 8). The selectivity towards $C_{16}O_2H$ increased with the amount of added vanadium compound which is in accordance to the expectations. Yet it is also to be seen that the molar amount of C_{14-16} compounds was greater than the amount of $C_{18}O_2H$. This clearly shows that other side-reactions besides chain shortening were happening. A decay of $C_{18}O_2H$ to shorter acids is rather unlikely as no significant amount of $C_{17}O_2H$ has been monitored. Yet again some compounds with longer retention times than $C_{18}O_2H$ were detected with GC-FID, which could not be identified with GC-MS.

Further investigations with this method were not done, as even 51 mol% of V(V) catalyst did not result in superior results and another method showed faster, more promising results at the same time (see HNO_3 conclusion and the following chapters).

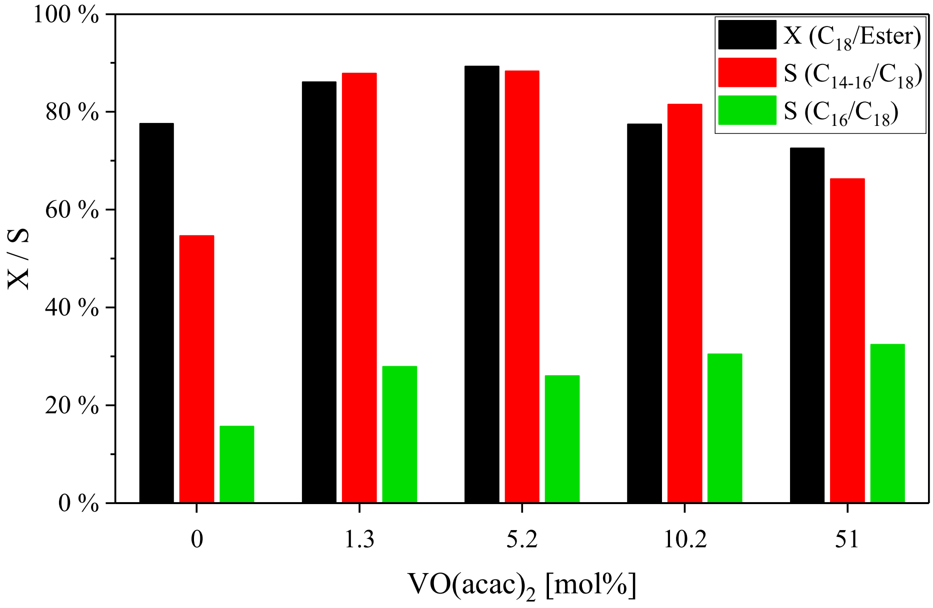


Diagram 8: Oxidation of $C_{16}-O_2C_{18}$ *with* HNO_3 *and differing amounts of* $VO(acac)_2$ *(compare table 20).*

Converting aldehydes to hemiacetals

Not only the addition of catalytic salts was investigated, but also the addition of organic compounds. The idea was developed when seeking an explanation to the different behaviour of $C_{16}OH$ in contrast to shorter alcohols often oxidized with nitric acid in literature-known procedures. Alcohols or organic compounds are in general more hydrophobic with the increasing number of “non-functional” groups. As a result, they are less soluble in water and interact less with water molecules. However, many suggested mechanisms of oxidations from alcohols to acids rely on the hydration of the aldehyde, forming a geminal diol that can be oxidized by the same mechanism as the alcohol. If the aldehydes are not oxidized to acids they may undergo side-reactions similar as in the adipic acid process, e.g. keto-aldehydes may be formed, which may then be oxidized into formic acid and the C_{n-1} corresponding acid, or another oxidation of a methylene group ($-CH_2-$) in α- position to the ketone might occur (compare figure 17). These side-reactions shorten the alkyl chain until a stable compound is reached (in the most extreme case: CO_2).[50,51,53]

As the herein used aldehydes are apparently not forming geminal diols but rather react in other ways, it was supposed to enhance the formation of a hydroxyl group by addition of catalytic compounds. One way to accomplish this would be a nucleophilic attack to the carbonyl carbon and the formation of a covalent bond. If the attack was committed by an oxygen atom, the aldehyde would form a hemi-acetal, which might react in the same way with HNO_3 as the alcohol group did before (compare figure 18). In theory also other atoms may bond to the carbonyl atom, forming hetero-hemi-acetals (e.g. thiols, amines or any other X-H group). However, considering the conditions of the reaction only a few of these groups are likely to have an acceptable probability to attack the aldehyde. Thiols and amines may be oxidized under the set conditions, so that both groups are unlikely to react in significant amounts with the in situ built aldehydes. Furthermore, both functional groups are connected to rather unfavourable smells. This leads back to the formation of “regular” hemi-acetals by reaction of aldehydes with alcohols. Primary alcohols and secondary alcohols cannot be used as these will be oxidized in similar ways to cyclohexanol or hexadecanol. The most reasonable chemicals would be tertiary alcohols or phenol like alcohols.

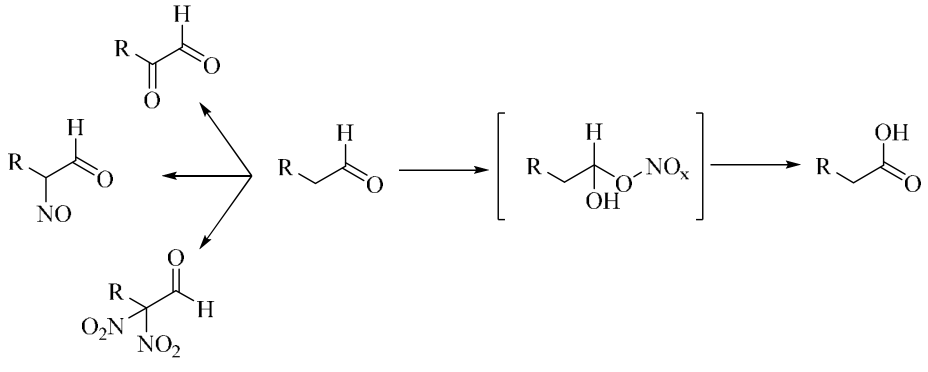


Figure 17: Possible reactions of aldehydes assuming similar reactivities as cyclohexanal.

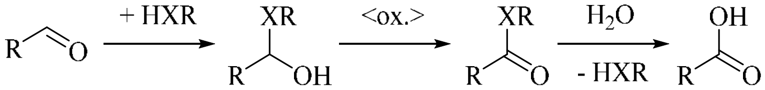


Figure 18: Schematic formation of a (hetero-) hemi-acetal, followed by oxidation and release of the acid.

Experiments with the model substrate showed that this approach seems to be working in principal. In diagram 9 the effects of different additives are depicted. App. 5 eq. ^{t}BuOH increased the yield of $C_{16}O_2H$ only slightly, yet the increase of $C_{15}O_2H$ was significant. These results were met by the addition of 0.4 eq. of phenol, outmatching the tertiary alcohol, when higher amounts were used. With 0.9 and 2.1 eq. of phenol the yield of $C_{16}O_2H$ only increased slightly, yet the yield of $C_{15}O_2H$ was increased to 18 and 27 %, compared to only 3 % without additive.

Yet both chemicals are not considered stable under such conditions. ^{t}BuOH may eliminate water under acidic conditions, forming 2-methylprop-1-ene (isobutylene), which can either evaporate or be oxidized. Phenol is likely to be nitrated, forming nitro-, dinitro- or even trinitro-phenols, 2,4,6-trinitrophenol being known as picric acid, an explosive substance similar to 2,4,6-trinitrotoluol (TNT). Handling wet picric acid at room temperature is safe, in dry form it is sensitive to shock and friction. Due to these issues the use of phenol in combination with nitric acid is not favourable and the investigations with phenol and its derivatives were only done to better understand the mechanism, possibly leading to another compound that actually catalyses the oxidation of the aldehyde to the corresponding acid. Further investigations were for example done with 2-, 3- and 4-nitro-phenol and chromotropic acid. The experiments with chromotropic acid showed reliable increase of $C_{16}O_2H$ and $C_{15}O_2H$, first results with nitro-phenols were inconsistent and were not illuminated more thoroughly as other experiments showed more promising results.

Pentafluorophenol (PFP) was expected to be less prone to nitration or protonation at the hydroxyl-group due to the electron withdrawing fluoric atoms. Therefore, it should be able to attack the aldehyde more readily and form a hemiacetal. The experimental results confirm this assumption. 0.95 eq. of PFP already showed very similar results to 2.1 eq. of phenol (app. 13 % $C_{16}O_2H$ and 27 % $C_{15}O_2H$) and 2.1 eq. of PFP attained app. 33 % $C_{16}O_2H$ and app. 34 % $C_{15}O_2H$.

In the production of adipic acid it is assumed that a great part of the KA oil reacts to 1,2-cyclohexan-di-one.[49] Assuming that the primary alcohol/aldehyde reacts in a similar way, the formation of hexadecane-2-one-1-aldehyde (or 1-carboxylic acid) is likely (such species were not detected in GC-MS). The lower decrease of $C_{15}O_2H$ yield compared to $C_{16}O_2H$ when lowering the amount of PFP may indicate that PFP more easily reacts with the assumed keto-aldehyde than with the aldehyde. Two possible binding modes for which neither proof nor proof of the contrary was produced in this work are shown in figure 19. Structure type **1** shows the formation of a hemi-acetal at the former carbonyl group, whereas structure type **2** is the result of a nucleophilic attack of the aromatic ring to the carbon atom of a carbonyl group, which is similar to the chromotropic acid reaction that is used to provide evidence of formaldehyde.[105-107] In literature no proof of such mechanism was found, yet it was found that PFP can be oxidized to Tetrafluorobenzoquinone (TFBQ), which may react differently.[108,109] Several quinone derivatives are known for their versatile oxidation capabilities. A well-known one is 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ), which can oxidize alcohols to aldehydes or ketones and can also oxidize saturated ketones to unsaturated ketones. It is further reported, that DDQ can abstract a hydride from alcohols, when a resonance-stabilized cation is formed thereafter. Both mechanisms might be valid for the oxidation of esters to two carboxylic acids if the phenol derivatives were oxidized to a quinone. The abstraction of hydrides could enhance the splitting of esters (compare figure 20), whereas the resulting aldehydes might react similar to saturated ketones, which are reported to react via their tautomeric enols. However, instead of forming an unsaturated aldehyde a carboxylic acid would be formed.[110-115]

Again, although these results showed some promising progress, investigations regarding this chemistry were not continued as another method showed faster, more promising results at the same time (see HNO_3 conclusion and the following chapters).

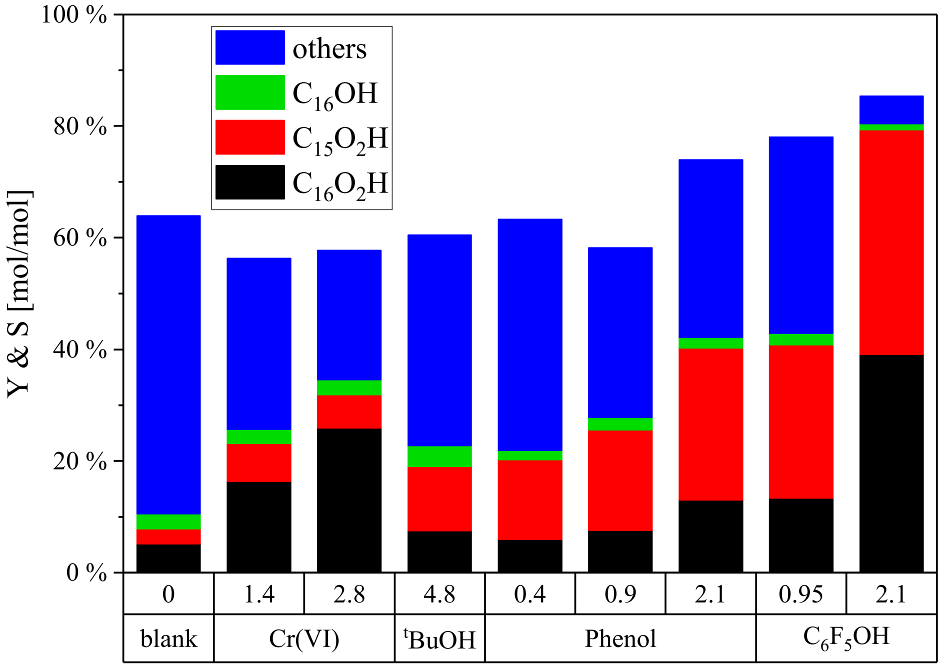


Diagram 9: Oxidation of C_{16}-O_2C_{18} with HNO_3 and different additives (compare table 21). Cr(VI) = $Na_2Cr_2O_7$.

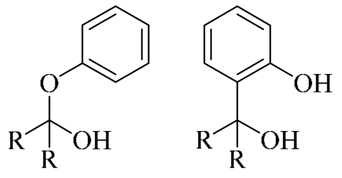


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Figure 19: Possible binding modes for phenol like chemicals at a carbonyl group which would result in an oxidizable hydroxyl group.

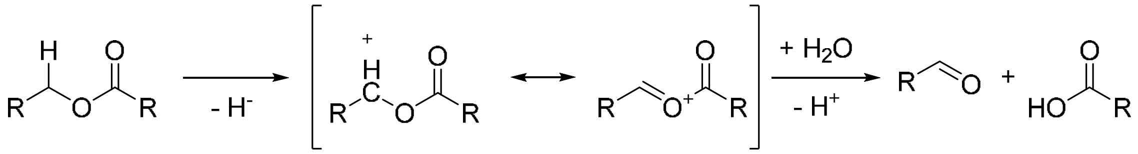

Figure 20: Possible mechanism of a simultaneous ester hydrolyses and oxidation by a quinone (Q).

HNO_3 conclusion

The results of oxidations with HNO_3 showed some promising improvement and the latest results suggested that even further improvement is possible. For the reactions with phenol derivatives it would be interesting to investigate what happens with the phenol-like reagents and which species are responsible for the successful oxidation to $C_{16}O_2H$. However, due to the likely formation of potentially explosive nitro-phenols and other nitro-compounds, I consider this method of rather academic interest and would not expect industrial companies to be too eager for upscaling a process with such chemicals. For the application of metal salts, vanadium compounds already showed some improvement for the selectivity and it would be interesting to see, whether a combination with other salts or even with phenol like reagents might boost the reaction.

Besides the GC analyses, there are also other qualities that are observable yet not that easily quantified. Depending on the conditions the ester/wax was sometimes soft, yellowy coloured and smelled unsavoury. To some extend there were compounds detected by GC-MS which contained nitrogen but these were not certainly identified.

Furthermore, before these issues could be handled and overall satisfying results could be produced, another method was developed which promised better results at higher robustness and variability. This method involving N-oxyl radicals showed some major advantages over any performed oxidation with HNO_3 and will be explained in the following chapters.

Annotation: Some people congratulated me to the realization that I was “riding a dead horse” and the decision to have “finally dismounted”. I absolutely agree that it was best to dismount at this point, but I do not consider oxidations with HNO_3 a “dead horse”. I would rather consider it a wild horse or animal which I attended to tame with the wrong harness and that eventually in the future it might become possible to “tame” this reaction with the right conditions and catalyst(s).

2.4. Basic Ester Cleavage

For basic cleavage of esters (or waxes in this case) there are several important conditions to be considered. A complete splitting of any ester can only be achieved with at least one equivalent of base. For the synthetic ester this is easy to calculate, for RBW it was necessary to calculate a medium molecular weight of the esters. This was done after the first successful splitting with NaOH dissolved in water at 120 °C (batch experiment 1). Identification of the main components and taking into account their portions lead to an approximate medium weight of 755 g/mol(RBW) (compare 1.8 Analyses). The next important condition is the concentration of the base. As depicted in diagram 10 a 10 wt.% sodium hydroxide solution did not affect the model substrate C_{16}-O_2C_{18} significantly at 110 °C, whereas a solution of 34 wt.% split the ester completely. For RBW these findings were not perfectly transferable, as RBW partially consists of monomers which may emulsify the reaction mixture and enhance the reaction. Simultaneously the esters are longer, exhibiting higher melting points and being more hydrophobic, thus possibly decelerating the reaction.

Most convenient for the laboratory experiments was using highly concentrated solutions of up to 50 wt.% base. Higher concentrated solutions might not be stable at room temperature, whereas low concentrated solutions are less efficient to split the wax unless they are concentrated by evaporation of water, which requires time and energy and results in foam formation. (It may be noted, that the process of splitting the wax esters was improved simultaneously with the oxidation of the split wax and due to this circumstance some later described oxidations will not use the "latest" splitting method described in this chapter.)[116]

A difficulty encountered with small scale experiments using magnetic stirrers was the insufficient mixing of the highly viscous reaction mixtures. Although the magnetic stirrers were the same in all small scale experiments, the viscosity and apparent differences in magnetic field led to inconsistent results with sodium hydroxide solutions. Experiments with 50 wt.% NaOH for example led to the inconsistent results depicted in diagram 11 exp. 1. Although the amount of base would have been sufficient, the splitting was simply hindered by inefficient stirring. The next experiments were started again with concentrated bases (50 wt.% NaOH and 42.5 wt.% KOH, diagram 11 exp. 2, 3 and 4) but when the reaction mixture solidified, water was added, thereby diluting the mixture. In these experiments complete splitting was attained with 1.3 eq. of base. It was noticed that the reactions utilizing KOH showed much lower viscosities than their NaOH equivalents.

Upscaling the "dilute" NaOH experiments to 30 g RBW by summing up the applied base and water did not lead to the same result. The splitting needed much more time to be complete. This seems quite logic, taking into account that the reaction mixtures of small scale experiments have much higher surface areas within comparably much bigger reaction vessels. Thus a great part of the water content can evaporate more easily and increase the concentration of the base faster than in the bigger experiments. Up-scaled experiments of 20 g (batch experiment 3) to 500 g (batch experiment 4) with concentrated NaOH (50 wt.%) however led to good results (especially compared to diagram 11 exp. 1). Supposedly this was mainly due to more efficient mixing by the utilized overhead stirrer, but also due to lower viscosities due to less evaporation of water. However, even with the help of a strong stirrer the high viscosity of the NaOH reaction mixtures could cause severe problems. In two instances the viscosity was so high that the glass stirrer broke (probably in combination with fractures in the glass).

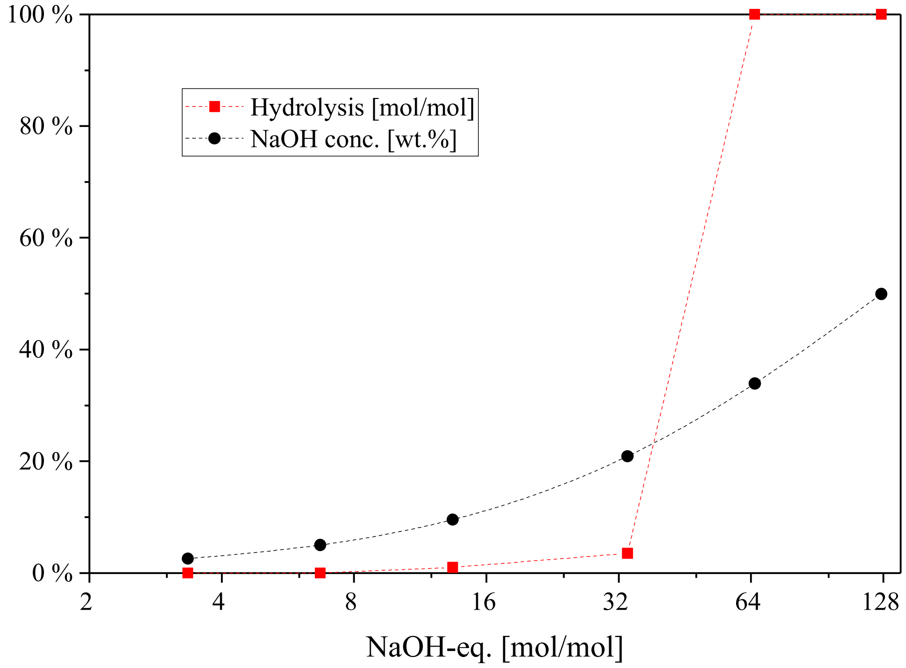

Diagram 10: Splitting of 0.2 g of C_{16}-O_2C_{18} in 2mL of H_2O at 110 °C for 4 h with various amounts of NaOH (compare table 22).

The high viscosity of the split waxes and esters could be attacked by using potassium hydroxide instead of sodium hydroxide. In soap manufacturing KOH is used to gain soft soaps, whereas sodium hydroxide is used to generate hard curd soaps. It proved to be similar with the straight chained esters of RBW. In small scale experiments the stirring was still not perfect, but the results were consistent with the amount of base used and using 1.3 equivalents of 42.5 wt.% KOH solutions were sufficient to split the wax (this concentration evolves from equal parts of water and KOH with 85 % purity). In up-scaled systems KOH worked as well and the viscosity of reaction mixtures was decreased so that stirring became easier. (Please note, that according to literature pure potassium salts of fatty acids are hard as well. The lower hardness of potassium soaps is probably due to a higher water content in the products, which is due to higher enthalpy of hydration for potassium compounds compared to analogue sodium compounds.)[116-118]

Comparing prices, KOH is more expensive than NaOH by a factor of 2 regarding mass, resulting in app. factor 3 regarding molar equivalents (table 53). For industrial purposes it is therefore questionable whether the easier handling and lower viscosities are worth this extra pricing. For laboratory scaled experiments KOH exhibits advantages that are indisputable worth such additional costs. Considering prices of other bases, calcium and magnesium hydroxide or oxide are both much cheaper than NaOH or KOH and would therefore be of interest for such a reaction. Hence, these chemicals were also investigated for the splitting of RBW. First attempts with app. 1.5 eq. of $Ca(OH)_2$ and $Mg(OH)_2$ did not result in significant splitting of the wax, even though the reaction mixtures were heated to 150 °C and total reaction time exceeded 5 hours (table 24). A second attempt was executed with 2 eq. of $Ca(OH)_2$ as app. 10 wt.% emulsion at 120 °C for 68 hours and did result in app. 64 % splitting of the esters (table 25). Due to these disillusioning results the idea to directly split RBW with CaO or MgO was dismissed. However, the thought of utilizing cheaper chemicals is still worth reconsidering the process, or rather parts of it. In connection with the later presented oxidation system the possibility to recycle the more expensive alkaline bases was developed and is further explained in chapter 2.7.3.

Besides chemical prices, the time needed to accomplish a reaction is an important aspect for industrial processes. Like any other reaction speeds up at higher temperatures, also the splitting of esters speeds up at increased temperatures. Lower viscosities are another advantage of higher temperatures, resulting in better mixing and less mechanical stress for the stirring devices. Up to the 1 kg scale it was most convenient to melt the wax at 110 °C, add the hydroxide solution and thereafter slowly heat the mixture to 115 °C. Conditions with temperatures above 115 °C led to the evaporation of water, forming bubbles and some sort of foam that expanded the volume of the reaction mixture. Similar things may happen when higher starting temperatures are used in this scale due to the high reaction enthalpy of app. 80 kJ/mol, i.e. app. 105 kJ/kg(RBW) (compare figure 21). For an isolated system the reaction of 1.3 equivalents of KOH as a 50 wt.% solution (app. 194 $g(KOH_{(aq.)})/kg(RBW)$) would result in a temperature increase of approximately 40 K if no water was evaporating.[a] Further acceleration of this step was neglected due to the potential risks associated with uncontrolled release of such energy.[116,119]

Compared to the alkaline splitting of RBW in a rather new patent, the herein presented method has several improvements. First of all, RBW was split at atmospheric conditions with only moderate excess of lye (app. 0.3 eq.) and without any additional organic solvent, despite the patents statement that “a pressureless saponification is possible only with a considerable excess of KOH or NaOH and […] additional solvent use (xylene)”. Secondly, the reaction time is much lower with less than 1 hour for the splitting of 1 kg of RBW (batch experiment 5).[18]

For larger systems the temperature protocol will have to be reconsidered, as the higher masses of reagents will produce more heat which needs either efficient cooling or some other way to hinder uncontrolled expansion of the reaction mixture. One such possibility would be headspace over the reaction mixture to let some of the water evaporate, which would take away 44 kJ/mol(H_2O), respectively 2453 kJ/kg(H_2O). For the theoretically mentioned approach this would mean that app. 43 g (2.4 mol) of water had to evaporate per kilogram of wax, resulting

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[a] Under the assumption that the heat capacities of 50 wt.% KOH and RBW would be 3 respectively 2 kJ/kg/K and further assuming that the heat capacity of the mixture could be calculated by the summation of the single heat capacities. Heat capacities for RBW were estimated from other hydrocarbons.

in app. 70 L of water vapour at 100 °C. Another way would be the application of a sealed reactor capable to resist higher water vapour pressures, thereby preventing extensive evaporation of water and expansion of the reaction mixture.

