Salt Effects in Hydrothermal Synthesis

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It is only those who know a little of nature, who fancy they know much. I have heard a young man say, after hearing a few popular chemical lectures, and seeing a few bottle and squirt experiments: Oh, water – water is only oxygen and hydrogen! – as if he knew all about it. While the true chemist would smile sadly enough at the youth's hasty conceit, and say in his heart: 'Well, he is a lucky fellow.'[1]

Charles Kingsley

ACKNOWLEDGMENTS

This work would not have been possible without the help of many people.

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SUMMARY

This work focuses on hydrothermal water as solvent and reaction medium. Water is abundant, non-toxic and environmentally benign, but at room temperature it does not dissolve most of the materials used in organic chemistry. When raising the temperature, though, its strong hydrogen bonds are weakened. At supercritical conditions water behaves similar to an unpolar solvent.

However, high pressure, temperature and corrosion are technical challenges when reaching supercritical conditions. Also, water in a temperature range of 150–200°C, also called hydrothermal water (HTW) is available from the cooling process of power plants. Therefore, experiments were placed in a temperature range around 180°C.

A lot of factors influence the yield and selectivity of HTW reactions. Hereby a special interest is taken in the impact of inorganic salts such as sodium chloride to the reaction mixture. Primarily hydrothermal conditions amplify the acidic or basic reactions of salts. In more complex mixtures other side reactions such as complex formation can take place.

More influences on HTW reactions studied in this work are the heating method, the reactor material and the creation of temperature-switchable liquid-liquid phase systems.

Model reactions were chosen that simulate aspects of the more complex hydrothermal carbonization of carbohydrates. Results include besides dehydration and rearrangement reactions the industrially important formation of carbon-carbon bonds (e.g. aldol condensation). Furthermore, HTW is applied in the extraction of aromatic monomers from Kraft lignin.

In conclusion, hydrothermal water is an interesting medium for organic and biomass reactions. Framework knowledge opens a lot of possibilities for development of new techniques and improvement of existing processes.

ZUSAMMENFASSUNG

Diese Arbeit beschäftigt sich mit Wasser unter hydrothermalen Bedingungen als Lösungsmittel und Reaktionsmedium in der organischen Synthese. Wasser ist ungiftig, umweltfreundlich, und im Überfluss vorhanden, aber unter Normalbedingungen lösen sich die meisten in der organischen Chemie verwendeten Substanzen nicht darin. Eine Erhöhung der Temperatur hat jedoch die Schwächung seiner Wasserstoffbrückenbindungen zur Folge. Jenseits des kritischen Punktes verhält sich Wasser wie ein unpolares Lösungsmittel.

Die Rahmenbedingungen für überkritisches Wasser beinhalten jedoch technische Herausforderungen wie hohe Temperatur, Druck und Korrosion. Ein zusätzlicher Aspekt ist die Verfügbarkeit von Wasser im Temperaturbereich von 150–200°C, das in den Kühlprozessen thermischer Kraftwerke anfällt. Deshalb wurden die Versuche im Bereich von 180°C durchgeführt. Wasser bei diesen Temperaturen wird im Folgenden als hydrothermales Wasser, kurz HTW, bezeichnet.

Viele Faktoren beeinflussen die Ausbeute und Selektivität organischer Reaktionen. Besonderes Augenmerk richtet sich dabei auf die Einwirkung anorganischer Salze, wie Natriumchlorid NaCl, zum Reaktionsgemisch. Ergebnisse zeigen, dass der pH-Wert durch eine Verstärkung der Protonierungs-/Deprotonierungsreaktionen unter hydrothermalen Bedingungen verändert

wird. In komplexeren Systemen finden zudem andere Konkurrenzreaktionen wie zum Beispiel Komplexbildung statt.
Andere untersuchte Kriterien hydrothermaler Reaktionsausbeuten sind die Heizmethode, das Reaktormaterial oder die Einstellung eines temperaturveränderlichen flüssig-flüssig Phasengemisches.

Modellreaktionen wurden ausgewählt, um das komplexere Phänomen der hydrothermalen Karbonisierung zu simulieren. Die Ergebnisse beinhalten neben Dehydratisierungs- und Umlagerungsreaktionen auch die Bildung neuer Kohlenstoff-Kohlenstoff Bindungen wie zum Beispiel Aldol Kondensationen. Des weiteren wird die hydrothermale Gewinnung aromatischer Monomere aus Kraft Lignin untersucht.

Hydrothermales Wasser ist ein interessantes Reaktionsmedium für die organische Synthese und zur Biomasseverwertung. Genaueres Wissen um die Rahmenbedingungen öffnet viele Möglichkeiten für die Entwicklung neuer Prozesse und Verbesserung bereits bestehender Verfahren.

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I

INTRODUCTION

This work origins in a series of different fields of interest. First among them was the area of hydrothermal carbonization HTC. A natural process commonly known for decades, it was only recently introduced into organic synthesis by Prof. Markus Antonietti and coworkers. They used it to fabric carbon nanostructures[2,3] and templates for catalysis,[4] and proposed deployment as fertilizing soil additive.[5]
The explicit mechanism of hydrothermal carbonization is still not entirely clear, mainly because of the complex interwoven reactions implicated in the carbon formation from complex molecules. Also they observed a peculiar phenomenon: The addition of a seemingly inert salt, as for example sodium chloride, greatly improves the conversion of sugars to carbon.