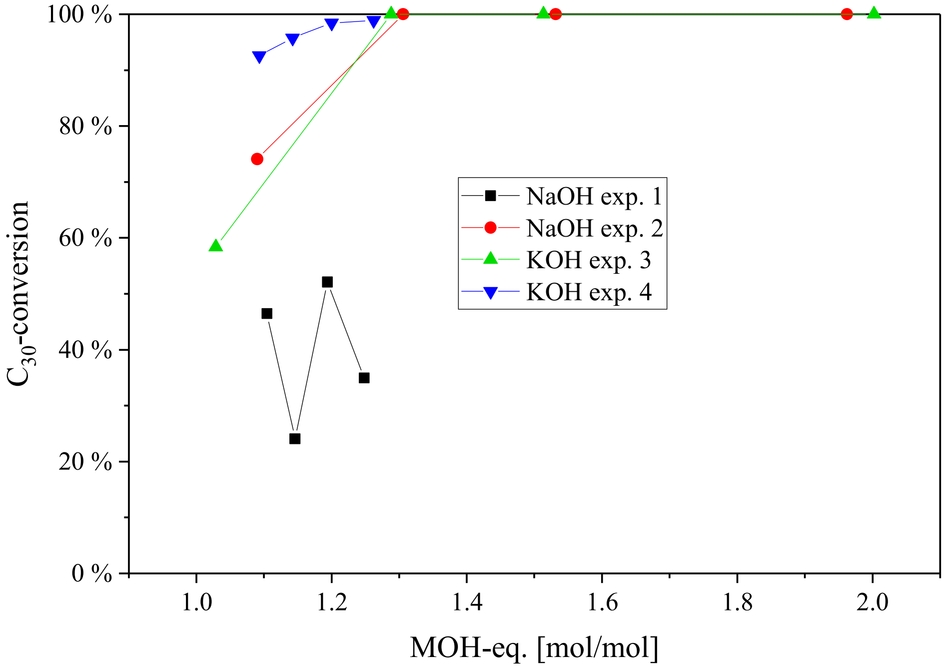
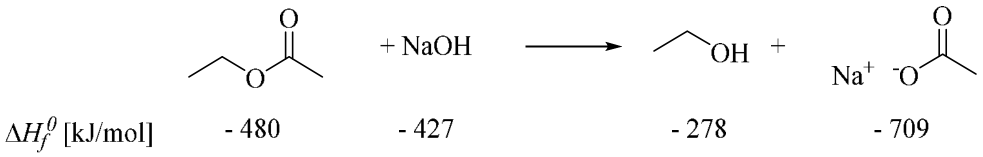


Diagram 11: RBW split with different amounts of base (compare table 23).



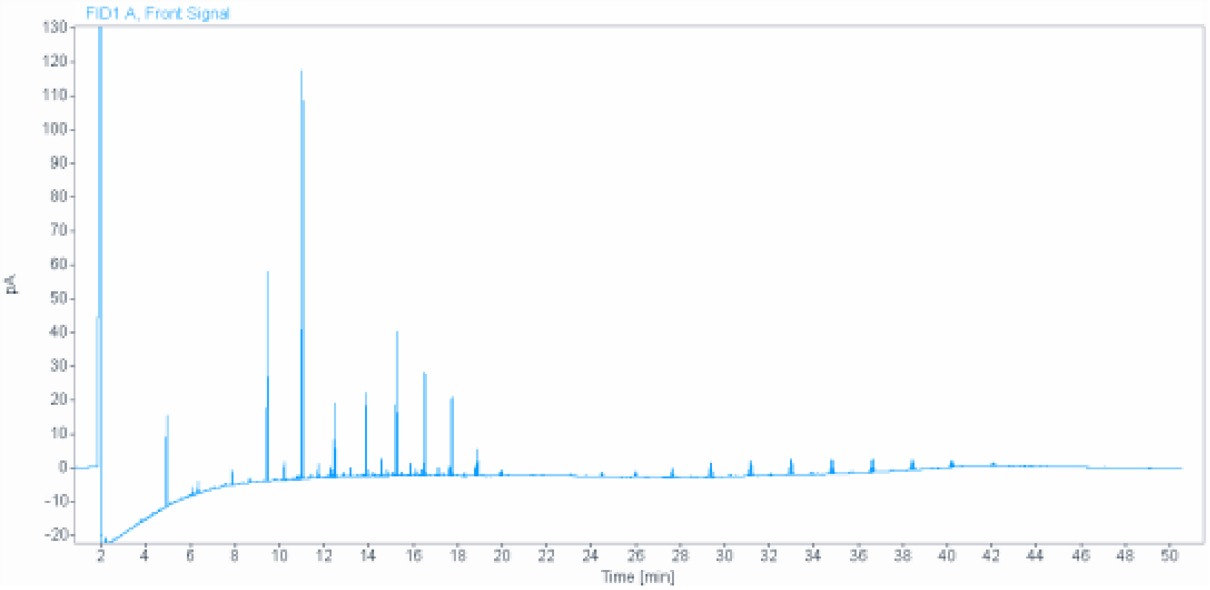
$$\Delta\Delta H_f^0 = -80 \text{ kJ/mol}$$

Figure 21: Standard enthalpies of formation for the alkaline hydrolysis of an ester. This calculation is neglecting the enthalpies of solution and for estimation.[116,120,121]

2.5. Oxidation of split RBW with Cr(VI)

With the esters of RBW sufficiently split and having free acids and alcohols, it seems reasonable to apply known and industrially established alcohol oxidation systems. In this case the oxidation with chromosulfuric acid.

For this proof of principle 1 g of split RBW, 1 g of 50 wt.% H_2SO_4 and 0.3 g of $Na_2Cr_2O_7$ (1.5 eq. Cr(VI)) were heated up to 90 °C and stirred overnight (table 26). The result depicted in chromatogram 6 was excellent (compared to the prior trials with NO_x). There was only minor formation of esters, and most alcohols were transformed to their corresponding acids. For $C_{30}OH$ a successful oxidation of 85 % to $C_{30}O_2H$ was calculated. Chain shortening is responsible for the biggest part of the "loss" in successful oxidation (compare 1.7).



Chromatogram 6: Oxidation of priorly split RBW with 1.5 eq. of Cr(VI).

Another experiment with 0.97 g of $Na_2Cr_2O_7$ (5.0 eq. Cr(VI)) showed a slightly different result. More chain shortening occurred and the successful oxidation of $C_{30}OH$ to $C_{30}O_2H$ was calculated to be app. 81 % (as more $C_{29}O_2H$ was observed). Therefore, for this reaction a vast excess of oxidant does not lead to better oxidation.

Compared to the direct application of chromosulfuric acid to RBW, this system is not only more efficient converting RBW, but also cheaper regarding chemicals (table 5). Compared to the experiment conducted in 2.1, which was developed from patents, and *Herrlich et al.'s* patent (compare chapter 1.5.3) the chemicals for this oxidation cost less than one third and may be reduced even further with optimization. For the oxidation of MW, chromosulfuric acid is applied two or three times (according to patents), which makes the processing of split RBW with this method even more attractive in comparison. The oxidation in *Herrlich et al.'s* patent may be compared to the oxidation with 5 eq. Cr(VI), as 496 g CrO_3 used for 500 g RBW correlate to app. 7.5 eq. Cr(VI) (calculating with an average molecular weight of 755 g/mol for

RBW). It is expected that these reactions result in higher ANs due to chain shortening and formation of di-acids. Optimization of this method may include the use of cheaper chemicals (NaOH instead of KOH), recycling of chemicals (see also chapter 2.7.3) and/or by inserting the split wax directly into chromosulfuric acid (instead of prior acidification with acetic or citric acid as done in chapter 2.4). However, as the preferred aim of this work was the avoidance of Cr(VI) reagents, further research focussed on the oxidation with environmentally more sustainable reagents and methods.

Table 5: Estimated costs for chemicals if RBW was split and subsequently oxidized with Cr(VI). Regarding prices compare the appendices.*

Chemical	**MW-oxidation (2nd stage)**		**RBW splitting and oxidation**[a]	
	[t/t(MW)]	**[€/t(MW)]***	**[t/t(RBW)]**	**[€/t(RBW)]***
KOH	-	-	0.097 (1.3 eq. OH^-)	75
H_3(CA)	-	-	0.22 (2.6 eq. H^+)	135
H_2SO_4	3.0	45	0.5 (8.0 eq. H^+)	8
$Na_2Cr_2O_7$	1.56	1 484	0.3 (1.5 eq. Cr(VI))	285
Total costs		**1 529**		**503**

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[a] The process is probably more work intensive as 5 instead of only 3 chemical reagents are involved but may already be worth for utilization for the chemical industry due to lower costs for reagents, good product quality and especially a significantly lowered utilization of chrome reagents. There was only the cheapest of typically two to three stages for the MW-oxidation taken into account.

2.6. Oxidation utilizing H_2O_2

As described earlier in chapter 1.6.2 rather few (successful) investigations were done utilizing H_2O_2 for the oxidation of primary alcohols to the corresponding acids.[64,68-70]

Investigations with hexanol already showed tungsten based catalysts are able to oxidize primary alcohols efficiently and better than the expensive MTO. Similar to reactions catalysed by TEMPO it was not certain, whether this method could be applied to the longer and less hydrophilic hexadecanol or even alcohols of RBW. To oxidize hexanol tris(tetrabutylammonium)tetrakis(oxodiperoxotungsto)phosphate ($[Bu_4N]_3[PO_4(WO(O_2)_2)_4]$, Bu_4-TATTP) was efficiently used

First screening experiments

First tests with $C_{16}OH$ revealed that Bu_4-TATTP is not sufficient for this reaction ($Y(C_{16}O_2H) < 1$ % within 2.5 h, table 27). As the essential reaction was not changed, it was suspected that the cation Bu_4N^+ is not sufficient enough as phase transfer agent (PTA). It was suggested to switch to more hydrophobic cations, e.g. tetrahexylammonium (Hex_4N^+) or hexadecyltrimethylammonium ($C_{16}Me_3N^+$). As TATTP-catalysts were not commercially available, but had to be synthesized via one or two step syntheses, it was decided to try sodium tungstate as precatalyst and have the active catalyst been produced in situ by addition of an ammonium salt and a hydrogen sulfate salt, ideally an ammonium hydrogen sulfate.[76] This would allow faster screening of different cations and thus possible advantages and weaknesses of the system could be spotted earlier. The first screening reactions (table 27 and 28) showed, that the assumption of Bu_4N^+ being too hydrophilic was correct. It was possible to oxidize $C_{16}OH$ to app. 90 % with Hex_4N^+ cations and it was also possible to at least partially (45 %) oxidize $C_{16}OH$ with $C_{16}Me_3N^+$. A first test reaction with an imidazolium cation did not result in any significant oxidation.

Following, the principle ability of these catalysts to oxidize the alcohols in RBW was tested. This was done in a similar manner to the prior experiments and showed that $C_{16}Me_3N^+$ in combination with W(VI) is able to oxidize the alcohols of RBW. Addition of various organic solvents is apparently not preferred and led to lowered oxidation values in the experiments. The decrease was only minor for rather polar solvents like DMSO, MeCN and EtOAc, but severe for the unpolar solvents heptane and toluene (table 29). It is suspected, that the unpolar solvents diluted the organic phase, thereby lowering the probability of an active catalyst meeting an oxidizable group. Possibly the low polarity of these solvents also inhibited the metal oxides of entering the organic phase. For the more polar solvents, it can be argued that they also diluted the organic phase but at the same time supported the phase transfer of the metal oxide into the organic phase.

In order to see, whether other metals might be interesting as well molybdate and phosphotungstic molybdate were tried for the oxidation of $C_{16}OH$ (table 30). It turned out that TATTP and WO_3 derivatives are apparently most active and easily accessible for this reaction. As with 0.64 mol% C_{12}-TATTP over 97 % oxidation of $C_{16}OH$ was possible. Similarly, interesting was an experiment which was executed with an in situ generated catalyst derived from Hex_4N^+ and Na_2WO_4. With less than 2 mol% of each component app. 90 % conversion of $C_{16}OH$ were accomplished. This performance is comparable with the performance of 0.64 mol% C_{12}-TATTP, as TATTP holds 3 cations and 4 tungsten atoms within its formula. The silicon equivalent of phosphotungstic acid, $H_4[SiW_{12}O_{40}]$ did not yield any oxidation in this experiment. A molybdenum derivative on the other hand showed at least some oxidation, reaching 15 % with 1.3 mol% of $Na_3[PMo_{12}O_{40}]$. Interestingly the performance decreased, when twice the amount of metal was used. This may either be due to the difference in ratio of ammonium cation to metal oxide, or due to an increase of pH value induced by the sodium salt. Further experiments with app. 21 mol% of Hex_4N^+ and 9.5 mol% Na_2MoO_4 resulted in 80 % conversion of $C_{16}OH$, whereas less than 2 mol% of Hex_4N^+ and Na_2WO_4 reached app. 90 % conversion.

Experiments with RBW

With these preliminary results, the focus was turned to the actual substrate, split RBW. The first experiments were conducted using C_{12}-TATTP, one of the most active catalysts of the prior screening. For 0.5 g substrate and otherwise similar conditions 1.3 mol% C_{12}-TATTP reached > 99 % conversion of $C_{16}OH$, whereas only 79 % C_{30}-oxidation was observed in split RBW with 2 mol% C_{12}-TATTP. An explanation for this result might be side-reactions of H_2O_2, but for reactions with 1 mol% of catalyst and two or four times the amount of oxidant, the C_{30} oxidation (app. 40 %) did not change significantly. However, increasing the amount of catalyst to 3.9 mol% with the same amount of hydrogen peroxide resulted in 92 % $C_{30}OH$ conversion. Quite interesting was also another observation of these experiments: With increased concentrations of H_2O_2 there was a significant re-esterification observed (table 31). The re-esterification that happened when increasing the amount of hydrogen peroxide was not expected, but seems logical, as the higher amount of H_2O_2 lowers the concentration of H_2O and therefore pulls the equilibrium to the ester side. Repeating the experiment by lowering the additional water instead of raising the amount and concentration of H_2O_2 confirmed the prior findings. Oxidation of $C_{30}OH$ was not increased significantly with higher peroxide or catalyst concentration (regarding amount per volume), whereas over 20 % of esters were found when no water was added.

Experiments with 9.5 mol% Na_2WO_4 instead of TATTP and shorter alkyltrimethylammonium cations showed very interesting results: When oxidizing 0.5 g split RBW with 0.5 mL H_2O_2 and 20 mol% of $C_{10}Me_3N^+$, an oxidation of app. 69 % was observed, regardless whether 1.5 mL H_2O were added, or not. When using 20 mol% C_8Me_3NCl the

C_{30}-oxidation was 48 % with H_2O_2, whereas with additional 1.5 mL of water the oxidation fell to less than 13 %. This shows quite significantly what difference a length increase of 2 methylene groups in the catalyst can induce to the oxidation under otherwise identical conditions. It furthermore shows the possible dependency of the oxidation on the ratio of organic to aqueous phase. In contrast to the experiment with C_{12}-TATTP no significant increase in re-esterification was noticed in both cases (table 32). The cause for these differing reactivities is not solved conclusively. It may be due to the different cations or anions or their concentrations, or the pH value which is induced by the utilized chemicals.

These quite scattered first experiments lead to several conclusions and suggestions:

- An oxidation of split RBW with H_2O_2 using metal oxides is possible. Possible metals for this purpose are tungsten and molybdenum (in oxidation state VI).
- Bu_4N^+ has apparently too short alkyl chains to be used for facile oxidations of $C_{16}OH$ or split RBW. Hex_4N^+ and $C_{\geq 8}Me_3N^+$ showed their principle capability of oxidizing split RBW.
- A higher hydrogen peroxide concentration at the same amount of aqueous phase may lead to an increase of re-esterification.
- Shorter alkyl chains in RMe_3N^+ may lead to a lowered oxidation under similar conditions.
- Shorter alkyl chains in RMe_3N^+ lead to an increased dependency of the oxidation towards the ratio of the two phases. But for reasonable substrate to total volume ratios of 1:2 – 1:4 very low to no dependency was observed for using 20 mol% of $C_{10}Me_3N^+$.

Acid influence

Basic chemical knowledge and literature suggest, that the pH value may play an important role in the oxidation of alcohols with H_2O_2 and metal oxides.[75,122] Therefore a series of experiments were conducted, which showed the significant dependency of this reaction to the amount of added acid. When utilizing 11.7 mol% Na_2WO_4 and 5.7 mol% $C_{12}Me_3NCl$ C_{30}-oxidation was calculated to be app. 8 %, which is according to diagram 1 virtually no oxidation at all. With the addition of 11.7 mol% $KHSO_4$ the oxidation was increased to 37.5 %, whereas excessive $KHSO_4$ (45 mol%) lead to a slight decrease again (32 mol% C_{30}-oxidation). Further increase of oxidation could be achieved by increase of PTA, achieving 62.5 % and 79.5 % oxidation when 11.5 mol% respectively 22.9 mol% $C_{12}Me_3NNO_3$ were added (table 33).

To see whether the complete process of splitting and oxidizing RBW would be suitable for a "one-pot-reaction" without intermediate work-up, acetic and citric acid were tested to their ability of acidifying the reaction mixture (depicted in figure 22). Citric acid appeared to have no positive effect on the oxidation whatsoever, as the C_{30}-oxidation did not change with up to 6.5 mol% CA and decreased when 40 mol% were added. The latter decrease may be due to a less efficient mixing of the two phases, as CA is quite polar and may enhance the lipophobicity of the aqueous phase, another possible aspect would be CA's potential chelating properties, which may allow it to interact with tungstate or the ammonium cations. Acetic acid on the other hand increased the oxidation slightly from 42 % to 50 % when 21 mol% acid were added and no drop in oxidation was monitored when raising the amount to 1.3 eq. This may be due to HOAc being a possible solvent for polar and unpolar substances with less chelating properties than CA. Therefore, HOAc would not hinder the mixing or phase transfer of substances. With addition of $KHSO_4$ on the other hand, 4.6 mol% additional acid already raised the oxidation to over 60 % and further increase was possible with more acid. 18.5 mol% raised the oxidation to over 70 %.

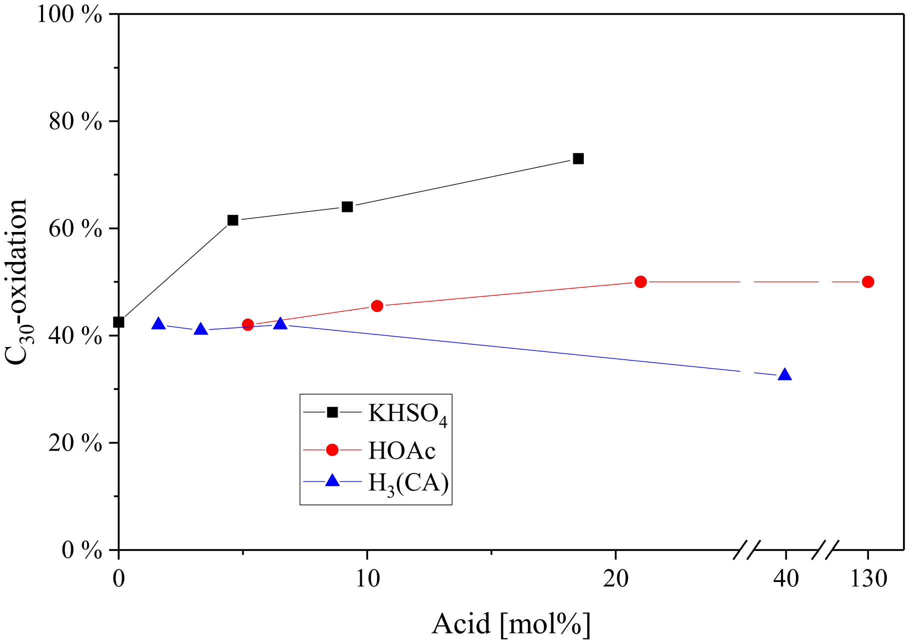


Figure 22: Influence of different acids on the C_{30}-oxidation (compare table 34).

Although these experiments are not solely controlled by pH, they show two things. On the one hand acetic and citric acid do not hinder the reaction too much and are in principle compatible with the oxidation system. On the other hand, lower pH values are necessary to obtain ideal performance of the catalyst (compare chapter 1.6.2) and it is yet uncertain how buffered systems would perform. As the catalyst is rather expensive, recycling will presumable be necessary in any process. It is expected that for a one-pot-reaction with CA/HOAc more catalyst would be needed (than with $KHSO_4$) and the recycling matrix would be rather complex. However, a 3-step process with intermediate work-up of the split wax would be more complicated by process management and would bear a greater risk of re-esterification, which might disagree with product quality.

These so far observed results all show one major drawback. The obtained turnover numbers (TON) are very low, not reasonably above 10 oxidations per tungsten molecule. To see whether the TON regarding tungsten could be increased experiments with lowered catalyst loadings were performed. With app. 2.5 mol% W(VI) and twice the amount of $KHSO_4$ reasonable oxidation was only achieved with comparatively high PTA loadings. 51 % C_{30}-oxidation could only be achieved with 20 mol% $C_{12}Me_3Cl$, referring to a TON of app. 20 regarding tungsten (table 36). As monitored before excessive increase of $KHSO_4$ would not have significant effect, but alternating the ratio of organic to aqueous phase might achieve some change in oxidation. It had also been monitored that the change in C_{30}-oxidation when diluting the aqueous phase from 1 volume to 3 volumes compared to the organic phase was dependent on the used PTA (compare table 32). With 10 mol% Na_2WO_4 and twice the amount of PTA, the oxidation with C_8Me_3NCl showed a significant decrease with higher dilution, whereas with $C_{10}Me_3NCl$ it was not significantly affected. It was now observed that with lower PTA loading even $C_{12}Me_3NCl$ was affected by the amount of aqueous phase. By increasing the ratio of organic to aqueous phase from 1:6 to 1:3 and otherwise identical conditions the oxidation with 5 mol% PTA increased from 24.5 to 46.5 % and with 10 mol% PTA from 38.0 to 61.5 % (table 36 and 37).

These experiments were furthermore interesting in another aspect. When conducting them with 2 or 4 mol% $KHSO_4$ per mol% W, it was observed, that the re-esterification was lower in experiments with higher $KHSO_4$ loading (table 37). This is contra-intuitive as the expected pH value should decrease with higher amounts of $KHSO_4$ and hence higher amounts of ester should be formed. However, the pH decrease may not have been that severe as all reagents were still rather diluted and furthermore hydrogen sulfate or potassium might act as phase transfer agents for water into the organic phase. Both ions can be considered rather hygroscopic and have a low molecular charge. If the general method could be developed further, experiments with sodium hydrogen sulfate might show whether the cation, anion or both were responsible for this effect.

Summarizing the effects of different acids and assuming their influence is mostly due to their acid strength leads to the following conclusions: CA and HOAc are too weak to influence the oxidation positive (high amounts of HOAc supposedly may rather act as phase transfer agents). HSO_4^- is good for acidification but already so strong that it may induce esterification.

With 5 mol% W(VI) and 15 mol% PTA it was tried to further narrow down the ideal pH by adding different amounts of $KHSO_4$. Starting point was the necessary amount of $KHSO_4$ to acidify Na_2WO_4 to HWO_4^- as literature and already executed experiments had shown the necessity for this species.[76] In addition to $KHSO_4$ an acid was sought which may be strong enough but not too strong, yet cheap and without any discomforting properties (smell, toxicity, etc.). Phosphoric acid came to mind. Its pK_A of app. 2.2 is slightly higher than the pK_A of HSO_4^- (~2.0) yet more acidic than HOAc (pK_A ~ 4.7).[12,123] Questionable was how phosphoric acid would interact with the tungstate, as phosphotungstic acid or a TATTP derivative might be formed. The results of these experiments are depicted in figure 23. For the addition of H_3PO_4 it can be seen that the esterification increased and oxidation decreased with higher amounts of this acid. It is suspected that phosphoric acid and tungstate formed conglomerates that may be less active or less soluble in the organic phase.

For $KHSO_4$ the trend seems a bit more complex. With the first 5 mol% the esterification increased steadily while the oxidation was monitored in a range between 74.5 to 83.5 %. Further increase of $KHSO_4$ led to an increase in oxidation (87.5 to 90.5 %), while the esterification had a drop when 15 mol% $KHSO_4$ were used. It might be that the speedup of the esterification constantly increased with higher amounts of acids, yet only dominated the trend of the first three experiments, whereas the speedup of the oxidation kicked in from between 5 and 15 mol% $KHSO_4$. This would also explain the lower ester ratio for this experiment as oxidizing the alcohols to acids changed the equilibrium for esterification. With a given concentration for the sum of alcohols and acids, the driving force towards the ester is greatest when alcohols and acids have the same concentration (which is the case when no oxidation has been performed). Therefore, a fast oxidation hinders extensive esterification and would explain the “drop” of ester ratio.

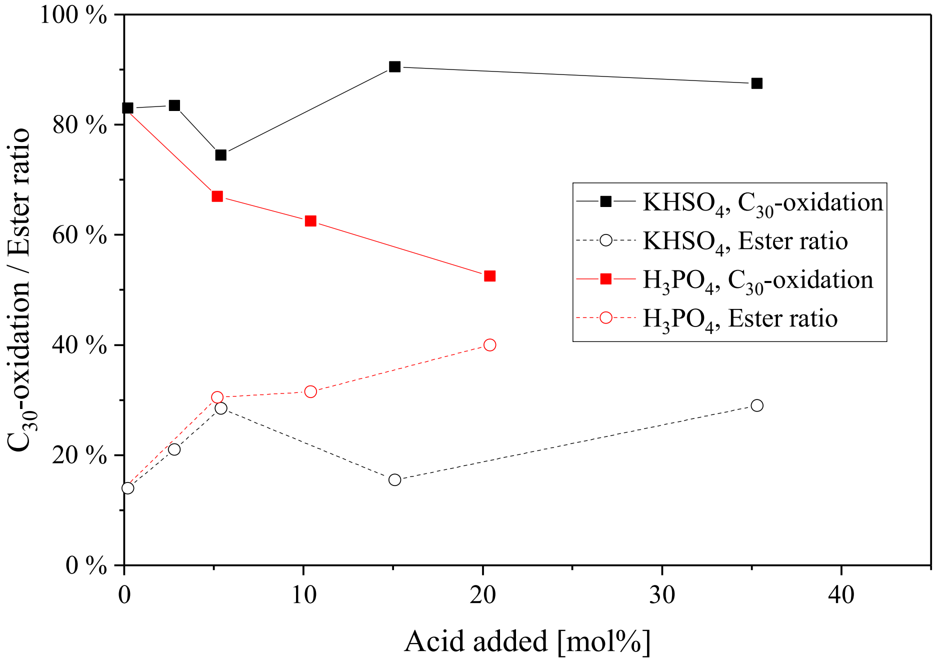


Figure 23: Influence of $KHSO_4$ and H_3PO_4 with 5 mol% HWO_4^- and 15 mol% PTA(table 38).

W(VI)/H_2O_2 evaluation and conclusion

The prior described experiments may seem scattered and to have produced more questions than to have answered. However, just this proves that this method shows a great dependency on a number of parameters when oxidizing long chained alcohols. To narrow down the window of variability for each influence would take a huge amount of time.

With W(VI) the yet best results for oxidizing split RBW were achieved with 3.9 and 4.9 mol% C_{12}-TATTP, gaining 92 and 93 % C_{30}-oxidation without significant re-esterification (2.0 mol% reached 79 %, table 31). Other experiments with less C_{12}-TATTP (2 and 3 mol%) also reached oxidation beyond 80 %, however with more significant re-esterification. It may therefore be assumed that 2.5 mol% C_{12}-TATTP may reach C_{30} oxidations of 85 to 90 % without too much re-esterification. C_{12}-TATTP consists of 3 $[C_{12}Me_3N]^+$ cations and one $[PO_4(WO(O_2)_2)_4]^{3-}$ anion, the chemical costs may be estimated by calculation of the tungsten and ammonium content, as the other reagents for synthesis of the catalyst are less expensive (H_3PO_4, H_2O_2 and HCl). If one assumes that 2.5 mol% of C_{12}-TATTP and 3 eq. of H_2O_2 could gain a product sufficient for the intended applications, the costs for chemicals would be app. 660 €/ton(RBW) (compare table 6). (The amount of H_2O_2 in the experiments was significantly higher but for the estimation one may assume that a reduction is possible with slow addition of H_2O_2 under "perfect" conditions.)

*Table 6: Estimated costs for chemicals under the assumption of using 2.5 mol% C_{12}-TATTP and 3 eq. H_2O_2 to oxidize split RBW (compare table 31). * Regarding prices compare the appendices.*

Chemical	Assumed amount	Amount for 1 t (RBW)	Costs for 1 t (RBW)*
W(VI)	10 mol%	39 kg Na_2WO_4	432 €
PTA	7.5 mol%	26 kg $C_{12}Me_3NCl$	131 €
H_2O_2	3 eq.	270 kg H_2O_2 (50 wt.%)	94 €
Total costs			**657 €**

Other good results include the experiments depicted in figure 23. With 5 mol% W(VI) and 15 mol% PTA an oxidation of 90.5 % was reached. Some re-esterification took place but may be neglected for this estimation of chemical costs. With 3 eq. of H_2O_2 the costs for chemicals would be app. 570 €/ton(RBW) (compare table 7).

Both cost estimations (table 6 and 7) are much higher than the estimated costs for the un-enhanced oxidation with Cr(VI) (app. 290 €, compare table 5). Even if one compares current literature-known procedures, the "best" experiments used 1.5-2 mol% W(VI) with 2-2.5 eq. of H_2O_2 (but only showed yields of less than 90 %, all experiments being performed with alcohols with shorter chains). Now simply assuming it was possible to further develop this process to a similar performance with RBW, the costs for chemicals might be as low as app. 199 €/t (see table 8). This would be cheaper than the not adapted Cr(VI) oxidation system, beating it by app. 100 €/t or 30 % (compare table 5) and further reduction of costs for chemicals might be achieved by recovery of tungsten. However, one has to consider that the recycling of tungsten may not be easy and will add up to the total costs. Furthermore, the removal of the PTA will not be as easy as the removal of any chemical in the Cr(VI)-system, nor as easy as the system that is described in the following chapters. This is due to the fact that long-chained PTAs (which would be necessary) have a high K_{OW} and hence cannot be washed out easily with water. Another point of consideration is that the price of tungsten (or another metal) is dependent on mining output and in some cases politics. Latest by 2021 the handling of tungsten and its products will get more complicated, and prices may rise as tungsten will be included in the "Conflict Mineral Regulation" law of the EU.[69,76,81,124]

All in all, these issues might be handled within reasonable time. However, similar to the oxidation of esters with HNO_3, these issues were not addressed due to the development of the more promising method involving N-oxyl radicals as catalysts, further explained in the following chapters.

*Table 7: Estimated costs for chemicals under the assumption of using 5.0 mol% W(VI), 15 mol% PTA and 3 eq. H_2O_2 to oxidize split RBW (compare table 38). * Regarding prices compare the appendices.*

Chemical	**Assumed amount**	**Amount for 1 t (RBW)**	**Costs for 1 t (RBW)***
W(VI)	5 mol%	20 kg Na_2WO_4	216 €
PTA	15 mol%	52 kg $C_{12}Me_3NCl$	262 €
H_2O_2	3 eq.	270 kg H_2O_2 (50 wt.%)	94 €
Total costs			**572 €**

*Table 8: Estimated costs for chemicals under the assumption of using 2.0 mol% W(VI), 2.0 mol% PTA and 2.5 eq. H_2O_2 to oxidize split RBW. * Regarding prices compare the appendices.*

Chemical	**Assumed amount**	**Amount for 1 t (RBW)**	**Costs for 1 t (RBW)***
W(VI)	2 mol%	8 kg Na_2WO_4	86 €
PTA	2 mol%	7 kg $C_{12}Me_3NCl$	35 €
H_2O_2	2.5 eq.	225 kg H_2O_2 (50 wt.%)	78 €
Total costs			**199 €**

2.7. Oxidation with N-oxyl radicals

Former research showed, that short-chained alcohols could be oxidized with $NaClO_2$ and catalytic amounts of TEMPO without the need of organic solvents. However, the used alcohol hexanol is quite soluble in water (app. 6 g/L), at least compared with the alcohols and acids contained in (split) RBW (palmitic acid, $C_{16}O_2H$: app. 7 mg/L). Therefore, it was not certain whether this expertise could be transferred to the given problem. .[64,116,125]

2.7.1. Small scale experiments

First experiments with TEMPO

First experiments with the model substrate hexadecanol showed, that 0.6 mg of TEMPO (0.5 mol%) with 94 mg of $NaClO_2$ (1.05 eq.) in 0.5 mL of water and a catalytic amount of hydrochloric acid (HCl) were sufficient to oxidize 0.2 g of $C_{16}OH$ (batch experiment 2). Without HCl no oxidation occurred for one hour, while the addition of a catalytic amount of HCl led to 99 % oxidation of $C_{16}OH$ to $C_{16}O_2H$.

Besides the absence of organic solvents, this reaction is a modification of *Zhao's* modification of *Anelli's* oxidation (compare 1.6.3). The hydrochloric acid ensured two conditions, which are critical for alcohol oxidation that shall gain acids with TEMPO and chlorite. First, a catalytic amount of hypochlorite ions was ensured by either synproportion of chloride (Cl^-) with chlorite (ClO_2^-) ions, or disproportion of chlorite ions. As depicted in figure 13 the hypochlorite is necessary to oxidize the precatalyst and start the catalytic cycle. The second not so obvious reason is a decrease in pH-value, which accelerates the reaction(s). The oxidation potential of ClO_2^- is higher in acidic than in alkaline mediums and TEMPO is faster oxidized to its corresponding nitrosonium ion under more acidic conditions.[126,127]

Similar reactions with split RBW showed no satisfying results in oxidation. When all $NaClO_2$ was added at the beginning of the reaction regularly chlorine gas evolved (detectable due to its green appearance) which is dangerous in higher amounts and should be reliably omitted before any up-scale of the reaction (furthermore the production of chlorine gas is also a way of decaying the oxidant thereby increasing the necessary amount thereof for complete oxidation). A possible solution was found in literature, as it suggested the use of buffered systems and continuous addition of the $NaClO_2$ over time.[90]

The first buffered system employed was the acetic acid / acetate system (HOAc/NaOAc). Acetic acid proved to be well working in the acidification of the split ester (compare 2.4) and should not interact undesirably with the chlorine chemistry, as carboxylic acids are already present from the acyl side of the esters and will be produced in the reaction. In order to certainly be able to start the catalytic cycle NaOCl was added in catalytic amounts. A series of reactions with 0.5 g of $C_{16}OH$, 1 mL of aqueous phase, 20 µL of NaOCl (5 % free Cl_2) and 1 mL of 24 wt.% $NaClO_{2(aq.)}$ (added over 20-60 minutes) at 95 °C led to the conclusion, that the buffer should have a certain minimum concentration, otherwise phase transfer agents are necessary for the reaction (compare table 39). In 0.5 M HOAc/NaOAc buffer TEMPO oxidized $C_{16}OH$ sufficiently. With a 0.2 M buffer medium no reaction occured without further additives, whereas with 2.5 mol% of sodium dodecyl sulfate (SDS) oxidation reached app. 80 %.

With these experiments done with $C_{16}OH$ it was possible to do the first successful reactions with split wax. At this point in time the wax had been split successfully with 1.9 eq of NaOH. In order to gain a 1:1 HOAc/NaOAc buffer 3.8 eq. of HOAc were needed. The C_{30}-oxidation was thereafter successfully accomplished to 92 % with 0.9 mol% of TEMPO, 0.5 mol% NaOCl and 1.5 eq. of $NaClO_2$ (compare batch experiment 3). Already at this point the method applied demonstrated a certain superiority compared to the original oxidation process for MW and the patented method to oxidize RBW (compare 1.5.1 and 1.5.3). The method does not only omit the use of any transition or heavy metal, but regarding chemical costs it is also cheaper than the MW-process and comparable with the oxidation of split RBW with Cr(VI) or H_2O_2. Table 9 shows all used chemicals and their projected costs for 1 ton of RBW.

Table 9: Estimation of the costs for chemicals to oxidize 1 t of RBW oxidation with TEMPO/$NaClO_2$ in a NaOAc/HOAc-buffer.

RBW splitting and oxidation			
Chemical	**Eq. or mol%**	**[kg/t(RBW)]**	**[€/t(RBW)]**
NaOH	1.9 eq. OH^-	106	36
HOAc	3.8 eq. H^+	318	85
TEMPO	0.9 mol%	1.9	139
NaOCl (11-14 % Cl_2)	0.5 mol%	7	6
$NaClO_2$ (80%)	1.5 eq.	225	286
Total costs			**552**

This first estimation of chemical costs offered several points for improvement: As already known from chapter 2.4 the amount of sodium hydroxide can be lowered to 1.3 equivalents without lowering the conversion or quality of the product, thus also reducing the amount of HOAc to 2.6 eq. (if the method had not been evolved further). Similarly, the amount of $NaClO_2$ seemed rather high with 1.5 eq., as in theory 1.0 eq. of this oxidant would be sufficient and a reduction of the amount should therefore be possible.

The costs for hypochlorite were rather difficult to find, as it is not stable in its pure form but only in solution. Therefore, it is usually not produced and transported in high quantities. Its concentration is usually specified by “% free chlorine”, often in rather vague ranges. Due to this comparable low stability (in comparison with the other herein used chemicals) the concentration may change and it is worth the question whether this could affect the overall reaction. In this reaction $HOCl/OCl^-$ acts as a reaction accelerator and is an important intermediate in the catalytic cycle. Hence, a certain minimal amount of $HOCl/OCl^-$ is necessary in the reaction mixture. However, due to the quality of the sodium chlorite, which is usually available as “technical quality”, and the tendency of chlorite ions to disproportionate in acidic solutions to hypochlorite and chlorate (OCl^- and ClO_3^-) it may not be necessary to add this reagent at all. If the disproportionation was not sufficient, there would also be alternative ways to in-situ create HClO with more stable chemicals. In general, this could be done by utilizing chlorine gas, hydrochloric acid, some chloride salt (e.g. NaCl), trichloroisocycanuric acid (TCCA), addition of an aldehyde or electrolyses. Chlorine gas might not be the best alternative due to safety issues (gas, corrosive, extremely toxic). If hydrochloric acid, NaCl or KCl were applied the chloride ions should synproportionate with chlorite ions to form hypochlorite ions. TCCA is most notably known for its application in swimming pools, setting free hypochlorous acid to disinfect the water. An additional aldehyde would generate hypochlorite by reduction of chlorite.[35,128]

Last but not least, the costs for the catalyst TEMPO needed to be taken into account. With 25 % of the whole chemical costs these were not to be underestimated. TEMPO is usually not sold in bulk, therefore it is rather a speciality with a high price. For laboratory applications there are many derivatives existing of which the following were investigated regarding their catalytic ability to oxidize alcohols in comparison with TEMPO: 4-acetamido-TEMPO (AA-TEMPO), 4-methoxy-TEMPO (MeO-TEMPO), 4-hydroxy-TEMPO (OH-TEMPO), 4-oxo-TEMPO (Oxo-TEMPO), 2-azaadamantane-N-oxyl (AZADO) and 9-azabicyclo[3.3.1]nonane N-oxyl (ABNO). Reactions performed with AZADO and ABNO derivatives are often much faster due to less steric hindrance at the radical group, but these chemicals are also much more expensive, whereas many direct derivatives of TEMPO are considerably cheaper than TEMPO. Especially OH-TEMPO is much cheaper, costing less than 10 % of TEMPO due to being a precursor to TEMPO (compare table 55 and 56).[129-132]

In agreement with the cooperation partner derivatives of TEMPO were tested and also the use of other acids. HOAc has a distinctive smell with an odour threshold of approximately 1-5 ppm and is painful in high concentrations.[125] For laboratory experiments and even for large-scale productions in factories this may rather be a minor issue, but not for end-consumers. Products for private consumers, e.g. cosmetics may not smell displeasingly. To avoid smelling products intensive work-up (washing or evaporation of acetic acid) and a reliable analytical test would be necessary. Even with such precautions it may always happen, that some customers are more sensitive than any analytical device or the analyst in the quality management. Hence an alternative to acetic acid with no smell would be much preferred.

Addition of catalyst

For industrial chemists, probably the most interesting of these parameters is the necessary catalyst loading. A perfect catalyst should still be active in minimal amounts, as it shall not decay due to the performed reactions. However, TEMPO is considered instable to heat and "oxidizing conditions" (which both apply in this reaction).[133] One possibility to lower decomposition of TEMPO is to shorten the time it is exposed to such conditions without actually catalysing the reaction. This can for example be achieved by simultaneous addition of TEMPO and oxidant. Compared with an equal amount of catalyst added before the oxidant, the simultaneously added TEMPO molecules have to perform the same number of molecular reactions, however, a great ratio of the catalyst is only exposed to the heat for shorter duration. As expected, experiments with simultaneous addition of TEMPO and the oxidizing agent $NaClO_2$ resulted in higher conversions (compare diagram 12 and table 40). These experiments were performed with lowered catalyst loading not sufficient to achieve complete conversion in order to reveal differences in performance. With a catalyst loading of 0.06 wt.% (0.3 mol%) C_{30}-oxidations of app. 63 % (catalyst added prior to oxidant) were increased up to app. 76 % (catalyst and oxidant added simultaneously). At the same time another experiment was performed in which catalyst and $NaClO_2$ were added simultaneously but no hypochlorite was added to the reaction. Results showed a C_{30}-oxidation of 65 %, which is still higher than the oxidation when the hypochlorite and TEMPO were added prior to $NaClO_2$. This experiment assured that additional hypochlorite is no set necessity in the overall reaction and might be neglected in following reactions and cost calculations. Due to uncertainty whether this may or may not apply to all conditions, NaOCl was still added to reactions by default and its avoidance would be reconsidered as one of the very last steps. The next question to be examined was how much catalyst is actually needed to achieve full or at least sufficient oxidation.

Two sets of experiments are reported here regarding this question. In one set of experiments catalyst and $NaClO_2$ were added simultaneously within two hours, whereas the other set of experiments were conducted by prior addition of the catalyst and faster addition of the oxidant within one hour. As can be seen in diagram 13 there was significant difference at very low catalyst loadings of app. 0.25 mol% for which the simultaneous addition turned out with 16 % higher C_{30}-oxidation. When going to catalyst loadings of 0.5 mol% and higher there was no significant difference observable anymore and both methods gained high oxidation rates. As the experimental effort is slightly higher for the simultaneous addition and the amount of necessary catalyst did not alter significantly for the intended high C_{30}-oxidations, further experiments were done by adding the catalyst prior to the $NaClO_2$.

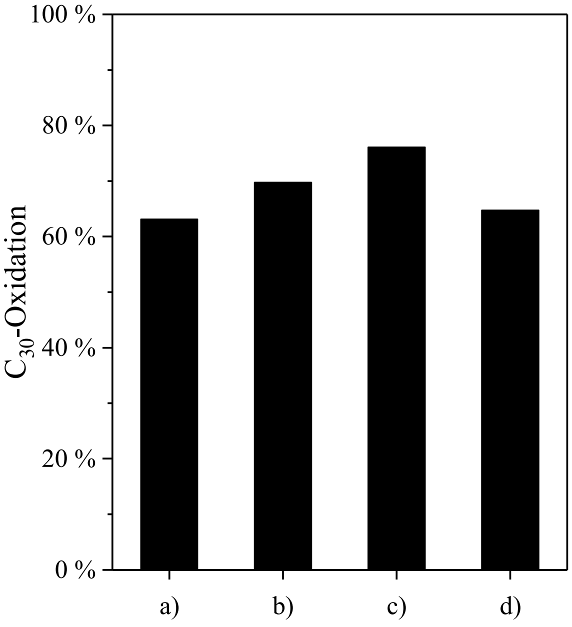


Diagram 12: Difference when adding TEMPO a) prior to $NaClO_2$, b) 50 % prior and 50 % simultaneous to $NaClO_2$, c) simultaneous to $NaClO_2$, d) simultaneous to $NaClO_2$ without NaOCl.

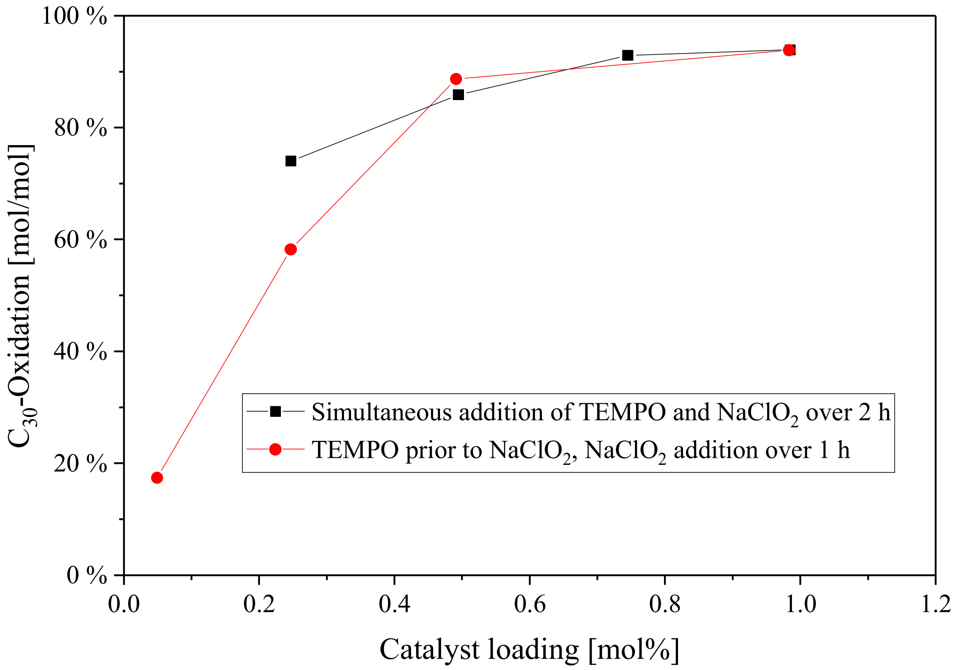


Diagram 13: Influence of catalyst loading for TEMPO (compare table 40).

Effect of phase transfer agent SDS

Due to using water as the only liquid besides the molten wax/alcohol the reaction is two-phased and the utilization of a phase transfer agent (PTA) might increase the oxidation. However, the addition of SDS (sodium dodecyl sulfate) proved to influence the oxidation with TEMPO only slightly. In a first attempt 0 to 3 mol% of SDS were added, achieving a slight increase of oxidation with 0.7 and 1.4 mol% but a decrease with 2.7 mol% (compare diagram 14). Examining low amounts of SDS revealed, that it generally increased the oxidation slightly but not significantly (up to 5 %). As the effect was rather small and other parameters have greater influence on the reaction, it was decided to keep the system as simple as possible and go without PTAs.

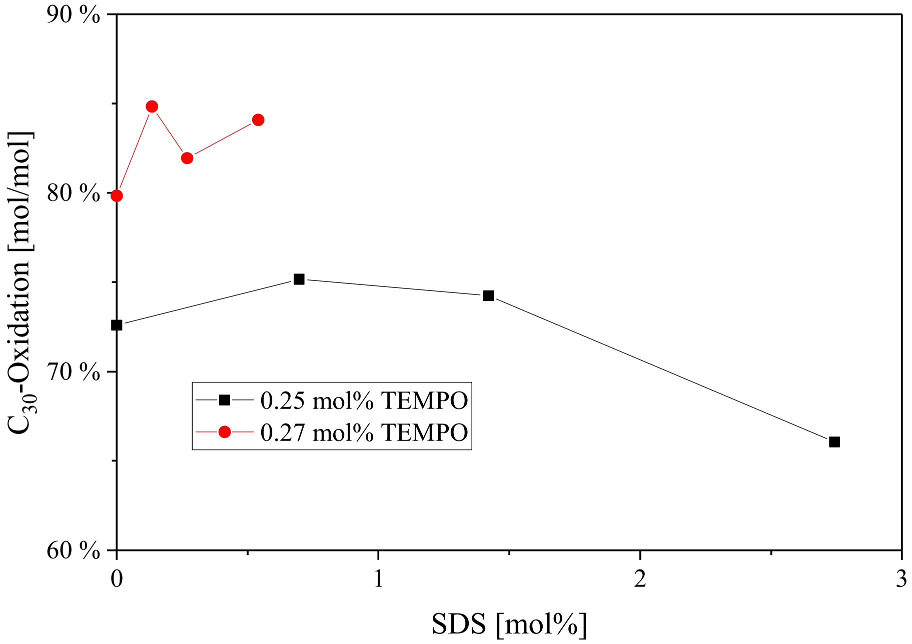


Diagram 14: Influence of sodium dodecyl sulfate on the oxidation of split RBW (table 41).

Amount of $NaClO_2$

Using unnecessary high amounts of $NaClO_2$ has several disadvantages besides simply being a waste of chemical reagents and therefore money. During the reaction the formation of chlorine (Cl_2) is more likely with higher chlorite concentrations. As this gas is highly reactive and poisonous, precautions have to be made for its potential occurrence, but most preferable none of this gas is formed due to the right process control. After the reaction the waste water needs to be disposed of or recycled. For waste water with higher chlorite concentrations, these processes might be more complex and therefore more expensive. Furthermore, possible side-reactions may become more likely with higher chlorite concentration, possibly decaying the catalyst or lowering the product quality.

As RBW derives from natural products the necessary amount of oxidant may vary for different batches and should therefore always be determined before oxidizing an unknown substrate. Similarly, $NaClO_2$ is usually sold as a rather unpurified (bulk) chemical with only 80 % pureness and each batch should be tested to its actual oxidizing capability.

The experienced coherence of the amount of oxidant and C_{30}-oxidation is displayed in diagram 15. For up to 1.1 eq. $NaClO_2$ the C_{30}-oxidation increased nearly linear, whereas for higher amounts of $NaClO_2$ the oxidation only increased marginally. With 1.3 eq. the highest oxidation was accomplished whereas with 1.4 eq. the oxidation decreased in these experiments. This may be due to already mentioned not perfect mixing, solubility effects, side-reactions (destruction of the catalyst) or chlorine formation, which was difficult to monitor in the small scale experiments. The following experiments would be done with 1.2 to 1.3 eq. of $NaClO_2$, as this slight excess of oxidant should compensate for possible varieties of RBW or $NaClO_2$.

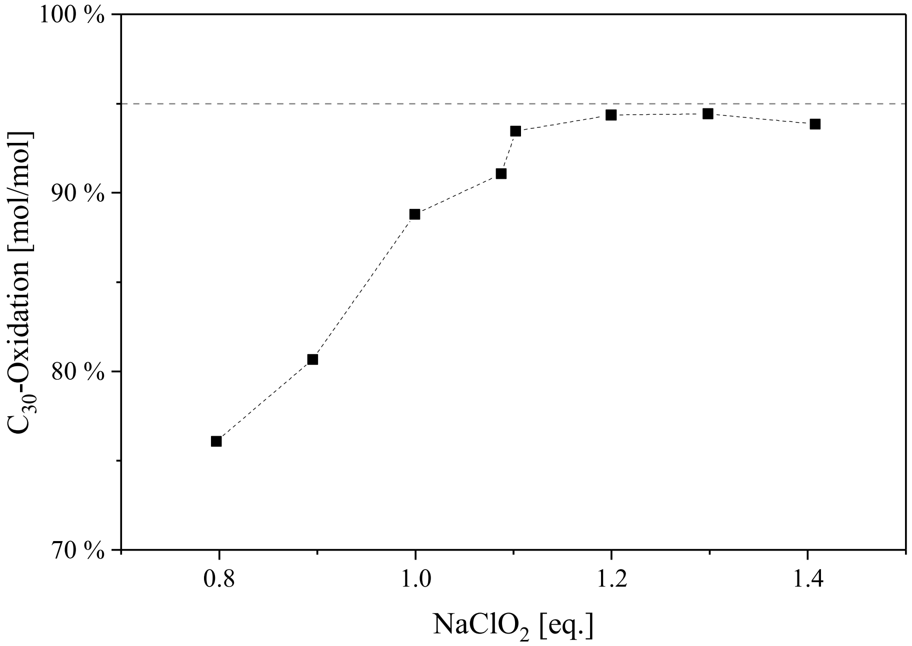


Diagram 15: Oxidation of split RBW depending on the amount of $NaClO_2$ (compare table 42). 95 % C_{30}-oxidation was the expected maximum, compare diagram 1.

Cheaper catalyst: OH-TEMPO

As stated earlier, TEMPO is not the only N-oxyl radical catalysing alcohol oxidations. The most interesting derivative or rather precursor being OH-TEMPO. This chemical is easily formed by a four step synthesis, starting by condensing three molecules of aceton to phorone, addition of ammonium, reduction of the keto-group and oxidation of the amine-group (compare figure 24). In academia OH-TEMPO is used rather for the synthesis of other TEMPO-derivatives like MeO-TEMPO or polymer-bound TEMPO than as a catalyst. In industry it is used as a radical controlling agent for the production of polymers.[134]

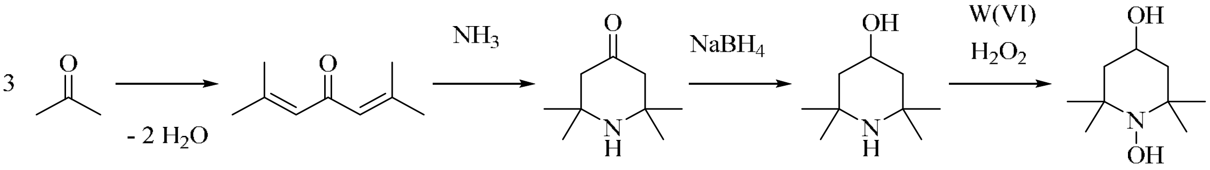


Figure 24: Schematic synthesis of OH-TEMPO.

First experiments with $C_{16}OH$ revealed, that at the same conditions OH-TEMPO was less active than TEMPO, only achieving app. 32 mol% $C_{16}O_2H$ in a 0.5 M HOAc/NaOAc buffer. An interesting tendency was observed, as OH-TEMPO was more active if the reaction was acidified with pure acetic acid instead of a buffered solution (compare table 43). This may not be contradictive but at least interesting if compared to other research results using *Anelli's* oxidation with NaOCl.[126,135] In these reactions fastest oxidations with TEMPO and AA-TEMPO are achieved at pH values of 8-9 although the formation of the nitrosonium ion, which is stated as the active oxidation state, is faster at lower pH values. This may be due to another mechanism for the oxidation of the aldehyde, as these reactions were conducted using NaOCl as oxidant and water soluble substrates which therefore are more prone to hydration in water forming geminal diols that are oxidizable by TEMPO. In *Zhao's* modification the aldehydes are oxidized by ClO_2^- which shows higher oxidation potentials at lower pH values.[127]

As the ideal pH value for the oxidation with OH-TEMPO was unknown, it was decided to use 1 mol% of citric acid (CA) to acidify the reaction. CA is a three based acid with pK_a values of 3.1, 4.8 and 6.4 so that a buffer medium from pH 3 to 7 might be established. As no literature procedure was found regarding oxidations with a CA buffered medium and OH-TEMPO as catalyst, it was decided to lower the amount of oxidant in order to lower the risk of "overshooting" the ideal pH-value. 0.5 eq. of $NaClO_2$ were added within one hour, slowly raising the pH value. Under these conditions 26 % $C_{16}O_2H$ were gained with 0.8 mol% OH-TEMPO, whereas with additional 0.9 mol% of SDS oxidation was increased to 41 mol%. This proved the general ability of utilizing OH-TEMPO instead of TEMPO. To generalize this approach and to exclude the possibility of citric acid being critically involved in the catalytic cycle, experiments with phosphoric acid were conducted (this time aiming at full oxidation of the alcohol with 1.2 eq. of $NaClO_2$). 1.7 mol% OH-TEMPO with 0.6 mol% H_3PO_4 achieved over 67 % oxidation of $C_{16}OH$ to $C_{16}O_2H$, being increased to 80 % when the amount of acid was doubled (interestingly, these values were beaten when using 0.9 or 1.4 mol% of AA-TEMPO, achieving ≥95 % successful oxidation to $C_{16}O_2H$; table 44).

Performing similar reactions with split RBW as substrate revealed that OH-TEMPO and other derivatives thereof oxidize split RBW very well, whereas TEMPO is inactive under such conditions (diagram 16). It is remarkable, that nearly any TEMPO derivative besides TEMPO itself and 4-Oxo-TEMPO showed high activities under these conditions and work as catalysts for this reaction. As TEMPO is active under more acidic conditions (HOAc/NaOAc buffer) and also under more alkaline conditions (usual oxidation under *Anneli's* conditions), it is assumed that TEMPO is not soluble enough in the aqueous phase and rather stays in the organic phase. In this case its oxidation by NaOCl cannot occur sufficiently and hence the substrate may not be oxidized.

Looking at the structures of these TEMPO-derivatives (figure 25) brings up the assumption, that OH-TEMPO may show lower conversions than some other derivatives due to instability of its hydroxyl group. By oxidation of this functional group Oxo-TEMPO would be formed which is practically inactive under these conditions. Protection of the hydroxyl-group therefore might increase the stability of the compound and result in better oxidation of the substrate. Regarding the costs OH-TEMPO is by far the cheapest catalyst (compare table 55 and 56) and at this point it would only be reasonable to use another derivative if it showed an exorbitantly higher turnover number (TON) or could easily be synthesized from OH-TEMPO or its precursors.

Exemplarily MeO-TEMPO and AA-TEMPO were tested regarding their oxidation capabilities at lowered catalyst concentrations (diagram 17). The activity of MeO-TEMPO decreased rapidly by lowering its concentration to 1.4 mol%. However, AA-TEMPO still converted the wax quantitatively with a catalyst loading of 1.4 mol% and over 50 % C_{30}-Oxidation was monitored with 0.7 mol% AA-TEMPO. Without further proof or tests there are two theories for this diverging behaviour at lowered catalyst concentrations. For MeO-TEMPO it is possible that an oxidation of the ether group occurs and the catalyst becomes inactive by formation of 4-Oxo-TEMPO or another inactive compound. Another possibility is that due to the ether group MeO-TEMPO is less soluble in water and therefore not sufficiently oxidized by NaOCl. The functional group of AA-TEMPO is more polar and it will therefore be more easily reoxidized in the aqueous phase.

Besides these soluble TEMPO derivatives there are a number of immobilized catalysts. Two of them were exemplarily tested, TEMPO immobilized on Silica and on a styrene derived polymer. Some oxidation was achieved with these, but they were not nearly as efficient as molecular derivatives and also re-esterification was monitored (see diagram 16).

Due to the "unbeatable" low price of OH-TEMPO (compare table 55 and 56) and no observed superiority justifying the use of another catalyst, further experiments were done with OH-TEMPO.

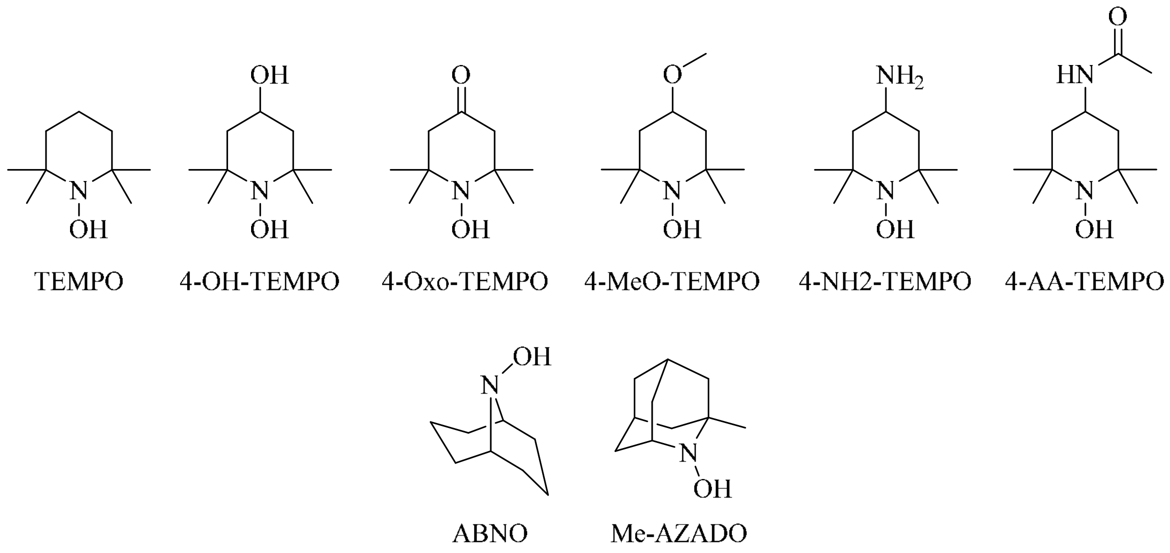


Figure 25: TEMPO derivatives investigated for oxidation of RBW.

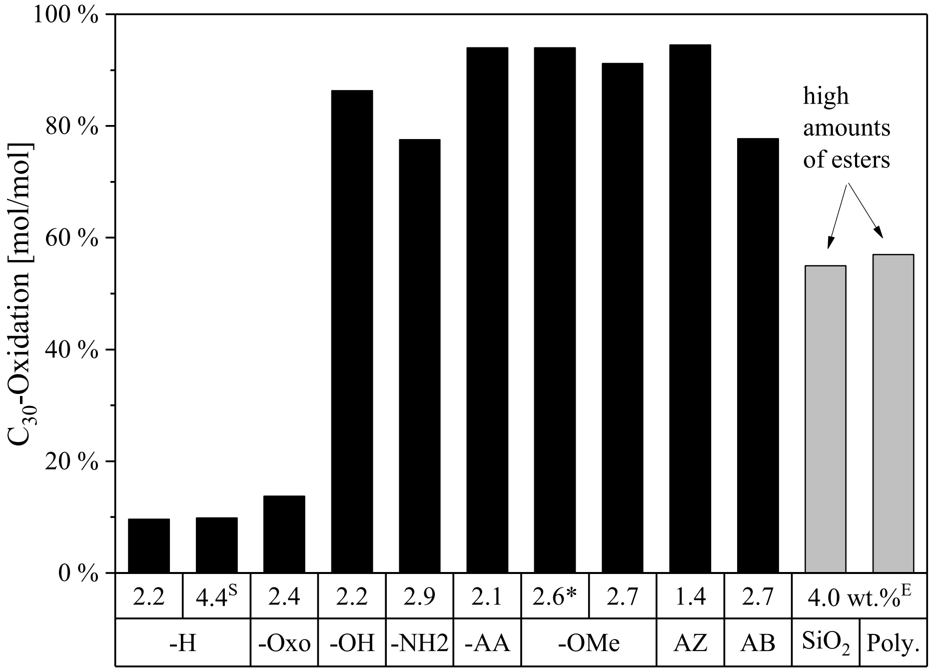


*Diagram 16: Oxidation of split RBW with different N-oxyl radicals (compare table 45). For direct derivatives of TEMPO the functional group at position 4 is given (compare figure 25). AZ = Me-AZADO, AB = ABNO, SiO_2 = TEMPO on SiO_2, Poly. = polymere bound TEMPO. [S] 0.1 mol% SDS added. * H/NaOAc-buffer instead of H_3(CA) was used. [E] High amounts of re-esterification, app. 32 % for SiO_2 and 21 % for Polymer based TEMPO.*

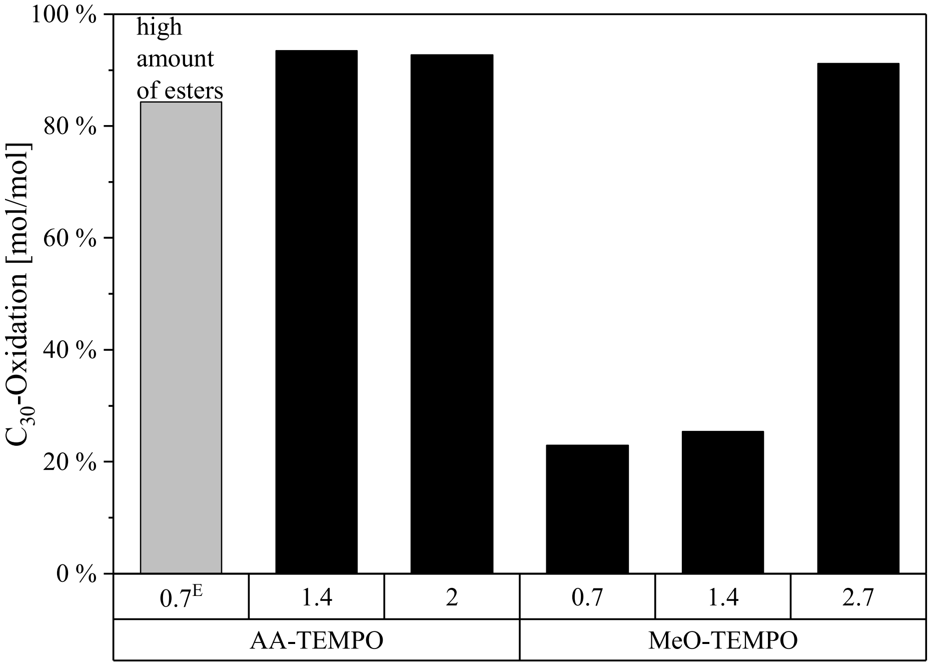


Diagram 17: Oxidation of split RBW with differing catalyst concentrations of MeO-TEMPO and AA-TEMPO (compare table 46). ^{E} App. 40 % of re-esterification.

Finding the right pH-value for OH-TEMPO

As experienced before, OH-TEMPO cannot be used as efficiently as TEMPO in the very same NaOAc/HOAc system, yet technically OH-TEMPO can take over the catalytic function to oxidize alcohols with $NaClO_2$.

The so far applied separation of aqueous and organic phase prior to oxidation with OH-TEMPO complicated the overall process and also bore an increased probability for re-esterification. It would be of great benefit, if an acid could be added to the split wax that established a buffered system in which OH-TEMPO is comparably active as TEMPO in its NaOAc/HOAc system. A valid replacement might be citric acid (CA) which already showed its general compatibility with OH-TEMPO. As stated before, CA is a three-basic acid with pK_a values of 3.1, 4.8 and 6.4 and therefore all pH-values between 3 and 7 could be buffered. CA is a natural intermediate of the citric acid cycle, food approved, highly water soluble (K_{OW}(CA) = -1.7; compare K_{OW}(HOAc) = -0.3), without odour for humans and industrially produced, therefore reasonable in price for large-scale applications.[136-138]

In order to avoid major re-esterification because of too acidic conditions the following experiments with CA were conducted in the rather high pH ranges of the buffer. Another benefit of oxidation in “high” pH ranges would be a lower amount of acid, making the overall process cheaper.

Having a look at the acid constants of citric acid, Na_3(CA) would show a basic pH value, whereas $Na_{2.5}H_{0.5}$(CA) should have a pH of 6.4, Na_2H_1(CA) of about 5.1 and $Na_{1.5}H_{1.5}$(CA) of 4.8. These values are rather theoretical, as with split RBW there are also the long-chained acids of the wax present. These have a low solubility in water, but will interact in the acid-base equilibrium to a certain degree, depending on the water-wax ratio and other parameters.

The results show an interesting progress of oxidation depending on the buffer medium used. As can be seen in diagram 19, buffered media with higher salt concentrations (1.2 or 1.5 eq. Na^+) showed best oxidation if the buffer consisted of Na_2H_1(CA) and it was still good when Na_3(CA) or $Na_{1.5}H_{1.5}$(CA) were used. Systems consisting of $Na_{2.5}H_{0.5}$(CA) were by far worst in this scenario. For systems with lower salt concentrations this trend still persisted, albeit that the oxidation was best in the system with the highest amount of CA, being the $Na_{1.5}H_{1.5}$(CA) system. This was probably due to the fact, that this system could better cope with the addition of alkaline $NaClO_2$.

Overall these results were very promising, as they stated the possibility to acidify the split wax and subsequently oxidize it with OH-TEMPO without the need to separate the split wax from the aqueous phase. This means one less individual production step, simplifying the process, reducing the probability of re-esterification, therefore increasing the product quality, saving time and money.

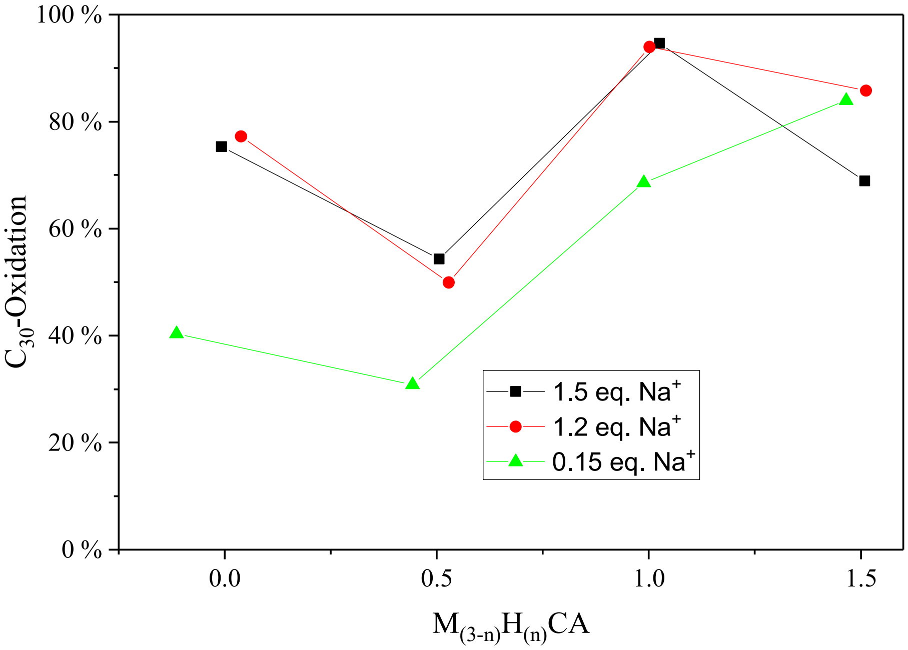


Diagram 18: Different buffer concentrations and compositions influencing the C_{30}-oxidation (table 48).

Increasing volume efficiency

Another aspect, which is rather unimportant in (small) lab scale experiments, but of considerable importance for large scale applications is the yield per volume. For total synthesis often high amounts of solvents are used to avoid undesirable side-reactions. In the reactions performed in this work rather high volumes of water were used, in order to lower the effect of evaporation and admittedly also for ease of preparation. To react 1 g of wax usually 3-4 mL of water were used in total, resulting in app. 1 g(RBW)/5 mL volume efficiency.

In order to see, what influence the wax/water ratio has on the reaction, experiments with varying water volumes were conducted (initial wax/water ratios ranging from 6:1 to 1:1). Each experiment was performed with 1.5 g split wax, 2 mol% CA, 2.9 mol% OH-TEMPO and slow addition of 1.2 eq. $NaClO_2$ in 0.5 volumes of water (total wax/water ratio after $NaClO_{2(aq.)}$ addition: 3:2 to 2:3). The results showed no significant difference in oxidation, all being excellent with C_{30}-oxidations in the range of 93.8 to 94.4 % (compare table 47).

Testing again pH dependency of OH-TEMPO with lower water volume and KOH instead of NaOH resulted in an overall increase of oxidation. By lowering the total amount of water from 3 mL/g(wax) to 1.5 mL/g(wax) the variation of oxidation was reduced significantly. As depicted in diagram 19, oxidation varied between 90 to 94 % with buffer systems ranging from K_3(CA) to K_2H(CA) (compare table 49). As an increase in oxidation was already monitored with just increased buffer concentrations, the change from NaOH to KOH is considered less important than the decreased water volume. Due to lower volumes the concentrations per volume of catalyst, oxidant and substrate were increased significantly. Therefore, reactions between any two species have higher probabilities and the overall reaction is faster.

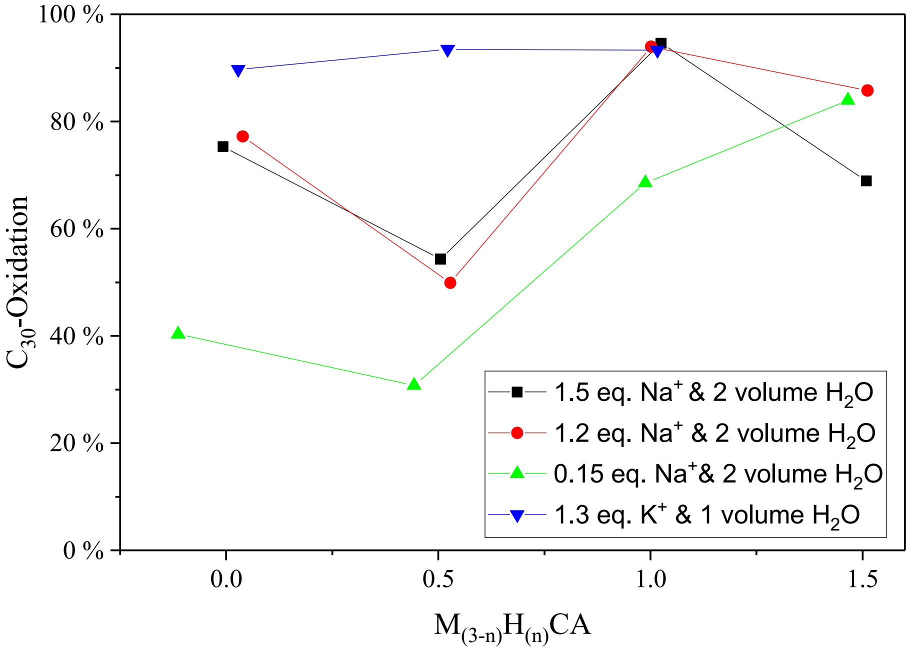


Diagram 19: Influence of higher overall concentrations on the C_{30}-oxidation (compare table 48 and table 49).

Avoiding NaOCl

As stated earlier NaOCl is an intermediate in the catalytic oxidation with N-oxyl radicals. In academic literature it is often used as oxidant or added in catalytic amounts to accelerate the oxidations with $NaClO_2$. To oxidize split RBW in combination with the NaOAc/HOAc buffer it was already proven that it is not necessary to add NaOCl (compare diagram 12). In order to see, whether this is valid for only these conditions or more generally applicable, further experiments were conducted.

To eliminate influences by impurities of the wax, experiments were executed with $C_{16}OH$. As depicted in diagram 20 the alcohol is not oxidized in a system containing 0.6 mol% CA without NaOCl. However, if 0.3 mol% NaOCl are added or the amount of CA is tripled to 1.9 mol%, the alcohol is converted to the corresponding acid in significant amounts. Conversion was also achieved when 0.6 eq. $K_2H(CA)$ was applied (compare table 51).

Additional glyoxal, NaCl, or $C_{18}O_2H$ did not result in significant alteration of the product distribution (diagram 20). The slightly lowered oxidation with glyoxal can be explained by utilization of oxidant by the reagent. In the experiment with $C_{18}O_2H$ more esterification occurred, presumably due to the higher concentration of carboxylic acids. For the split RBW similar results were obtained, no NaOCl is needed under acidified (2 mol% CA) or buffered (0.6 eq. $K_2H(CA)$) conditions for the oxidation (compare table 52).

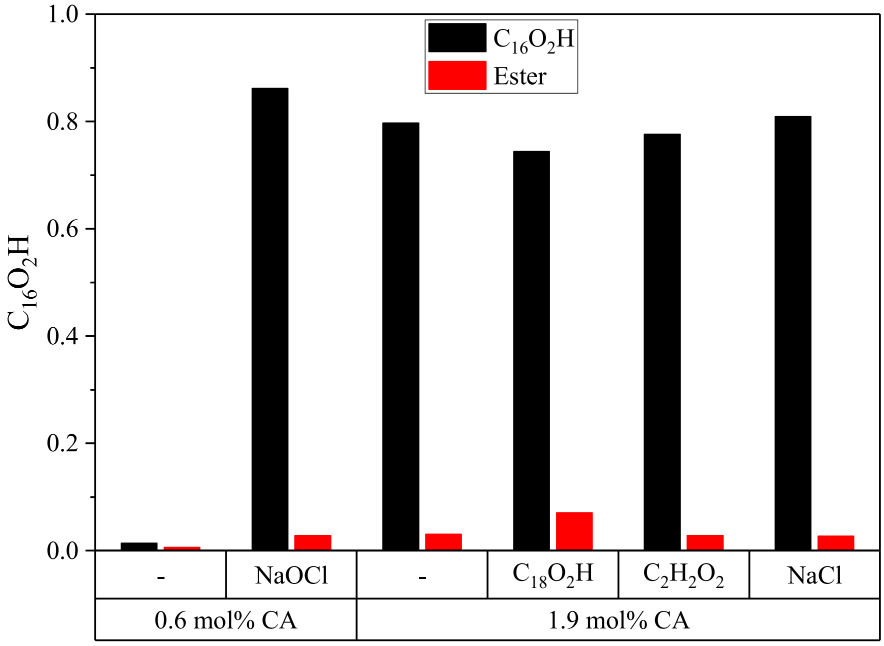


Diagram 20: Oxidation of $C_{16}OH$ proving additional NaOCl unnecessary under the right conditions (compare table 51).

Speeding up of the reaction

Last but not least another general aspect of interest is whether the time for addition of $NaClO_2$ is relevant for the oxidation. As prolonged addition was not considered of interest for industry and addition within two hours already yielded excellent results, time intervals were shortened to 15 and 30 minutes in exemplary experiments. The results showed that the sped up addition of $NaClO_2$ is no problem for these small scale experiments. With 1.3 mol% of OH-TEMPO the reactions reached >93 % C_{30}-oxidation, when lowering the amount of catalyst the oxidation did not decrease significantly but higher amounts of esterification were monitored which is undesirable for the reaction in general (table 50).

For large scale experiments the addition of oxidant needs to be reconsidered in agreement with the cooling capabilities of the reactor as the reaction is quite exothermic and may heat up the reaction beyond the boiling point of the aqueous phase. In one up-scaled experiment just this still happened. The cause is supposed to be not thoroughly molten wax. When the split wax had been acidified and the catalyst was added, the addition of $NaClO_2$ was started. Apparently the temperature meanwhile had dropped so far that the wax had partially solidified upon addition of the acid and the oil bath had not accomplished complete liquefaction of the wax before the oxidant was added. Due to the addition of oxidant with room temperature the two-phase reaction was not heated up thoroughly, until at some point the oxidation reaction reached a critical point and was exothermic enough to heat up the whole reaction mixture. As can be seen in figure 26 the reaction mixture only had a temperature of app. 82 °C and slowly started to heat up 75 min after starting the addition of $NaClO_2$. The temperature increased steadily until app. 105 min and 90 °C, when the temperature increased rapidly up to the boiling temperature of the aqueous phase. That temperature was kept for app. 10 minutes until most alcohols had reacted and no additional heat of the reaction was freed.

The overall reaction enthalpy can be considered to be app. 596 kJ/mol, i.e. 795 kJ/kg(RBW), as can be calculated from enthalpies of formation from shorter chained derivatives (i.e. the reaction of ethanol to acetic acid, compare figure 27). For comparison, the reaction enthalpy of the splitting is app. 80 kJ/mol (compare chapter 2.4 and figure 21). Estimating the possible "heating potential" of this reaction, 1 kg of RBW may cover for 2 kJ/kg/K and app. 1.5–2 kg of aqueous phase with app. 4 kJ/kg/K sum up to app. 8-10 kJ/K for the reaction mixture to oxidize 1 kg of RBW. This means that the temperature of an isolated system would be increased by app. 80-100 K if no wax melting or water evaporation took place. If all heat was used to evaporate water (app. 44 kJ/mol), app. 325 g (18 mol) of water would evaporate, forming app. 550 L of water vapour (at 100 °C, per 1 kg(RBW)). Similar to the reaction enthalpy of the splitting this energy needs to be taken care of. Either by efficient cooling without (partially) solidifying the wax, controlled evaporation of water or a mixture of these effects.[116]

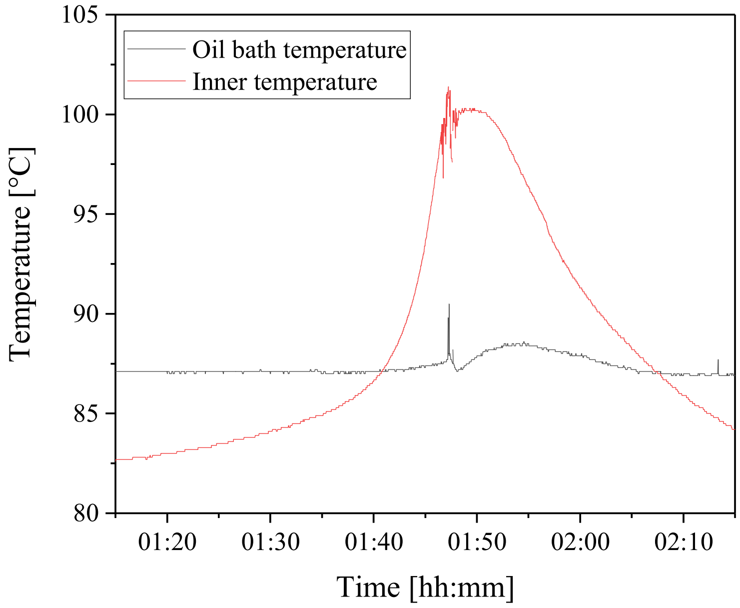
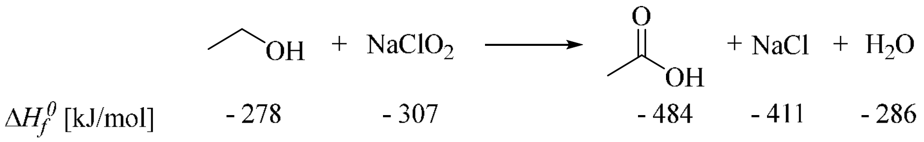


Figure 26: Temperature profile of a reaction in which the oxidation reaction was not under control.



$$\Delta\Delta H_f^0 = -596 \text{ kJ/mol}$$

Figure 27: Enthalpic consideration of the oxidation reaction. The calculation does not consider enthalpy of solvation and is only for the purpose of estimation.[116,121]

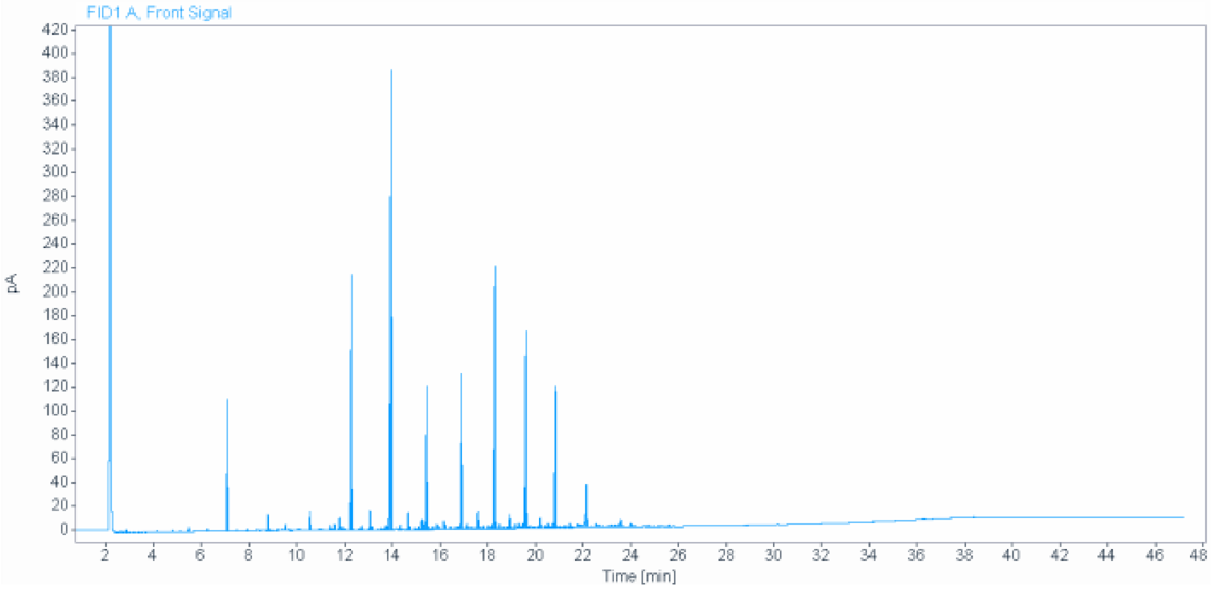
2.7.2. Up-Scaling

Simultaneously to optimizing reaction conditions of splitting and oxidizing RBW on small scale basis, experiments on larger scales were conducted. This was done in order to investigate possible challenges and conditions for further up-scaling beyond lab-scale and also to produce samples that could be analysed and reviewed by *Kahl GmbH & Co. KG*.

20 g batch reaction

One of the first larger batches was conducted with 20 g of RBW, using TEMPO in an acetic acid buffered system (batch experiment 3). Thereto the wax was split with 1.9 eq. of NaOH, acidified with 3.8 eq. of HOAc and oxidized with 1.5 eq. of $NaClO_2$, 0.9 mol% of TEMPO and 0.5 mol% NaOCl. The complete process was done as a one-pot-synthesis within a day and provided the “latest” reaction process at that point.

The measured acid value of 130 mg (KOH)/g(wax) and the “clean” chromatogram 7 show proof of a clean and efficient conversion of the wax. No re-esterification was observed and the chromatogram does not show any unexpected signals. For comparison with other (small scale) experiments, an oxidation of 92 % was reached for $C_{30}OH$ to $C_{30}O_2H$.



Chromatogram 7: 20 g scale oxidation of RBW, utilizing splitting with NaOH and a TEMPO/$NaClO_2$-mediated splitting in NaOAc/HOAc-buffer.

Experience gained by this first upscaling includes the knowledge, that the splitting is by far easier executed in bigger scales, due to the use of an over-head stirrer and slower water evaporation due to a lower surface/volume ratio. Head-space was necessary for this reaction, as the splitting was done with “diluted” base (less than 20 wt.%) and some water needed to evaporate before complete splitting. Therefore, the vessel should not be closed in order to release built up pressure.

500 g batch reaction

In this experiment H_2SO_4 instead of HOAc was used in order to see whether cheaper inorganic acids may be used for the acidification step (batch experiment 4). The mixing with the wax was expected to be hindered due to the high polarity of H_2SO_4 and its salts. Therefore, some HOAc was added prior to the inorganic acid in order to act as “phase transfer acid” and as a buffer for the highly acidic reagent. Furthermore, this experiment showed the capability of OH-TEMPO oxidizing the alcohols in only mildly acidified media.

500 g of RBW were split with 40 g of NaOH (1.5 eq.) and afterwards acidified with 20 g HOAc (0.5 eq.) and 40 g of H_2SO_4 (1.33 eq. of H^+) in app. 1.1 L of water. After settling the aqueous phase was disposed of and the wax was washed with water. 2.5 g of H_3CA (6 mol%), 3.0 g OH-TEMPO (2.6 mol%) and 12.4 g NaOCl(aq.) (5 % free Cl_2, 1.2 mol%) were added with 880 mL of water. Thereafter, 90 g $NaClO_2$, dissolved in 300 mL of water were added within 2.5 hours. The result is not perfect, as esters are present and the oxidation reached “only” 90 % with an acid value of 113.

The esters are probably due to re-esterification during the acidification. An incomplete splitting due to improper mixing cannot be ruled out completely, but is less likely as samples after the splitting did not show any sign of remaining esters. It is suspected that the sulfuric acid lead to partial re-esterification. The acid strength is for sure one reason therefore, but also less efficient mixing of aqueous and organic phase was monitored during the acidification, which is probably due to the high polarity of the acid and its corresponding salts. However, it proved that H_2SO_4 in combination with HOAc as “phase transfer acid” is in principle capable of doing this purpose, just not ideal.

1 kg batch

When the method had been further developed (one-pot-reaction, increasing volume efficiency, etc.) and the method had been tested in scales of up to 500 g, the method was tested by a further up-scaling to 1 kg (batch experiment 5).

This experiment was conducted in a 4 L flask with 1 kg of RBW. The aim was to gain experience with bigger amounts, an increased volume efficiency and also to test the behaviour of OH-TEMPO at its “worst” pH-value, in the $K_{2.5}H_{0.5}(CA)$ buffer in a large scale experiment.

The wax was split with 182 g of a 52 wt.% KOH solution (1.28 eq.) at 110-115 °C. When the wax was split after 50 minutes, the oil bath temperature was set to 95 °C and 132 g of CA were added with 900 mL of water. 6 g of OH-TEMPO in 20 mL of water and 40 mL NaOCl solution (5 % free Cl_2) were added. 180 g of $NaClO_2$ dissolved in 300 mL water were added within approximately 2.3 hours. 15 minutes thereafter the oxidation seemed to be completed (regarding GC analyses). The C_{30}-oxidation was determined to be 93.2 % and the AN could be determined to be 132 (the prior 500 g batch with the same chemicals and conditions reached 92.6 % C_{30}-Oxidation and an AN of 129). 1031 g of wax were yielded after washing (1042 g would have been the theoretical yield for a wax consisting of 100 % ester with an average molecular weight of 755 g/mol).

This reaction proved the small-scale developed principle of lowered reaction volume and further showed that the reaction does not need extensive acidic conditions in order to gain high oxidations and ANs. Recalculating the costs for an up-scaled process using the same equivalents of chemicals would result to app. 425 €/t(RBW) (compare table 10).

Table 10: Chemical cost calculation for the 1 kg batch.

RBW splitting and oxidation			
Chemical	**Eq.**	**[kg/t(RBW)]**	**[€/t(RBW)]**
KOH (90 %)	1.28 eq.	106	74
Citric acid	1.56 eq. H^+	139	85
4-OH-TEMPO	2.6 mol%	6.0	28
NaOCl (14 % Cl_2)	2.0 mol%	14	11
$NaClO_2$ (80%)	1.20 eq.	180	229
Total costs			**424**

2.7.3. Possible recycling of certain chemicals

In theory any chemical but the catalyst is converted to other chemicals in the described process. In practice the catalyst decays, as can be seen when low amounts of catalysts were utilized and the conversion is not complete. However, in contrast to the decay of the catalyst the conversion of all other chemicals is reversible if the products can be separated. NaOH or KOH can be set free from salts with the addition of another lye, citric acid can be set free from its salt by addition of another acid and $NaClO_2$ (and NaOCl) can be regained from NaCl by electrolysis (and follow-up steps).

As depicted in table 11, neither NaOH, KOH or CA can compete with prices of MgO, CaO or H_2SO_4. However, these more expensive chemicals do a much better job in the herein developed process. A combination of such both advantages (cheap price, good performance) would be favourable and can be achieved for this process by recycling the alkaline lye and CA (see figure 28).

After completion of the oxidation the aqueous phase would be separated from the organic (wax) phase. This aqueous phase will contain a high amount of alkali citrate. By addition of limewash (emulsified $Ca(OH)_2$) calcium citrate ($Ca_3(CA)_2$) will precipitate and a solution of alkali hydroxide and alkali chloride will remain. After sedimentation and separation, the calcium citrate can be converted into free citric acid by acidification with sulfuric acid, and the gained CA can be reused to acidify the next batch of split wax (pretty much the same method is used in industry to isolate citric acid synthesized by fermentation). The alkali hydroxide/chloride solution could be concentrated, precipitating sodium chloride before the hydroxide. The alkali hydroxide solution could then be reused for the next batch of wax, while the sodium chloride could be sold or electrochemically reoxidized to sodium chlorite.[35,138]

*Table 11: Prices of different industrially relevant bases and acids, potentially useful in this process. *Regarding chemical prices compare appendices.*

Chemical	**M [g/mol]**	**Costs [€/kg]***	**Costs [€/kmol(H^+/OH^-)]**
Base			
NaOH	40.0	0.34	14.2
KOH	56.1	0.70	43.7
MgO	40.3	0.09	1.9
CaO	56.1	0.07	2.1
Acid			
H_2SO_4	98.1	0.02	0.78
HOAc	60.0	0.27	16.8
$H_3(CA)$	192.1	0.56	41.3

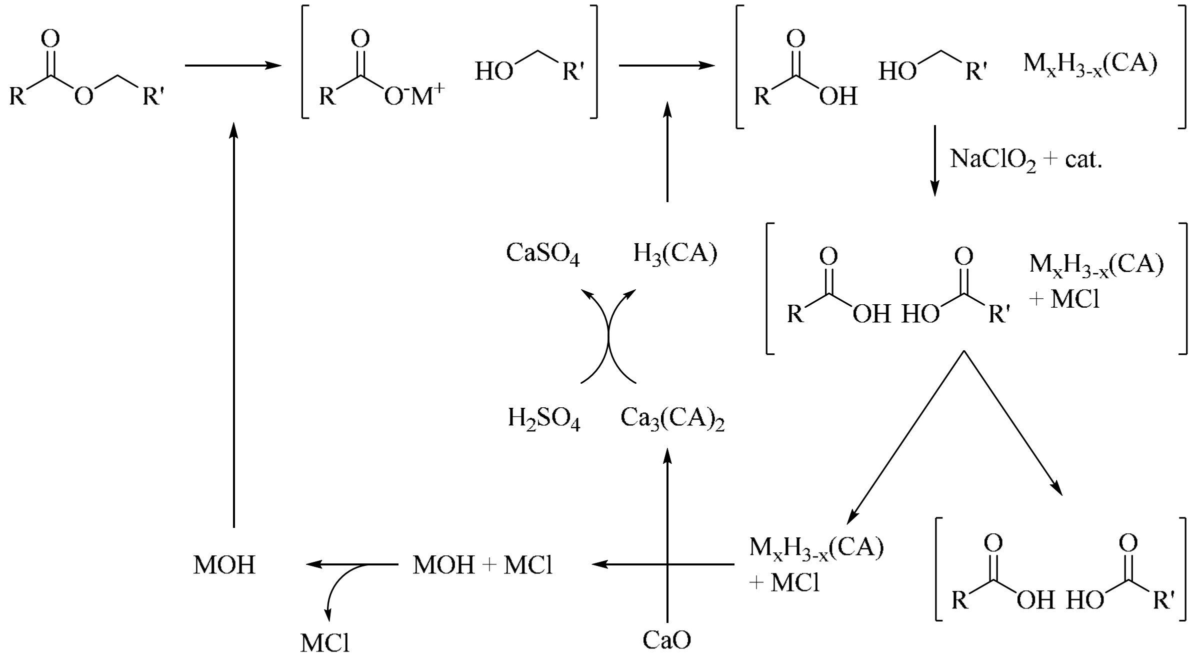


Figure 28: Schematic approach to reuse the alkaline hydroxide and citric acid by recycling them with the cheaper CaO and H_2SO_4.

In principle this seems very easy and straightforward. However, there are two uncertainties, being the behaviour of not consumed chlorite and the question whether the benefit of using KOH for lower viscosities would be compatible with this recycling.

Regarding some not consumed chlorite, it is not clear whether the chlorite would synproportionate with chloride and form chlorine, or rather disproportionate to chloride and (per)chlorate when the lye was concentrated. To circumvent this uncertainty, the slightly acidic mixture of citrates and chlorides gained after oxidation of the wax and separation of the two phases could be concentrated and if necessary slightly acidified with H_2SO_4. Thereby the equilibrium should be pushed towards the formation of HCl, ClO_2 and Cl_2, which could be reused for the production of chlorite. The following steps would not have to be altered, only more CaO would have to be added to compensate for the additional H_2SO_4 ($CaSO_4$ would precipitate alongside or prior to $Ca_3(CA)_2$).

Regarding the benefit of lower viscosities of potassium "soaps" (compare 2.4), this might not be entirely lost as a mixture of Na^+/K^+ OH^- could be used for the splitting. Therefore, the alkali hydroxide/chloride solution may only be as much concentrated as potassium chloride was still soluble but sodium chloride would precipitate. The calculation of such a system is not facile, as the aim would not be a diluted solution but a concentrated mixture consisting of the four ions Na^+, K^+, OH^-, Cl^- with less than 80, possibly even less than 50 wt.% of H_2O (compare 2.4 basic ester cleavage). However, to get some impression what might be possible, one might reduce the problem theoretically to a system consisting of Na^+, K^+ and Cl^- in water. In such a system one can calculate with the help of solubility products that by only precipitating NaCl without KCl, the potassium content might be in the range of 40 – 45 % (in mol(K^+)/mol(M^+), compare figure 29).[b] Whether this content in potassium would be beneficial enough to justify this complication in the work-up procedure can only be decided with further knowledge of the reaction at up-scaled conditions. As explained before, KOH was mainly used to prevent damage from the laboratory instruments and to ease the overall process. For industrial facilities the use of NaOH or the use of fresh KOH for each run are presumably the easier and overall more cost efficient methods.

Coming back to the potential benefit of recycling the alkaline citrate; the costs for chemicals to split and acidify could theoretically be diminished to less than 10 € per ton of RBW (compared to app. 160 €/t(RBW), compare table 10). Thus the chemical costs of the overall process would mainly depend on the oxidation itself, for which the catalyst OH-TEMPO might cost less than 30 € and the oxidant $NaClO_2$ might cost less than 230 €. Summed up the process could in theory be accomplished with less than 270 €/t(RBW) for chemicals. Whether this theoretical recycling of alkali hydroxide and citric acid is economically beneficial in reality will depend on the amount of used chemicals, the costs for the respective facilities and the running costs.

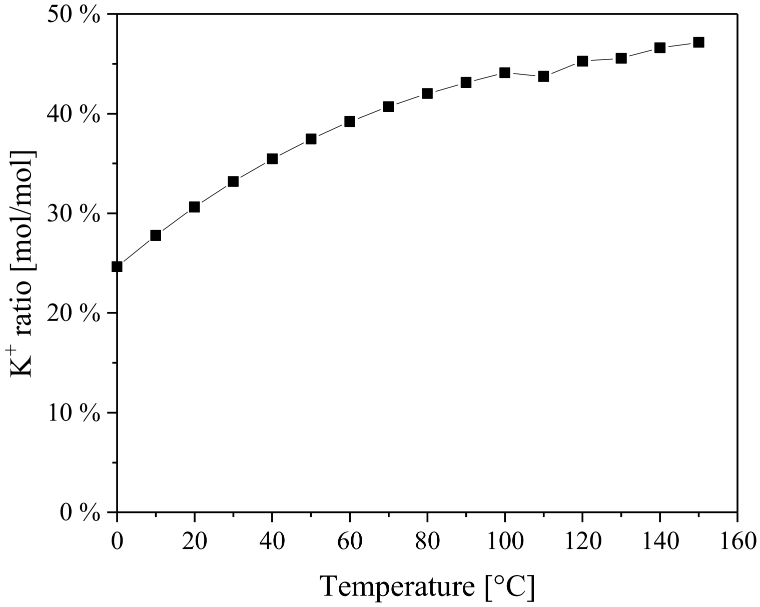


Figure 29: Calculation of maximum potassium content in a Na^+, K^+, Cl^- system by comparison of solubility products of NaCl and KCl at different temperatures (neglecting any inter-ion interferences).

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[b] As solubility products are interfering with each other to some extend and as no literature regarding the mixture of the four ions (Na^+, K^+, OH^- & Cl^-) was found, this only aids for an initial estimation.

2.7.4. N-oxyl radical conclusion

The decision to examine the oxidation of split wax instead of raw wax was probably the most critical decision in this work. With this decision many procedures from literature were in general applicable to the task and could be evaluated. The use of N-oxyl radicals quickly led to promising results when the reaction conditions were modified to fit the substrate. In contrast to literature procedures the temperature of oxidation was considerably increased and organic solvents were omitted. The turnover numbers of the catalysts were not outstanding (as catalyst loads below 0.2 mol% did not yield sufficient results, compare diagram 13). Yet in combination with the low molecular weight of the catalyst(s), its comparable low price and other favourable properties this method proved its theoretical suitability for the use in an industrial application. The method was developed and improved in several steps and is now at a point where further reduction of chemicals might (only) decrease the costs from app. 420 €/t(RBW) to app. 300 €/t(RBW) if only 1.0 eq. of KOH, CA and $NaClO_2$ were used, no NaOCl was applied and the catalyst was recycled to 100 %. This would be more than 25 % of the chemical costs, however, such reagent reduction would affect the performance and necessary reaction time of each individual reaction and the overall process. Besides the only theoretically possible recovery of 100 % still functional catalyst, the reduction of the other chemicals to 1.0 eq. would most certainly lead to lower AN and hence lower product quality. Therefore, I do not see any plausible cause to further reduce the amount of chemicals at this laboratory stage. When process parameters are found for the industrial application the amount of chemicals have to be adjusted to fit the qualities of the reagent batches and the intended quality of the final product. From an economic point of view, it might then even be beneficial to increase some chemical equivalents, if reaction times can be shortened or uncertainties of substrate or reagent quality may be bypassed.

The overall process may rather be improved in chemical costs by recycling of certain chemicals, as explained in 2.7.3, or by the use of a different oxidation method which should utilize a cheaper oxidant, which ideally is also environmentally more friendly, such as hydrogen peroxide or oxygen. The latter being especially interesting, as oxygen can be derived from air, which is free to use.

The sum of the most striking advantages and disadvantages of oxidizing split RBW with the herein represented method is listed in table 12 in comparison to the bleaching and oxidation of MW with Cr(VI).

Table 12: Detailed advantages and disadvantages of each step in the developed process.

	Advantage	**Disadvantage**
RBW instead of MW	• Cheaper, renewable resource • By-product of food industry • Already less colourful raw product	• User awareness not yet given • Acceptance of product not yet given
Splitting and acidification before oxidation	• Quantitative conversion of esters and therefore alcohols possible	• Additional steps (compared to oxidation in an acidic media) • Potential re-esterification
Chlorite based oxidation process	• No heavy or transition metals • Cheaper than MW-oxidation • High selectivity (no chain shortening) • Low toxicity (table 59) • Salts are colourless/white (Cr(III) salts are usually green)	• Catalyst needed
Work-up (washing with water)	• Easy • Cheap • All chemicals exhibit rather low toxicity • In principle established in Cr(VI) process	• Possibly high amount of waste water (although probably much less than in the Cr(VI) process)

3. Summary and Conclusion

The pursuit of this work was the development of a process that is able to transform rice bran wax (RBW) into a wax with similar properties as oxidized Montan Wax (S-wax). Indispensable requirements by the cooperation partner were the absence of stoichiometric chromium(VI) compounds or any other compound mentioned in Annex XVII of REACH. Further preferable conditions like temperature, solvents and further chemical reagents were defined considering properties of RBW, economic and environmental aspects (compare table 3). Strategic design and synthesis of the model substrate hexadecyl octadecanoate (C_{16}-O_2C_{18}) in combination with the development of an analytical method suitable for fast and efficient screening were next in line before actual screening experiments were conducted.

Screening in order to create a process performing the splitting and oxidation in an acidic medium did achieve some promising results with nitric acid. It was possible to convert all ester in experiments and free the acyl part sufficiently. However, the selective oxidation of the alkyl part was not achieved efficiently as major chain shortening occurred. Several approaches were able to address this issue and to increase selectivity, yet none was exceedingly efficient. As the outcome of this method was uncertain, other approaches were done simultaneously to increase the probability to develop at least one working method in the given time.

This involved the division of the overall process into the two individual steps of splitting and oxidizing. This approach bore the advantage of utilizing less aggressive oxidation methods, of which numerous are at hand from academic research. Possible disadvantages of two individual steps instead of simultaneous splitting and oxidizing are for instance a more complicated reaction control and higher chemical costs (the more complex reaction control also bears a higher number of occasions to corrupt the quality of the final product).

The splitting of RBW can be achieved efficiently with alkaline reagents, as the salt formation is a sufficient driving force to convert the ester quantitatively. The alkaline reagent should be used in slight excess compared to acylic compounds in order to gain complete splitting. For batch reactions, a rather fast addition of the alkaline reagent might suit the process best due to the otherwise increased viscosity of the reaction mixture (for a process under constant flow conditions this obviously might be different). Experimental results showed that concentrated solutions of sodium or potassium hydroxide are best suited for this purpose. They are reasonable in price, easily manageable, highly soluble in water, odourless and their metal ions can be considered non-toxic in reasonable amounts.

Thereafter two reactions have to be conducted, the oxidation of alcohols and the acidification of the wax. Due to the viscosity of the (split) wax under basic conditions and the formation of acids, which influence the pH value, it is favourable to first acidify the split wax and oxidize the alcohols thereafter.

The acidification is probably the most sensitive step in the overall process, in order to achieve highest yields of acids with no esters. The wax has to be completely split (or at least sufficiently for the later intended applications), which is achieved fastest by a rather low water content. However, for the next step the water content should be high enough in order to cool down the wax without solidification. The cooling is done in order to prevent re-esterification of free alcohols and acids, and to prevent extensive boiling of water which would result in foam formation (as this is unfavourable and with lab equipment even slightly dangerous). The solution used to acidify the wax may not have a too low pH value as this favours re-esterification as well, neither should it be too dilute as this increases the overall volume needed for the reaction which may increase the amount of needed catalyst, time and reactor volume. Besides these reasons, a higher concentrated aqueous salt solution would also make work-up in order to re-use some of the reagents more profitable (less water had to be evaporated, compare 2.7.3).

A valid acid for the acidification of the split wax is acetic acid (HOAc). HOAc is cheap in acquisition, can be applied in any concentration due to being liquid and completely miscible with water. It is non-toxic (in reasonable amounts) and shows excellent buffer properties from app. pH 3 to 5. However, HOAc also has some disadvantages. These are its distinctive odour and its slightly corrosive behaviour. The constant will to improve the method further brought up citric acid (CA) as a near to perfect alternative. CA is like NaOH or KOH reasonable in price, easily manageable, highly soluble in water, odourless and non-toxic in reasonable amounts being the eponymous intermediate of the citric acid cycle. Furthermore, it shows excellent buffer properties on a wide pH range (app. 2 to 7). It is less corrosive to metals and organic matter than HOAc and most other acids, and a recovery of CA could be achieved easily (compare 2.7.3). Without recycling the theoretical costs for chemicals of splitting and acidification would be app. 160 €, whereas recycling with CaO and H_2SO_4 could reduce these costs to less than 10 €/t(RBW).

The last reaction step of the process, the oxidation of the alcohols, may be achieved by various methods. These methods are in general only limited by a few factors. As the use of organic solvents was omitted, the probably most crucial parameter is the efficient mixing of the reaction mixture, which originates from its two-phased nature. As efficient mixing is achieved by two liquid phases, the preferred temperature of any oxidation is limited by the melting point of the wax and the boiling point of the aqueous phase. In case of RBW the temperature range being approximately 80-100 °C (most reactions were performed at 90 °C).

As one of the first examples, the split RBW was oxidized with chromosulfuric acid. The resulting wax showed a high acid content, with only minor chain shortening. Compared to the oxidation of MW or the tried benchmark experiment with raw RBW, the amount of Cr(VI) and H_2SO_4 was drastically reduced. The estimated costs for chemicals of an up-scaled, non-optimized process being less than 510 €/t(RBW) (including 210 € for splitting and acidification), thereby being less than one third as expensive as one of two or three oxidation stages of MW.

Another method involved the utilization of hydrogen peroxide with tungsten based oxidation catalysts and ammonium based phase transfer agents (PTA). High C_{30}-oxidations were achieved and the amount of involved transition metals was reduced as only catalytic amounts of W(VI) were needed. However, the amount of catalyst to achieve good results was rather high. In combination with the (comparable) high prices for tungsten and PTAs no oxidation was achieved that would be economically beneficial against the oxidation with Cr(VI) reagents. Efficient recycling and work-up would be needed. Furthermore, the work-up might be complicated itself as good oxidations were only achieved with long chained tetraalkylammonium reagents which are difficult to extract with water from an organic phase.

As other methods were investigated, the oxidation with TEMPO and $NaClO_2$ turned out to be very promising. Although such oxidation systems are rather used by academic research with high amounts of organic solvents and at low temperature, the system turned out to be able to oxidize alcohols very efficiently without any organic solvent but the molten substrate itself. The method was further developed by establishing a one-pot-process starting from raw RBW. Due to the comparable high costs of TEMPO, possible application of cheaper N-oxyl radicals was focused. Trials with OH-TEMPO, the probably cheapest derivative of TEMPO, revealed its slightly different behaviour and suggested a modification of reaction conditions. With the adjustment OH-TEMPO proved to be an excellent catalyst for this application and even outperformed TEMPO under certain conditions. It turned out that switching from acetic to citric acid was not only beneficial for the smell during the reaction and the smell of potential products but also for the utilization of OH-TEMPO, as it was (again) possible to develop a one-pot-process.

Further improvement did not affect the actual chemistry but rather focussed on economic numbers as the necessary amounts of base, acid, catalyst, oxidant and water were optimized. These investigations demonstrated the high robustness of this method against many reaction conditions without relevant corruption of the product quality. Under the presumption that enough catalyst is used, “slight” changes in the amount of water, the time frame to add the oxidant, the pH value of the aqueous phase and the temperature are not decisive to the final product quality. All of these investigations were first developed in theory and tried and optimized in small scale experiments (1 g RBW). These experiments were followed by slightly up-scaled experiments (~20 g RBW), proving the idea of easy up-scaling by successful oxidation of 1 kg RBW.

Besides the high selectivity and a low price, the developed method also has the advantage of an easy work-up procedure. All reagents are water soluble and can easily be removed from the wax by washing with water. The product does not need complicated or cost intensive work-up like distillation, chromatography or solvent extraction. Therein it is somewhat similar to the old and still used chromosulfuric acid process, however, with the advantage that lower reagent amounts are needed for conversion and all reagents are lower in toxicity and water hazard class than the currently used Cr(VI) compounds.

Regarding the costs of chemicals, the herein developed OH-TEMPO/$NaClO_2$-system is not only cheaper than the oxidation of MW, but is as well comparable in price with the prior described oxidation of split RBW with Cr(VI) reagents. The upscaling of the latest oxidation step might cost app. 270 €/t(RBW) compared to app. 290 €/t(RBW) for the (non-optimized) oxidation step with Cr(VI). Without recycling the overall chemical costs might be as low as 425 €/t(RBW), whereas with recycling of lye and CA the chemical costs can be calculated to be less than 280 €/t(RBW). Aside of environmental aspects also the potential chemical costs in comparison with just one stage of oxidizing MW (~1500 €/t(MW)) clearly prove the superiority of this new method.

Table 13: General comparison of using RBW with the herein developed process compared to using MW with the old chromosulfuric acid process.

	RBW + new process	**MW + Cr(VI)/H_2SO_4 process**
Substrate	Similar in price	
Substrate origin	Rice bran: side product from dehusking of Rice: natural product grown in vast amounts Not in competition with food crops or wildlife habitats	Lignite, fossil resource, with differing compositions Will not be available forever
Process chemical costs	Cheaper (app. 25 % of 1 stage), depending on exact implementation	Without recycling quite high
Number of process steps	3 individual steps, each with its own conditions	1 general step, which may be repeated several times
Time for process, without heat-up & work-up	< 6 h is expected to be possible without problems when the reaction is routinely executed (< 10 h in lab scale, with sample taking and evaluation within)	5-7 hours for one general step, adding up to 10-21 hours for 2-3 steps (without washing; according to patents)
Washing	All chemicals well water soluble Low toxicity	All chemicals water soluble, but limiting values for chromium compounds need to be met
Waste disposal	Mainly non-toxic, remaining oxidant is of low toxicity (table 59)	High concentration of heavy metal (Cr), high amounts of acid (H_2SO_4), Cr(III) may be used as tanning agent
Yield per volume	1 kg RBW was successfully oxidized in a 4 L flask with less than 1.8 kg other reagents (incl. H_2O)	1 kg MW need app. 4 kg other chemicals (incl. H_2O) for one general step

4. Outlook

With this work, it was managed to develop a process that is able to convert natural RBW to a wax with similar properties to S-wax derived from MW. In the near future the new process should be up-scaled further in pilot plants to gain experience with increased reaction volumes. It will be necessary to choose the right reactor and stirrer type and to develop suitable temperature and process profiles for the higher amounts of wax and therefore higher energies that will be set free during the process. This pilot phase would also be great to investigate whether NaOH should be used to split the wax or whether a lower viscosity justifies the higher price of KOH. Furthermore, economical calculations should be performed to evaluate whether batch or constant-flow conditions are preferable and at which scale the proposed recycling of chemicals and regeneration of chlorite would be suitable or whether the disposal of the side-products would be more profitable.

Up-scaled to a similar quantity, the product will be competitive to the currently available S-wax not only due to the cheaper, environmentally friendlier RBW, but also due to the developed process which is superior to the currently used MW oxidation process. The new process is highly efficient, environmentally less challenging and even cheaper in regards to reagent costs (costing less than a third of one of 2-3 stages in MW oxidation). Additionally, the production of RBW is neither dependent on fossil resources, nor is its production competing against the production of food, as carnauba wax may do, when areas are mainly used to grow palms for wax production instead of growing food crops.

This process is only one of many possible steps towards more efficient and environmentally friendlier processes in industry. I expect that an enhancement of the new process will utilize H_2O_2 or oxygen/air for the oxidation of the wax. Of course, the development of an air utilizing oxidation step would be more favourable. As there are several literature-known procedures existing to oxidize shorter alcohols with oxygen, I expect that one of these will be adaptable to the here discussed matter in future.

5. Experimental Section

5.1. Materials and Characterization

Chemicals

Unless otherwise stated, all chemicals were purchased from commercial suppliers and used without further purification. Moisture- and air-sensitive reactions were carried out using Schlenk techniques. Catalysts and products for determination of ANs were dried under reduced pressure. Wax samples were heated to melt and dried under vigorous stirring.

NMR

^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded at 298 K with an AV-400 spectrometer from *Bruker*. All NMR spectra were referenced internally to residual proton signal of the respective deuterated solvent and are reported relative to tetramethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants *J* (Hz). Signal multiplicities are abbreviated as follows: singlet – s, doublet – d, triplet – t, multiplet – m.

GC analyses

GC-analyses were done with an *Agilent* 7890B instrument with an *Agilent* DB-5ht column, length 15 m, ID 0.320 mm, film 0.1 µm. 1µL of sample was injected and analysed via Flame Ionisation Detection (FID). Flow and heat profiles were individually established for each substrate. The methods were changed during the process of this work due to deterioration of the column and only the last method for each substrate is reported. Mass spectra of monomers were measured with an *Agilent* 5977A Series GC/MSD system.

For $C_{16}OH$ and C_{16}-O_2C_{18} the initial temperature was set to 90 °C and hold for 1.5 min, followed by a temperature ramp of 20 °C/min until 140 °C was reached, followed by a temperature ramp of 10 °C/min until 180 °C was reached, followed by a temperature ramp of 40 °C/min until 280 °C was reached, and a final temperature ramp of 20 °C/min until 330 °C was reached which was hold for 12 min. Total runtime was 25 min, equilibration time was set to 3 min at 90 °C. The gas inlet was set to 340 °C with a split ratio of 40:1. The nitrogen flow was set to constant 0.5mL/min in the column. The FID detector was set to 350 °C with an air flow of 400 mL/min, hydrogen flow of 40 mL/min and a makeup flow of 30 mL/min.

For RBW the initial temperature was set to 150 °C and hold for 1 min, followed by a temperature ramp of 15 °C/min until 180 °C was reached, followed by a temperature ramp of 8 °C/min until 320 °C was reached, and a final temperature ramp of 3 °C/min until 380 °C was reached which was hold for 10 min. Total runtime was 50.5 min, equilibration time was set to 3 min at 150 °C. The gas inlet was set to 390 °C with a split ratio of 40:1. The nitrogen flow was set to constant 0.5mL/min in the column. The FID detector was set to 390 °C with an air flow of 400 mL/min, hydrogen flow of 40 mL/min and a makeup flow of 30 mL/min.

5.2. Reactions at atmospheric pressure

If not mentioned otherwise small scale experiments (<2 g) at atmospheric pressure were performed in a Carousel 12 Plus Reaction Station™ from *Radleys*. If not reported other, reactions were performed by addition of substrate and other reagents to the vessel, closure of the vessel and setting the vessel in the pre-heated carousel station. Slow stirring was applied at the beginning until all reagents were liquefied and stirring was turned to the highest level on the magnetic stirrer. If not reported differently, reagents that were added over a time period were added with the help of a syringe pump with a 4 syringe adapter. All reagent amounts and addition times are noted in the tables. After the indicated time frames, samples were drawn from the reaction vessels (if possible from a liquid product phase) and the reaction products were transferred into vials for later verification. Water and an organic solvent (heptane for C_{16}-O_2C_{18} and toluene for RBW) were added to the sample and the sample was heated to liquidation. The organic phase was thereafter washed 2-3 times with 1 M $HCl_{(aq.)}$, 2-3 times with distilled water and 2-3 times with $NaCl_{(aq., konz.)}$. A small portion of the organic phase was thereafter mixed with the silylating agent MSTFA and put up for gas chromatography.

5.3. Reactions performed

Benchmark experiments

Table 14: 0.50 g substrate and 3.0 g sulfuric acid (50 wt%) were added into the reaction vessel at room temperature, heated to 120 °C for 30 min, 1.3 g of 60 wt.% Cr(VI) solution was added over 2 h. The mixture was stirred for additional 3 h.

Substrate	**X** [$\mathbf{I_{Acids}/I_{Total}}$]	**X** $\left[1 - \frac{I(C_{16}-O_2C_{18})}{I_{Total}}\right]$
C_{16}-O_2C_{18}	7.0 %	31.0 %
RBW	21.0 %	-

Acidic splitting

Table 15: 0.20 g C_{16}-O_2C_{18} (0.39 mmol) and 1 g of diluted acid were added into each reaction vial, heated to 110 °C and stirred for 4 hours.

Acid	**Amount acid [mol%]**	**X [%]**	**S($C_{16}OH$) [%]**
-blank-	-	0.0	0.0
H_3PO_4	15.8	0.0	0.0
HCl	13.2	1.5	0.0
$MeSO_3H$	13.2	6.0	5.5
H_2SO_4	12.9	3.5	3.0
	18.3	9.0	3.5
HNO_3	13.1	9.5	9.5
	18.3	13.0	13.5

Table 16: 0.10 g C_{16}-O_2C_{18} (0.20 mmol) and 1 g of aqueous acid were added into each reaction vial, heated to 110 °C and stirred for 4 hours.

Acid	**Acid conc. [wt.%]**	**Eq. of acid [mol/mol]**	**X [%]**	**S($C_{16}OH$) [%]**
HNO_3	40	31.8	15.5	14.0
	45	35.7	17.0	13.5
	50	39.7	21.0	11.0
	55	43.7	24.0	8.0
	60	47.6	32.0	4.5
$MeSO_3H$	50	26.0	7.0	7.5
	75	39.0	4.5	4.0
	90	46.8	6.0	2.0
	100	52.0	14.5	0.0

HNO_3 oxidation

Table 17: 1.0 g C_{16}*-*O_2C_{18} *(2.0 mmol) and 0.655 mL* HNO_3 *(100 wt.%, 16 mmol, 8 eq.) diluted with water to the specified concentration were added into the reaction vessel, heated to the specified temperature and stirred for 4 hours.*

T [°C]	HNO_3 [wt.%]	X [%]
80	20	0
	40	6.2
	60	15.1
	80	20.9
	100	19.5
90	20	0.3
	40	6.5
	60	13.1
	80	30.2
	100	42.2
100	20	0.8
	40	14.2
	60	16.1
	80	56.5
	100	73.5
120	20	3.5
	40	17.2
	60	75.7
	80	88.2
	100	81.3
140	20	3.9
	40	16.6
	60	82.4
	80	87.9
	100	79.3

Table 18: 0.1 g C_{16}-O_2C_{18} (0.20 mmol) and 0.66 mL HNO_3 (100 wt%, 16 mmol, 80 eq.) diluted with water to the specified concentration were added into the reaction vessel, heated to 95 °C and stirred for 4 hours.

HNO_3 conc. [wt.%]	**X [%]**	**C_{16}/$C_{18}O_2H$ [%]**
40	8.9	100
45	10.8	98.5
50	13.2	84.6
55	14.6	69.6
60	15.5	58.2

Table 19: 0.1 g $C_{16}OH$ (0.4 mmol) and 0.66 mL of HNO_3 (100 wt%, 16 mmol 38 eq.) diluted with water to the specified concentration were added into the reaction vessel, heated to 95 °C and stirred for 4 hours.

HNO_3 conc. [wt.%]	**X [%]**	**S(Esters) [%(I)]**	**S($C_{16}O_2H$) [%(I)]**
50	93.1	76.7	0.8
55	98.3	36.4	6.0
60	99.4	6.2	19.0
65	99.3	7.7	17.6
70	99.4	4.1	18.2
75	99.6	2.0	15.2
80	99.8	1.5	14.0

Table 20: 0.4 g C_{16}-O_2C_{18} (0.8 mmol) and 1 g of HNO_3 (65 wt%, 14.4 mmol 18.5 eq.) and the specified amount of $VO(acac)_2$ were added into the reaction vessel, heated to 110 °C and stirred for 4 hours.

$VO(acac)_2$ [mol%]	**X [%]**	**S($C_{16}O_2H$) [%(I)]**	**S($C_{14\text{-}16}O_2H$) [%(I)]**
0.0	77.5	15.5	54.5
1.3	86.0	28.0	88.0
5.2	89.5	26.0	88.5
10.3	77.5	30.5	81.5
51.2	72.5	32.5	66.5

Table 21: 0.1 g C_{16}-O_2C_{18} (0.20 mmol), 1 mL HNO_3 (65 wt.%, 14 mmol, 73 eq.) and the specified reagent were added to the reaction vessel, heated to 110 °C and stirred for 4 hours.

Reagent	**Eq.**	**X [%]**	**S($C_{16}O_2H$) [%]**	**S($C_{15}O_2H$) [%]**
-blank-	-	64.0	5.0	2.5
$Na_2Cr_2O_7$ * 2 H_2O	1.41	56.5	16.5	7.0
	2.76	58.0	26.0	6.0
^{t}BuOH	~4.8	60.5	7.5	11.5
Phenol	0.44	63.5	6.0	14.0
	0.92	58.0	7.5	18.0
	2.15	74.0	13.0	27.5
C_6F_5OH	0.95	78.0	13.5	27.5
	2.14	85.5	39.0	40.0

Basic splitting

Batch experiment 1: 1.15 g RBW (1.5 mmol) and a solution of 347 mg NaOH (5.3 mmol, 3.4 eq.) in 3 mL H_2O were heated to 120 °C and stirred. After one hour the reaction mixture had solidified and 2 mL H_2O were added. After additional 3 hours the reaction product was dissolved in app. 15 mL toluene and 5 mL EtOAc. The organic phase was washed several times with slightly acidified water and brine. GC analysis revealed complete splitting of the esters.

Table 22: 0.2 g C_{16}-O_2C_{18} (0.39 mmol) and the specified amount NaOH dissolved in 2 mL of H_2O were added into the reaction vessel, heated to 110 °C and stirred for 4 hours.

NaOH [eq.]	**NaOH conc. [wt.%]**	**X [%]**
3.34	2.6	0.0
6.71	5.0	0.0
13.4	9.6	1.0
33.6	20.9	3.5
65.4	34.0	100
124.5	50.0	100

*Table 23: 1.0 g of RBW (1.3 mmol) and the specified amount of base as aqueous solution were added into the reaction vessel, heated to 110 °C and stirred for 3 hours. * Reactions were started with 50 wt.% NaOH / 42 wt.% KOH, after 10 and 35 min 0.25 mL H_2O were added. Stirring was conducted for 2 hours.*

Base	**Conc. of base [wt.%]**	**Eq. of base [mol/mol]**	**X [%($I_{Monomeres}/I_{Total}$)]**
NaOH	50.0	1.10	46.5
		1.14	24.0
		1.19	52.0
		1.24	35.0
	10.4*	1.08	74.0
	12.2*	1.31	100
	14.0*	1.53	100
	17.2*	1.96	100
KOH	15.3*	1.03	58.5
	18.4*	1.29	100
	20.9*	1.50	100
	26.0*	2.02	100
	42.5	1.09	92.5
		1.13	95.5
		1.21	98.5
		1.26	99.0

*Table 24: 1.0 g RBW (1.3 mmol) and 0.76 eq. of the specified base were added into the reaction vessel, heated to 125 °C and stirred for one hour. After another hour the temperature was raised to 140 °C and after another hour to 150 °C. After stirring for an hour a sample was drawn and the reaction stopped. * The base was added after melting the wax.*

Base	**X [$I_{Monomeres}/I_{Total}$]**
$Ca(OH)_2$	0.0 %
$Mg(OH)_2$	4.0 %
$Ca(OH)_2$*	2.5 %
$Mg(OH)_2$*	5.0 %

*Table 25: 0.50 g RBW (0.67 mmol) and 38.5 mg CaO (0.7 mmol, 2.1 e. OH^-) emulsified in 360 mL H_2O were added into the open reaction vessel, heated to 120 °C and stirred for 68 hours. * 0.18 eq. of KOH were added to accelerate the reaction.*

X [$I_{Monomeres}/I_{Total}$]
64.0 %
85.0 %*

Oxidation of split ester/wax with Cr(VI)

*Table 26: 1.0 g of substrate, the specified amount of H_2SO_4 and 1.5 eq. of Cr(VI) as $Na_2Cr_2O_7$ were added into the reaction vessel, heated to 90 °C and stirred for 18 h. * 5.0 eq.of Cr(VI) were used. ^{S} 0.5 g $C_{16}OH$ were used.*

Substrate	**H_2SO_4 (50 wt.%) [g]**	**Ester ratio [%(I)]**	**$S(C_{16}O_2H)$ [%(I)]**	**X_{C30} [%]**
$C_{16}OH$	3.24	27.5	65.5	
RBW (split)	1.02	8.5		87.0
$C_{16}OH^{*S}$	5.40	30.0	54.0	
RBW (split)*	3.40	13.0		87.0

Oxidations with Hydrogen peroxide

*Table 27: 0.5 g $C_{16}OH$ (2.1 mmol), 0.7 mol% of the TATTP derivative, 0.3 g H_2O and 0.3 g H_2O_2 (50 wt.%, 4.4 mmol, 2.1 eq.) were put into the reaction vessel, heated to 95 °C and stirred for 2 hours. After 1 hour additional 0.3 g H_2O_2 were added. For the experiments with SDS no water but two times 1 g H_2O_2 (50 wt.%, 14.7 mmol, 7 eq.) were added. * A lot of side products were observed in this experiment.*

Cation	**Additional SDS**	**$S(C_{16}O_2H)$ [%(I)]**
Bu_4N^+	-	0.5
Bu_4N^+	2.0 mg	0.5
$C_{16}Me_3N^+$	-	12.5
$C_{16}Me_3N^+$	1.7 mg	22.0*

Table 28: 0.5 g $C_{16}OH$ (2.1 mmol), 1.7 mol% Na_2WO_4, the specified amount of ionic compound, 0.5 g H_2O and 1.0 g H_2O_2 (50 wt.%, 14.7 mmol, 7.0 eq.) were put into the reaction vessel, heated to 90 °C and stirred for 4 hours. [1] 8 hours of stirring. [2] 1.5 mol% H_2SO_4 added.

Ionic compound	**Amount [mol%]**	**$S(C_{16}O_2H)$ [%(I)]**
$Bu_4N^+HSO_4^-$	1.9	1.0[1]
$Hex_4N^+HSO_4^-$	1.5	90.5
$Hex_4N^+HSO_4$	1.4	88.5[1]
$C_{16}MeN^+NO_3^-$	2.2	45.5
$C_{16}MeN^+NO_3^-$	1.7	22.0[2]
$OcMeIm^+Cl^-$	1.4	1.0

Table 29: 0.5 g split RBW (0.67 mmol), 10.5 mg $Na_2WO_4 * 2\ H_2O$ (32 µmol, 4.7 mol%), 16.0 mg $C_{16}Me_3NNO_3$ (46 µmol, 6.9 mol%), 10 mg $KHSO_4$ (73 µmol, 11 mol%), 1 g H_2O_2 (50 wt.%, 15 mmol, 22 eq.), 1 mL H_2O and 0.5 mL of the specified solvent were added into the reaction vessel, heated to 90 °C and stirred for 22 hours.

Additional solvent	**X_{C30} [%]**
-	66.0
Heptane	22.5
Toluene	26.5
DMSO	58.5
MeCN	58.5
EtOAc	59.0

Table 30: 0.5 g $C_{16}OH$ (2.1 mmol), the specified amount of catalytic reagents and 2 g H_2O_2 (12.5 wt.%, 7.4 mmol, 3.6 eq.) were put into the reaction vessel, heated to 90 °C and stirred for 22 hours. [1] 1 g of H_2O_2 (50 wt.%, 15 mmol, 7 eq.), 6 h of stirring.

PTA	**Amount [mol%]**	**Metal oxide**	**Amount [mol%]**	**$S(C_{16}O_2H)$ [%(I)]**
C_{12}-TATTP			0.16	50.0
			0.31	80.0
			0.64	97.5
			1.27	99.5
$[C_{12}Me_3N^+][Cl^-]$	4.0	$H_4SiW_{12}O_{40}$	1.0	<0.5
	4.4		2.0	<0.5
	4.1	$Na_3PMo_{12}O_{40}$	1.3	15.5
	4.3		2.6	7.5
$[Hex_4N^+][HSO_4^-]$	21.0	Na_2MoO_4	9.5	80.5[1]
	1.5	Na_2WO_4	1.7	90.5[1]

Table 31: 0.5 g split RBW (0.65 mmol), the specified amount of C_{12}-TATTP, 0.5 g H_2O_2 (50 wt.%, 7.4 mmol, 11.4 eq.) and the specified amount of H_2O were added into the reaction vessel, heated to 90 °C and stirred for 21 hours. [1] 17 instead of 21 hours stirring.

C_{12}-TATTP [mol%]	**H_2O_2 [mL]**	**H_2O [mL]**	**Ester ratio [%(I)]**	**X_{C30} [%]**
1.0	2.0	0.0	25.0	37.5
	1.0	1.0	30.0	44.0
	0.5	1.5	5.5	39.5
		1.5	9.0	46.0[1]
		1.0	7.5	51.0[1]
		0.5	8.5	50.0[1]
		0.0	20.5	71.5[1]
2.0	0.5	1.5	7.0	79.0
	0.5	1.5	15.5	84.5[1]
	0.25	1.75	20.5	87.0[1]
	0.125	1.875	8.0	74.5[1]
3.0	0.5	1.5	13.0	90.5[1]
3.9			5.5	92.0
4.9			5.0	93.0

Table 32: 0.5 g split RBW (0.65 mmol), 20.7 mg Na_2WO_4 ** 2* H_2O *(62 µmol, 9.5 mol%), app. 20 mol% of the specified ionic compound, 17.1 mg* $KHSO_4$ *(0.13 mmol, 19 mol%) and 0.5 mL* H_2O_2 *(50 wt.%, 7.5 mmol, 11 eq.) were added into the reaction vessel, heated to 90 °C and stirred for 16 hours.* ^{W} *1.5 mL* H_2O *were added.*

Ionic compound	X_{C30} **[%]**
C_8Me_3NCl	48.5
	12.5^{W}
$C_{10}Me_3NCl$	69.0
	68.5^{W}

Table 33: 0.5 g split RBW (0.65 mmol), 25.2 mg Na_2WO_4 ** 2* H_2O *(76 µmol, 11.7 mol%), 10.3 mg* $C_{12}Me_3NNO_3$ *(37 µmol, 5.7 mol%), the specified amount of* $KHSO_4$*, 1.0 mL* H_2O_2 *(50 wt.%, 14.7 mmol, 22 eq.)and 3.0 mL* H_2O *were added into the reaction vessel, heated to 90 °C and stirred for 17 hours.* ^{1} *11.5 mol%* $C_{12}Me_3NNO_3$ *were used.* ^{2} *22.9 mol%* $C_{12}Me_3NNO_3$ *were used.*

$KHSO_4$ **[mol%]**	X_{C30} **[%]**
0.0	8.0
6.3	21.5
11.8	37.5
45.0	32.0
	62.5^{1}
	79.5^{2}

*Table 34: 0.5 g split RBW (0.65 mmol), 20.1 mg Na_2WO_4 * 2 H_2O (61 mmol, 9.3 mol%), 16.0 mg $C_{12}Me_3NNO_3$ (61 mmol, 9.3 mol%), the specified amount of acid, 0.5 mL H_2O_2 (50 wt.%, 7.5 mmol, 11 eq.) and 1.5 mL H_2O were added into the reaction vessel, heated to 90 °C and stirred for 15 hours.*[122,139]

Acid	**Amount [mol%]**	**X_{C30} [%]**
-blank-	-	42.5
$KHSO_4$	4.6	61.5
	9.2	64.0
	18.5	73.0
HOAc	5.2	42.0
	10.4	45.5
	21.0	50.0
	130.0	50.0
CA	1.6	42.0
	3.3	41.0
	6.5	42.0
	39.9	32.5

*Table 35: 0.5 g split RBW (0.65 mmol), the specified amount of Na_2WO_4 * 2 H_2O, $C_{10}Me_3NNO_3$ and $KHSO_4$, 0.5 mL H_2O_2 (50 wt.%, 7.5 mmol, 11 eq.)and 1.5 mL H_2O were added into the reaction vessel, heated to 90 °C and stirred for 15 hours.*

W(VI) amount [mol%]	**$C_{10}Me_3NNO_3$ [mol%]**	**$KHSO_4$ [mol%]**	**X_{C30} [%]**
9.2	9.8	10.0	46.5
	19.3	19.7	70.0
	39.2	39.9	83.0
18.7	9.9	10.0	34.0
	19.3	19.7	85.5
	39.7	40.4	91.0

Table 36: 0.5 g split RBW (0.65 mmol), 5.2 mg $Na_2WO_4 * 2 H_2O$ (16 µmol, 2.4 mol%), the specified amount of $C_{12}Me_3NCl$, 4.4 mg $KHSO_4$ (32 µmol, 5.0 mol%), 0.5 mL H_2O_2 (50 wt.%, 7.4 mmol, 11 eq.)and 2.5 mL H_2O were added into the reaction vessel, heated to 90 °C and stirred for 18 hours. [1] 2.5 mol% $KHSO_4$ were used. [2] 20 mol% $KHSO_4$ were used.

$C_{12}Me_3NCl$ [mol%]	**Ester ration [%]**	**X_{C30} [%]**
2.5	18.4	15.5
2.5[1]	6.3	15.0
2.5[2]	14.6	15.0
5.0	7.7	24.5
10.0	9.8	38.0
19.9	13.3	51.0

Table 37: 1.0 g split RBW (1.3 mmol), 10.7 mg $Na_2WO_4 * 2 H_2O$ (32 µmol, 2.5 mol%), the specified amount of $C_{12}Me_3NCl$ and $KHSO_4$, 1.0 mL H_2O_2 (50 wt.%, 14.7 mmol, 11 eq.)and 2.0 mL H_2O were added into the reaction vessel, heated to 90 °C and stirred for 20 hours. [W] 5.0mol% Na_2WO_4 were used.

$C_{12}Me_3NCl$ [mol%]	**$KHSO_4$ [mol%]**	**Ester ratio [%]**	**X_{C30} [%]**
5.0	4.9	20.3	46.5
	10.0	10.4	44.0
9.9	4.9	17.2	61.5
	10.0	14.3	63.0
9.9[W]	10.0	16.4	87.0
	20.0	12.3	83.0

Table 38: 1.0 g split RBW (1.3 mmol), 21.2 mg $Na_2WO_4 * 2 H_2O$ (64 µmol, 5.0 mol%), 51.3 mg $C_{12}Me_3NCl$ (194 µmol, 15.1 mol%) and the specified amount of $KHSO_4$ and H_3PO_4, 0.83 mL H_2O_2 (50 wt.%, 12 mmol, 9.5 eq.)and 1.3 mL H_2O were added into the reaction vessel, heated to 90 °C and stirred for 20 hours.

$KHSO_4$ [mol%]	**H_3PO_4 [mol%]**	**Ester ratio [%]**	**X_{C30} [%]**
5.2	-	14.0	83.0
7.8	-	21.0	83.5
10.4	-	28.5	74.5
20.1	-	15.5	90.5
40.3	-	29.0	87.5
5.2	5.2	30.5	67.0
5.2	10.4	31.5	62.5
5.2	20.4	40.0	52.5

Oxidation with N-oxyl radicals

Batch experiment 2: 0.196 g of $C_{16}OH$ (0.81 mmol), 93.6 mg $NaClO_2$ (0.83 mmol, 1.02 eq.), 0.6 mg TEMPO (4 µmol, 0.5 mol%) and 0.5 mL H_2O were heated to reflux in a reaction vessel and stirred. After 5 minutes 10 µL $HCl_{(aq.)}$ (0.5 wt%, 1.4 µmol, 0.17 mol%) were added and a sample was taken after 1 hour. No conversion was monitored. 100 min after reaction start 10 µL of $HCl_{(aq., konz.)}$ (37 wt.%, 0.12 mmol, 15 mol%) were added and after additional 3 hours the reaction was stopped. The alcohol was by then quantitatively (98.8 %) converted to the acid.

*Table 39: 0.50 g $C_{16}OH$ (2.1 mmol) and 1 mL of buffer medium with the specified reagents were added into the reaction vessel, heated to 95 °C and the reaction was started by addition of 20 µL NaOCl (5 % free Cl_2, 13 µmol, 0.7 mol%). 1.3 eq. of $NaClO_{2(aq.)}$ (0.24g/mL) were added within 60 min by pipetting and the mixture was stirred for additional 2 hours. * No NaOCl added, $NaClO_2$ added within 25 min. ^{AA} AA-TEMPO instead of TEMPO.*

TEMPO [mol%]	**HOAc [mmol]**	**NaOAc [mmol]**	**Additive**	**Amount [mg]**	**S($C_{16}O_2H$) [%(I)]**
0.74*	-	-	Aceton	250	< 1
0.82	-	-	$BuSO_3Na$	106.4	< 1
0.88*	0.01	0.09			< 1
0.86*	0.01	0.09	Aceton	250	64.0
0.96*	0.05	0.05			< 1
0.65	0.1	0.1			< 1
0.62			$BuSO_3Na$	5.2	2.5
0.76			$BuSO_3Na$	34.5	2.5
0.83			SDS	15.2	80.0
0.81			SDS	30.9	63.5
0.86			SDS	61	89.5
0.76	0.25	0.25			98.0
0.78*	0.1	0.9			< 1
0.94*	0.5	0.5			87.5
1.06^{AA}	0.1	0.1			2.5
1.04^{AA}	0.1	0.1	SDS	14.9	77.0
0.94^{AA}	0.25	0.25			96.0

*Table 40: 1.0 g split RBW (1.3 mmol) and 3 mL 1 M HOAc/NaOAc buffer and the specified amount of TEMPO were added into the reaction vessel and heated to 90 °C. 20 µL NaOCl (13 µmol, 1.0 mol%) were added, before 225 mg $NaClO_2$ (2.0 mmol, 1.5 eq.) and the specified amount of TEMPO were added in 2 mL of H_2O via syringe pump over 2 hours. The mixture was stirred for 2 hours. * No NaOCl added.*

TEMPO prior $NaClO_2$ [mol%]	**TEMPO simultaneous to $NaClO_2$ [mol%]**	**X_{C30} [%]**
0.29	-	63.0
0.15	0.16	69.5
-	0.31	76.0
-*	0.31	64.5
0.05		17.5
0.25		58.0
0.49		88.5
0.98		94.0
	0.25	74.0
	0.49	86.0
	0.75	93.0
	0.99	94.0

*Table 41: 1.0 g split RBW (1.3 mmol) and 3 mL 1 M HOAc/NaOAc buffer and 0.51 mg TEMPO (3.3 mmol, 0.25 mol%) were added into the reaction vessel and heated to 90 °C. 20 µL NaOCl (13 µmol) were added, before 225 mg $NaClO_2$ (2.0 mmol, 1.5 eq.) was added in 2 mL of H_2O via syringe pump over 2 hours. The mixture was stirred for 2 hours. * 0.54 mg TEMPO (3.5 mmol, 0.27 mol%).*

SDS [mg]	**X_{C30} [%]**
-	72.5
2.6	75.0
5.3	74.0
10.3	66.0
-	80.0*
0.5	85.0*
1.0	82.0*
2.0	84.0*

Table 42: 1.0 g split RBW (1.3 mmol) and 3 mL 1 M HOAc/NaOAc buffer were added into the reaction vessel and heated to 90 °C. 20 µL NaOCl (13 µmol) was added, before the specified amount of $NaClO_2$ and 2.0 mg TEMPO (13 µmol, 1.0 mol%) were added in 2.2 mL of H_2O via syringe pump over 2 hours. The mixture was stirred for 14 hours.

$NaClO_2$ [eq.]	**X_{C30} [%]**
0.80	76.0
0.90	80.5
1.00	89.0
1.09	91.0
1.10	93.5
1.20	94.5
1.30	94.5
1.41	94.0

*Table 43: 0.50 g $C_{16}OH$ (2.1 mmol), app. 3.5 mg OH-TEMPO (22 µmol, 1.1 mol%) and 2 mL of buffer in the specified composition were added into the reaction vessel and heated to 90 °C. 20 µL NaOCl (13 µmol, 0.7 mol%) was added, before 247 mg of $NaClO_2$ (2.0 mmol, 0 96 eq.) were added within 45 min by pipetting and the mixture was stirred for 30 min. * C_{16}=O was observed.*

HOAc [mmol]	**NaOAc [mmol]**	**S($C_{16}O_2H$) [%(I)]**
0.50	1.50	14.0
0.50	0.50	32.5*
0.25	0.75	1.0
0.25	0.25	5.5
0.10	0.10	< 1*
0.10	-	< 1
0.05	0.05	< 1*
0.05	-	< 1*

Table 44: 1.0 g $C_{16}OH$ (4.1 mmol), the specified amount of catalyst and acid and 2 mL H_2O were added into the reaction vessel and heated to 90 °C. 20 µL NaOCl (10 % free Cl_2, 13 µmol, 0.7 mol%) were added prior to the addition of 561 mg $NaClO_2$ (5.0 mmol, 1.2 eq.) in 2 mL H_2O over 2 hours and stirred for 1 hour. [1] Only 0.5 eq. of $NaClO_2$ in 1 mL H_2O were added within 1 hour. [2] 0.88 mol% SDS were added.

H_3CA added [mol%]	**H_3PO_4 added [mol%]**	**OH-TEMPO [mol%]**	**AA-TEMPO [mol%]**	**$S(C_{16}O_2H)$ [%(I)]**
1.2		0.78		26.0[1]
1.2		0.85		41.5[1,2]
	1.2	1.7		80.5
	0.6	1.7		67.5
			0.93	95.0
			1.37	95.5

Table 45: 1.0 g split RBW (1.3 mmol), 5.1 mg CA (27 µmol, 2.0 mol%) 2 mL H_2O and the specified catalyst were added to the reaction vessel and heated to 90 °C. 20 µL NaOCl (10 % free Cl_2, 13 µmol, 2.0 mol%) were added before 180 mg $NaClO_2$ (1.6 mmol, 1.2 eq.) were added in 2 mL H_2O over 2 hours. [1] 1.5 eq. $NaClO_2$ in 1.125 mL über 4.5 h. [2] 3 mL 1 M H/NaOAc-buffer was used. [E] High amounts of esters were observed

Catalyst	**Amount [mol%]**	**X_{C30} [%]**
TEMPO	2.2	9.5[1]
TEMPO	4.4	10.0[1]
Oxo-TEMPO	2.4	14.0
OH-TEMPO	2.2	86.5
NH_2-TEMPO	2.9	77.5
AA-TEMPO	2.1	94.0
MeO-TEMPO	2.6	94.0[2]
MeO-TEMPO	2.7	91.0
Me-AZADO	1.5	94.5
ABNO	2.7	77.5
TEMPO on SiO_2	~2.2	55.0[E]
TEMPO polymer-bound	~3.1	57.0[E]

Table 46: 1.0 g split RBW (1.3 mmol), 5.2 mg CA (2.7 µmol, 2.1 mol%) 2 mL H_2O and the specified amount of catalyst were added to the reaction vessel and heated to 90 °C. 20 µL NaOCl (13 µmol, 1 mol%) were added before 180 mg $NaClO_2$ (1.59 mmol, 1.23 eq.) were added in 2 mL H_2O over 2 hours and the mixture was stirred for 24 hours. ^{E} High amounts of esters were observed.

Catalyst	**Amount [mol%]**	**X_{C30} [%]**
AA-TEMPO	0.68	84.0^E
	1.36	93.5
	2.05	92.5
MeO-TEMPO	0.68	23.0
	1.35	25.5
	2.71	91.0

Table 47: 1.5 g split RBW (1.9 mmol), 7.5 mg CA (3.9 µmol, 2.0 mol%), 10.1 mg OH-TEMPO (59 µmol, 3 mol%) and the specified amount of water were added to the reaction vessel and heated to 90 °C. 30 µL NaOCl (20 µmol, 1 mol%) were added before 270 mg $NaClO_2$ (2.39 mmol, 1.23 eq.) were added in 0.75 mL H_2O over 2 hours and the mixture was stirred for 20 hours.

H_2O [mL]	**X_{C30} [%]**
0.25	93.8
0.50	93.8
0.75	94.4
1.5	94.4

Table 48: 1.0 g split RBW (1.3 mmol), 5.0 mg OH-TEMPO (29 µmol, 2.2 mol%) and 2 mL aqueous buffer were added into the reaction vessel and heated to 90 °C. 20 µL NaOCl (10 % free Cl_2, 13 µmol, 2.0 mol%) were added prior to the addition of 180 mg $NaClO_2$ (1.6 mmol, 1.2 eq.) in 2 mL H_2O over 2 hours and the mixture was stirred for 15 hours. [1] Slight excess of 0.5 mol% NaOH.

NaOH [eq.]	**CA [eq.]**	**Resulting $Na_{(3-n)}H_{(n)}CA$**	**X_{C30} [%]**
0.155	0.050	$Na_3(CA)$[1]	40.5
	0.061	$Na_{2.6}H_{0.4}(CA)$	31.0
	0.077	$Na_{2.0}H_{1.0}(CA)$	68.5
	0.10	$Na_{1.5}H_{1.5}(CA)$	84.0
1.2	0.41	$Na_{3.0}(CA)$	77.0
	0.48	$Na_{2.5}H_{0.5}(CA)$	50.0
	0.60	$Na_{2.0}H_{1.0}(CA)$	94.0
	0.81	$Na_{1.5}H_{1.5}(CA)$	86.0
1.5	0.50	$Na_{3.0}(CA)$	75.5
	0.60	$Na_{2.5}H_{0.5}(CA)$	54.5
	0.76	$Na_{2.0}H_{1.0}(CA)$	94.5
	1.0	$Na_{1.5}H_{1.5}(CA)$	69.0

*Table 49: 2.0 g split RBW (2.6 mmol), 10.0 mg OH-TEMPO (58 µmol, 2.0 mol%) and 2 mL aqueous buffer were added into the reaction vessel and heated to 90 °C. 40 µL NaOCl (5 % free Cl_2, 13 µmol, 2.0 mol%) were added prior to the addition of 370 mg $NaClO_2$ (3.3 mmol, 1.25 eq.) in 1 mL H_2O over 2 hours and the mixture was stirred for 14 hours. * Disregarding the effect of the acids in split RBW.*

KOH [eq.]	**CA [eq.]**	**Resulting buffer***	**X_{C30} [%]**
1.3	0.44	$K_{3.0}H_{0.0}(CA)$	89.5
	0.52	$K_{2.5}H_{0.5}(CA)$	93.5
	0.65	$K_{2.0}H_{1.0}(CA)$	93.5
1.5	0.75	$K_{2.0}H_{1.0}(CA)$	93.0

Table 50: 1.0 g split RBW (1.3 mmol), the specified amount of OH-TEMPO and 1 mL aqueous buffer consisting of 182 mg $K_{2.5}H_{0.5}(CA)$ (0.64 mmol, 47.9 mol%) were added into the reaction vessel and heated to 90 °C. 15 µL NaOCl (10 % free Cl_2, 20 µmol, 1.5 mol%) were added prior to the addition of 315 mg $NaClO_2$ (2.8 mmol, 2.1 eq.) in 1 mL H_2O over 15 minutes. ^{30min} *All reagents were doubled, $NaClO_2$ added within 30 min.*

Amount of OH-TEMPO [mol%]	**X_{C30} [%]**	**Ester [%(I)]**
1.3	93.5	4.0
	94.0^{30min}	8.0
0.89	93.5	13.5
	90.5^{30min}	7.0

*Table 51: 1.0 g $C_{16}OH$ (4.1 mmol), 2 mL H_2O, the specified amount of OH-TEMPO, CA and additives were added into the reaction vessel, heated to 90 °C. The specified amount of $NaClO_2$ was added within the specified amount of time and the mixture was stirred for 2 hours. * 0.5 g C16OH were used.*

CA [mol%]	**OH-TEMPO [mol%]**	**Additive**	**$NaClO_2$ [eq.]**	**Time $NaClO_2$ [h]**	**$C_{16}O_2H$ [%(I)]**	**Ester [%(I)]**
-	2.1	$K_2H(CA)$ (0.6 eq.)	1.2	1.5	68.5	9.0
0.6	2.1	-	1.2	1.5	1.5	0.5
0.6	2.5	NaOCl (0.3 mol%)	1.2	2.0	86.0	3.0
2.1	1.9	-	1.0	1.0	79.5	3.0
2.1	1.9	$C_2H_2O_2$ (5.0 mol%	1.0	1.0	77.5	3.0
2.1	1.9	NaCl (5.0 mol%)	1.0	1.0	81.0	2.5
2.1	1.9	$C_{18}O_2H$ (1.0 eq.)*	1.0	0.5	74.5	7.0

Table 52: 2.0 g split RBW(2.65 mmol), 2 mL H_2O, 10.0 mg OH-TEMPO (58 µmol, 2.1 mol%), 10.0 mg CA (50 µmol, 2.0 mol%) or 0.6 eq. $K_2H(CA)$ (as KOH and CA) were added into the reaction vessel, heated to 90 °C. 360 mg $NaClO_2$ (3.2 mmol, 1.2 eq.) in 1 mL H_2O was added within 1.5 hours and the mixture was stirred for 2 hours.

Additive	**X_{C30} [%]**	**Ester [%(I)]**
CA	92.5	7.5
$K_2H(CA)$	94.0	7.0

Batch experiment 3: 20.02 g RBW (26.5 mmol) were heated in a flask equipped with an overhead-stirrer in an oil bath which was set to 110 °C. When the wax was liquefied, 2.027 g NaOH (50.7 mmol, 1.9 eq.) dissolved in 5 mL H_2O were added within minute 0-6. A sample was drawn at minute 10, showing partial first splitting. Due to an increase in viscosity 15 mL H_2O were added after minute 30 and a sample was taken at minute 90, showing complete splitting of all esters. 6.01 g HOAc (99 mmol, 3.7 eq.) were dissolved in 60 mL H_2O and slowly added, while simultaneously letting the oil bath cool to 100 °C (minute 170-180). pH value was 4-5 when 36.5 mg TEMPO (0.23 mmol, 0.9 mol%) were added in 3 mL HOAc (50 mmol, 1.9 eq.), followed by 0.2 mL NaOCl (5 % free Cl_2, 0.13 mmol, 0.5 mol%). 4.502 g $NaClO_2$ (40 mmol, 1.5 eq.) were added in 20 mL H_2O from minute 200-220. pH value was determined to be 4-5. At minute 230 a sample was taken, which showed app. 60 % oxidation of C_{30}. Evolution of a greenish gas, supposedly $Cl_{2(g)}$ was observed at minute 240. At minute 300 a sample was taken which showed app. 92 % oxidation. The aqueous phase was discarded and the organic phase was washed 3 times with 40 mL H_2O. The resulting product was dried under reduced pressure (10^{-1} bar) at 95 °C. The acid value was determined by *Kahl GmbH & Co. KG* to be 130.

Batch experiment 4: 500.0 g RBW (0.66 mol) were heated in a 4 L three-neck flask equipped with an overhead-stirrer and reflux-condenser, suspended in an oil bath which was set to 115 °C. To speed up the melting of the wax a heat gun was attached to one of the flask openings, heating the interior of the flask with 150 °C hot air. When the wax reached a temperature of app. 110 °C, 40.02 g NaOH (1.0 mol, 1.5 eq.) dissolved in 20 mL hot water were added hot (app. 110 °C). Within one minute a brown viscous mixture was formed. At minute 15 (after NaOH addition) the oil bath was set to 120 °C, at minute 25 the viscous mixture had partly solidified and was not stirred effectively anymore. The mixture was allowed to react overnight (GC showed complete splitting), before 500 mL H_2O were added, followed by 20 g HOAc (0.33 mol, 0.5eq.) in 1000 mL H_2O and the oil bath temperature was set to 95 °C. Thereafter 500 g diluted H_2SO_4 (8 wt.%, 0.41 mol, 0.6 eq.) were added slowly within 4 hours. Additional 5 g of H_2SO_4 (50 mmol, 0.07 eq.) were added with 800 mL H_2O before aqueous and organic phase separated. 1.5 L aqueous phase were subtracted from the liquid organic phase. 0.3 L H_2O were added and the whole mixture was allowed to cool to room temperature overnight. At the next day the aqueous phase was not clear and therefore not discarded directly. The whole mixture was heated without stirring to 90 °C, thereby melting the wax and allowing the aqueous phase to clear of any wax particles. The aqueous phase was then subtracted and the organic phase was washed 3 times with 20 mL of H_2O (GC showed some ester content, app. 5 %). 2.52 g CA (13 mmol, 2.0 mol%) and 3.02 g OH-TEMPO (17.5 mmol, 2.6 mol%) were added with 920 mL H_2O, before 12.4 g NaOCl (5 % free Cl_2, 8.3 mmol, 1.3 mol%) were added and the addition of 90 g $NaClO_2$ (0.8 mol, 1.2 eq.) in 300 mL H_2O was started with a peristaltic pump within 2.5 hours. The mixture was allowed to stir overnight before heating and cooling was turned off. Cooled to room temperature the aqueous phase was decanted, the wax was heated to 90 °C, washed with water and cooled down again. GC showed a C_{30} conversion of app. 90 % and the acid value was determined by *Kahl GmbH & Co. KG* to be 114.

Batch experiment 5: 1 000 g RBW (1.3 mol) were heated in a 4 L three-neck flask equipped with an overhead-stirrer and reflux-condenser, suspended in an oil bath which was set to 120 °C. The flask was covered with aluminium foil for heat isolation. To speed up the melting of the wax a heat gun was attached to one of the flask openings, heating the interior of the flask with 150 °C hot air. When the wax reached 110 °C, 112.1 g KOH (85 %, 1.7 mol, 1.28 eq.) dissolved in 70 mL H_2O were slowly added. 20 minutes after the addition over ¾ of the wax were already split, while 50 minutes after the addition the GC showed complete splitting of the esters. 500 mL H_2O were slowly added and the oil bath temperature set to 95 °C. With the first 50 mL H_2O strong foaming occurred. Thereafter 132.2 g CA (0.69 mol, 0.52 eq.) dissolved in 300 mL H_2O were added over 2 hours. The oil bath was set to 90 °C and 6.00 g OH-TEMPO (34.8 mmol, 2.6 mol%) were added in 120 mL H_2O. Successively 40 mL NaOCl (5 % free Cl_2, 26.9 mmol, 2.0 mol%) were added and the addition of 180 g $NaClO_2$ (1.59 mol, 1.2 eq.) in 300 mL H_2O over 2.5 hours was started. When approximately 90 % of the $NaClO_2$ were added, intense foam formation and a temperature of 99.9 °C in the reaction mixture were observed. The aluminium foil was removed. 1.5 hours after completed addition a sample showed >94 % conversion of C_{30}. 27.5 g H_2SO_4 and 20 mL H_2O were added to speed up separation of the two phases. The mixture gained a slight green colour thereafter, and was after 10 minutes of additional stirring allowed to cool to room temperature overnight. On the next day the flask was heated in the oil bath to 100 °C without stirring whereupon the phases separated. It was cooled to room temperature again and the aqueous phase was decanted. The organic phase was washed three times with acidified water, each washing being less acidic. Finally, 1 031 g of oxidized RBW were gained, whose acid value was determined by *Kahl GmbH & Co. KG* to be 132.

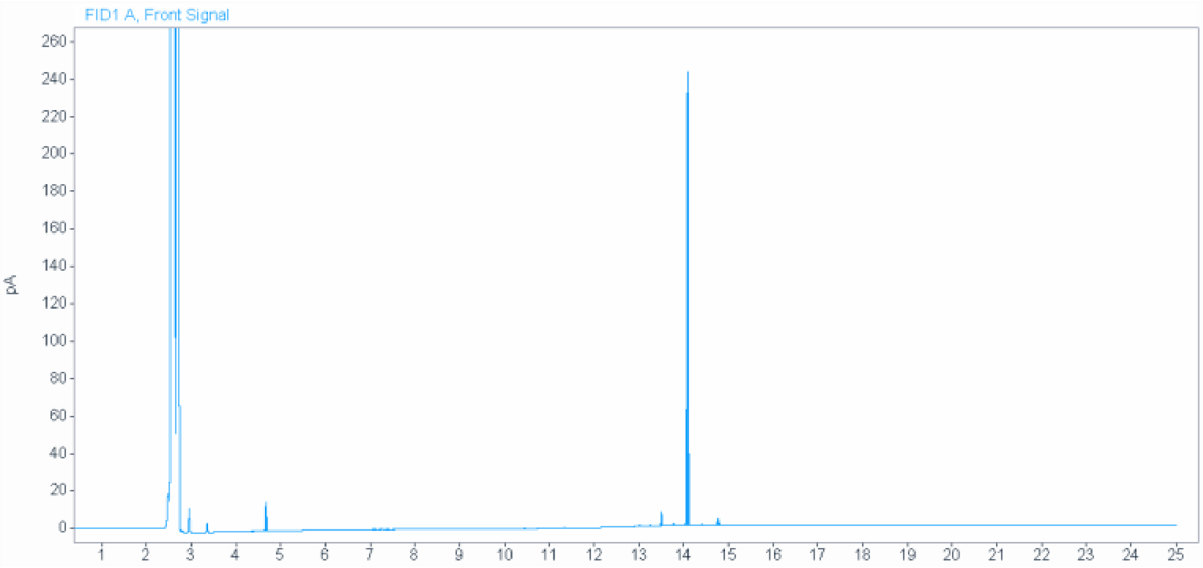
5.4. Syntheses

Hexadecyl octadecanoate[64]

A mixture of 120 g (0.50 mol) hexadecanol and 140 g (0.49 mol) octadecanoic acid was heated to 125 °C and stirred for 72 h. The resulting product was cooled, dissolved in hexane and purified by column chromatography. 183 g (0.36 mol, 73 %) of hexadecyl octadecanoate were received as a white powder.

^{1}H-NMR (400 MHz, C_6D_6): δ [ppm] = 0.85-0.95 (m, 6 H, CH_3), 1.15-1.35 (m, 54 H), 1.45-1.55 (m, 2 H, $C\underline{H_2}CH_2O$), 1.55-1.65 (m, 2 H, $C\underline{H_2}CH_2CO_2$), 2.18 (t, ^2J = 7.5 Hz, 2 H, CH_2CO_2), 4.04 (t, ^2J = 6.7 Hz, 2 H, CH_2O).

^{13}C-NMR (101 MHz, C_6D_6): δ [ppm] = 14.4 (2 C, CH_3), 23.2, 25.5, 26.4, 29.2, 29.6, 29.8, 29.8, 29.9, 30.0, 30.1, 30.1, 30.2, 30.2, 30.3, 32.4, 34.5 (1 C, $\underline{C}H_2CO_2$), 64.3 (1 C, CH_2O), 173.1 (1 C, $CH_2\underline{C}O_2$).



Chromatogram 8: Typical GC-result of C_{16}-O_2C_{18}. Purity by integral is 95.5 %, the main impurity is C_{16}-O_2C_{16} (app. 2 %) due to $C_{16}O_2H$ impurities in $C_{18}O_2H$ (2.5-3.5 min solvent heptane, 4.7 min dodecane as standard, 13.5 min C_{16}-O_2C_{16}, 14.1 min C_{16}-O_2C_{18}).

6. Appendices

*Table 53: Prices for basic metal hydroxides. * If no purity was given, 95 % purity was assumed. [M] The exchange rate was estimated to be 75 INR = 1 €.[44,140]*

Base (purity*)	**Shipment date**	**Amount [t]**	**Reported price [*1000 INR]**	**Price per mass [€/t][M]**	**Price per OH^- [€/kmol(OH^-)]**
NaOH	25.05.2015	25	633	337.70	14.22
KOH (90 %)	19.11.2016	20	1 052	700.97	43.70
MgO	04.10.2016	270	1 776	87.72	1.86
CaO	01.09.2016	228	1 200	70.25	2.07

*Table 54: Prices for basic acids. * If no purity was given, 95 % purity was assumed. [M] The exchange rate was estimated to be 75 INR = 1 €.[44,140]*

Acid (conc.*)	**Shipment date**	**Amount [t]**	**Reported price [*1000 INR]**	**Price per mass [€/t][M]**	**Price per H^+ [€/kmol(H^+)]**
H_2SO_4	20.10.2016	19 682	22 232	15.06	0.78
H_3PO_4 (75 %)	22.11.2016	11 780	442	500.31	21.79
HCl (36 %)[141]				40.00[X]	4.05
HNO_3 (68 %)	27.10.2016	22	467	277.66	25.73
HOAc	22.10.2016	55	1 097	265.82	16.80
H_3(CA)	21.11.2016	25	1 049	559.45	41.25

[X] “45 $/wet ton 22-degree Baume material ex works”.

*Table 55: Prices of large scale N-oxyl radicals. * If no purity was given, 95 % purity was assumed. [M] The exchange rate was estimated to be 75 INR = 1 €.[44,140]*

Reagent (purity*)	**Shipment date**	**Amount [t]**	**Reported price [*1000 INR]**	**Price per mass [€/t][M]**	**Price per Mol [€/kMol]**
TEMPO (99 %)	03.06.2016	0.125	694	74 045	11 668
OH-TEMPO	17.10.2016	9	3 007	4 455	807

*Table 56: Prices of N-oxyl radicals from one supplier. * If no purity was given, 95 % purity was assumed.*[142]

Reagent (purity*)	**CAS**	**Amount [g]**	**Price [€]**	**Price per mass [€/g]**	**Price per Mol [€/Mol]**
TEMPO (98 %)	2564-83-2	25	60.58	2.42	386
OH-TEMPO (95 %)	2226-96-2	100	140.00	1.40	254
Oxo-TEMPO	2896-70-0	5	114.72	22.94	4 111
MeO-TEMPO (97 %)	95407-69-5	5	74.42	14.88	2 858
NH$_2$-TEMPO (97 %)	14691-88-4	5	274.30	54.86	9 686
AA-TEMPO (97 %)	14691-89-5	25	341.25	13.65	3 002
4-CO$_2$-TEMPO (97 %)	37149-18-1	0.25	66.62	266.48	55 013
TEMPO methacrylate (98 %)	15051-46-4	1	93.00	93.00	22 806
TEMPO-4-mesylat (97 %)	35206-66-8	1	140.85	140.85	35 980
4-Hydroxy-TEMPO benzoate (97 %)	3225-26-1	1	58.63	58.63	16 704
AZADO (96 %)	57625-08-8	0.25	163.15	652.60	103 471
1-Me-AZADO (97 %)	872598-44-2	0.1	165.00	1 650.00	282 779
ABNO (95 %)	31785-68-9	1	153.40	153.40	22 639
TEMPO on Turbobeads (99 %)		2.5	275.40	110.16	1 112 727
TEMPO on Silica gel		25	247.00	9.88	14 857
TEMPO on Polymer		5	208.65	41.73	439 263

*Table 57: Prices of (basic) oxidants. * If no purity was given, 95 % purity was assumed.* [M] *The exchange rate was estimated to be 75 INR = 1 €.*[44,140]

Reagent (purity/conc.*)	**Shipment date**	**Amount [t]**	**Reported price [*1000 INR]**	**Price per mass [€/t]**	**Price per Mol active oxygen [€/kMol(O)]**
O$_2$	-	-	-	-	0.00
H$_2$O$_2$ (50 wt.%)	19.11.2016	30	780	347	23.59
NaOCl (14 %)	21.11.2016	1.4	82	780	415
NaClO$_2$ (80 %)	17.11.2016	21	2 914	1 274	72.04
NaClO$_3$	07.11.2016	21	710	451	16.83
NaClO$_4$	22.11.1016	25	1 633	871	32.19
Na$_2$Cr$_2$O$_7$	19.11.2016	21	1 498	951	87.45
CrO$_3$	10.10.2016	18	2 350	1 741	122
KMnO$_4$	22.01.2015	19	2 944	2 040	136
TBHP	27.05.2014	15	1 753	1 538	198

*Table 58: Prices of various chemicals. * If no purity was given, 95 % purity was assumed. ^{M} The exchange rate was estimated to be 75 INR = 1 €.*[44,140]

Reagent (purity*)	(Shipment) date	Amount [kg]	Reported price [*1000 INR]	Price per mass [€/kg]	Price per Mol [€/Mol]
W (99.95 %)	02.11.2016	1 500	2 999	26.65	4.90
Na_2WO_4	18.07.2016	10 000	7 904	10.54	3.26
Mo	08.11.2016	972	1 307	15.80	1.81
Re	17.09.2014	5	893	2 382	467
Re[143,144]	08.01.2018	1 pound	1 290 $	2 376	466
Re[145,146]	28.09.2017	1	~41 k RMB	5 250	978
Aliquat 336	26.03.2016	52	17 163	4.40	1.87

Table 59: Water hazard class ("Wassergefährdungsklasse", WGK) according to the online database of the German Umweltbundesamt (Federal Environment Office). No data was found for TEMPO and Oxo-TEMPO.[25]

	WGK		
	1	**2**	**3**
Bases	NaOH, KOH, CaO, MgO, $Ca(OH)_2$,		
Acids	H_3(CA), HOAc, H_2SO_4, H_2WO_4	HCl, $HClO_4$	
Salts	NaCl, KCl, $NaClO_4$, NaH_2(CA), Na_3(CA) * 2 H_2O, K_3(CA) * 2 H_2O, $Ca_3(CA)_2$, $CaSO_4$	NaOCl, $NaClO_2$, $NaClO_3$,	
Organics	OH-TEMPO, AA-TEMPO	Bu_4NHSO_4	$C_{12\text{-}16}Me_3NCl$, $C_{12\text{-}16}Me_3NBr$
Cr compounds	$CrCl_3$ (anhydrous), $Cr_2(SO_4)_3$ (anhydrous)	$CrCl_3$ * 2 H_2O, chrom(III)-potassium sulfate dodecahydrate, $Cr(NO_3)_3$ * 9 H_2O, Cr(III)-sulfat (basic)	chromosulfuric acid, CrO_3, "soluble Cr(VI) reagents"
Others	H_2O_2	$Cl_{2(g)}$	$KMnO_4$

7. Curriculum Vitae

Personal

Name	Tommy Alfred Hofmann
Date and place of birth	04.04.1991 in Bad Ems

Education

08.2015 – 06.2018	PhD candidate at Technichal University Munich (TUM), Professorship for Molecular Catalyses (Prof. Kühn)
10.2013 – 06.2015	Chemistry, M.Sc. (TUM). Grade: 1.2 Master's Thesis (1.3): Studies on the oxidation of renewable waxes utilizing a model substrate; Professorship for Molecular Catalyses (Prof. Kühn)
10.2010 – 09.2013	Chemistry, B.Sc. (TUM). Grade: 2.0 Bachelor's Thesis (1.0): Optimizing Silica doped Zirconia catalysts for producing Green Diesel from Microalgae oil; Technichal Chemistry II (Prof. Lercher)
2001 – 2010	Mons-Tabor-Gymnasium, Montabaur. Abitur 1.5 Facharbeit Chemie: Koffein – ein legales Dopingmittel? (15 MSS-points)

Professional Experience

Scientific Assistant (TUM)	08.2015 – exp. 07.2018, Development of an industrially applicable oxidation of rice bran wax in cooperation with Kahl GmbH & Co. KG, financially supported by BMBF
Tutorials (TUM)	Tutorials in Principels & Methods in Chemistry, Methods in Mathematics I, Organic Chemistry I, Practical Internships in Organic Chemistry
Kloeckner-Pentaplast, Montabaur	03.-04. 2011, 2-month internship in the field of process technology

Foreign Experience

Edinburgh, Scotland	09. – 10.2014, 6 weeks internship in the research group of Jason B. Love (University of Edinburgh)
Nashville, Tennessee, USA	08. – 09. 2010, 8 weeks internship in the research group of Jens Meiler (Vanderbilt University)

Qualifications

Languages	English Latin (“Großes Latinum”) Spanish
Further	Driving licence A, BE, T sport boat licence see & inland (Germany) CMAS ** (diver’s licence) Weaponry expertise according to §7 WaffG

Miscellaneous

Interests	Swimming (competitive 2000-2007) Sport shooting (competitive 2005-2010) Diving Working in olive groves
Selection procedure of the IChO 2009 & 2010	Reaching the last round (15 pupils) both times, in 2010 achieving the 6th place
Stipends	Scholarship of Rhineland-Palatinate (04.2009 – 03.2010) Internship sponsored by the Meiler-Lab (08.-09.2010) e-fellows.net stipend (since 10.2010) Travel expense stipend by the Bavarian State Ministry for Education and Culture, Science and Art (for the internship 09. – 10.2014 in Edinburgh)
Co-author in publications	Cadenbach, T., Pankhurst, J.R., Hofmann, T.A., Curcio, M., Arnold, P.L., Love, J.B. (2015). Macrocyclic Platforms for the Construction of Tetranuclear Oxo and Hydroxo Zinc Clusters. Organometallics, 34 (11), 2608–2613. Lindert, S., Hofmann, T., Wotzel, N., Karakas, M., Stewart, P.L., Meiler, J. (2012). Ab initio protein modelling into CryoEM density maps using EM-Fold. Biopolymers, 97, 669-677.

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