The last observation raised the interest of Prof. Werner Kunz, specialized in the field of water-ion-interactions.[6] At a meeting in April 2008 with Prof. Antonietti and with Dr. Frédéric Goettmann, former postdoc in the group of Prof. Antonietti, a plan to investigate hydrothermal organic synthesis was developed. For this a PhD thesis topic was given out in all three cooperating institutes: The Max-Planck-Institute for Colloids and Interfaces in Golm (Potsdam), the University of Regensburg, and the ICSM in Marcoule, France.

While in Golm the chemistry of carbohydrates was examined by Daniel Kopetzki, different organic reactions were investigated in Marcoule by Bernhard Smutek and the physicochemical background was the main thesis topic in Regensburg. At regular meetings results were discussed and new ideas exchanged. Results were published in the respective doctoral theses and various research articles.[7–10]

Integration of the concepts of Green and Sustainable Chemistry was a fundamental part of the newly developed ideas and will be discussed in detail in chapter II. Also background information on hydrothermal water properties, technical challenges, and biomass composition will be given there.

The experimental part includes impact of different salt additions to the dehydration reaction of the model alcohol 1-phenyl-1-propanol and the aldol condensation of benzaldehyde and acetophenone. Results show this correlation to be mainly originated in the influence of salts on the pH at higher temperatures.

Next the extraction of aromatic monomers from Kraft lignin was examined. The main problem was identified to be repolymerization reactions onto the lignin strands. Solving these problems efficiently calls even more fine-tuning of HTW reactions and also better equipment. Minor recovery of aromatics, however, should be easily to integrate within existing plants, since Kraft cooking is very similar to HTW conditions.

In the following conventional heating of HTW reactions were compared with heating in a novel synthesis microwave oven. This method is growing more and more popular in chemistry for its advantageous heating properties, yet it has not been ascertained for sure if there are other, specific microwave effects that increase reaction yields. The collected data showed, though, that there are several competing factors in the experimental setup which influence the reaction yield.

Lastly the introduction of a temperature-dependent HTW phase system was presented. Polyethylene glycol PEG is completely soluble in water at ambient conditions, but separates into two liquid phases at higher temperatures. This is extensively used in industrial phase partitioning. 1,8-octanediol, on the other hand, forms two liquid phases with water upon melting. At higher temperatures they mix and a single liquid phase appears instead. Based on these observations, the effects of these variable phase systems on known reaction yields were examined.

Overall some of the experiments led to unexpected results. These were investigated, evaluated and interpreted. In conclusion, it has to be noted that hydrothermal synthesis undergoes a variety of different influencing factors, some of which are not fully evaluated until today.

II

FUNDAMENTALS

This part discusses the theoretical framework of knowledge of the main topics in this PhD project. Important concepts and terms are explained in detail, and put into the necessary context.

1 Hydrothermal Water

Hydrothermal water or high-temperature water (HTW) is hereby defined as liquid water in a temperature range of 100°C – 300°C under its autogenous pressure. Other important terms in this regard are supercritical water (SCW, above the critical point) and near-critical water (NCW, approaching the critical point of water). The critical point of water is 647.096 K ($\hat{=}$ 374°C) and 22.6 MPa, with a density of 322 kg/m^3.[11]

1.1 Physicochemical Properties

Water is one of the most important substances on earth. Due to its extended application in industry information on its properties at high temperatures is needed. Therefore, "The International Association for the Properties of Water and Steam" (IAPWS) was founded. As an assembly of national organizations, it provides a lot of data on numerous properties of water, steam, and aqueous solutions through Releases and Guidelines on their webpage.[12] Also it identifies "Certified Research Needs" (ICRNs) to close the gaps of missing data for potential industrial application.

Consequently the available data on the properties of water at elevated temperatures and pressures is too substantial to be mentioned here. Thus only a few selected properties important to synthesis will be presented in the following.

Hydrogen bonding

Hydrogen bonding is one of the key factors for the properties of liquid water. At ambient temperature and pressure they form an infinite network with a unique structure based on a tetrahedral coordination.

With increasing temperature and pressure, the relative amount of hexagonal structures increases, converging towards the behaviour of other simple liquids.[13]

The number of hydrogen bonds decreases, in consequence water also loses its strong hydration power. This can be seen e.g. in the so-called clouding, a phenomenon seen on nonionic surfactants and short chain amphiphiles (hydrotropes). For a given composition, they undergo phase separation above a certain temperature (the cloud temperature), because their solvation with water molecules is no longer sufficiently high to ensure miscibility.

Nevertheless, even above the critical point hydrogen bonding is still present. Here water tends to form clusters that are strongly dependent on temperature and pressure.[14,15]

Dielectric Constant

The dielectric constant ϵ or permittivity describes the ability of a material to interact with an electric field. Regarding solvents, it directly relates to their polarity and is thus an important unit concerning solvent properties.[11] The common way to refer to it is the relative dielectric constant ϵ_{rel}, which is dimensionless.[16]

A solvent having a high dielectric constant generally means that it dissolves easily ionic species and polar compounds. Solvents with a low dielectric constant dissolve preferentially small organic molecules, while ions form contact pairs.[17] Another effect that relates to the permittivity of a material is the microwave dielectric heating effect (see also chapter V.1). A general overview of some dielectric constant values are found in table II.1.

cyclohexane	2.015
benzene	2.274
ammonia	16.9
ethanol	24.30
water	78.54

Table II.1: Relative dielectric constant at 298 K.[16]

With increasing temperature the dielectric constant of water decreases (see figure II.1). In consequence, at high temperatures water behaves like a non-polar solvent, making it thus an ideal medium for organic synthesis.[17] After cooling down the initial properties reemerge, and the organic phase can easily be separated from the solvent.

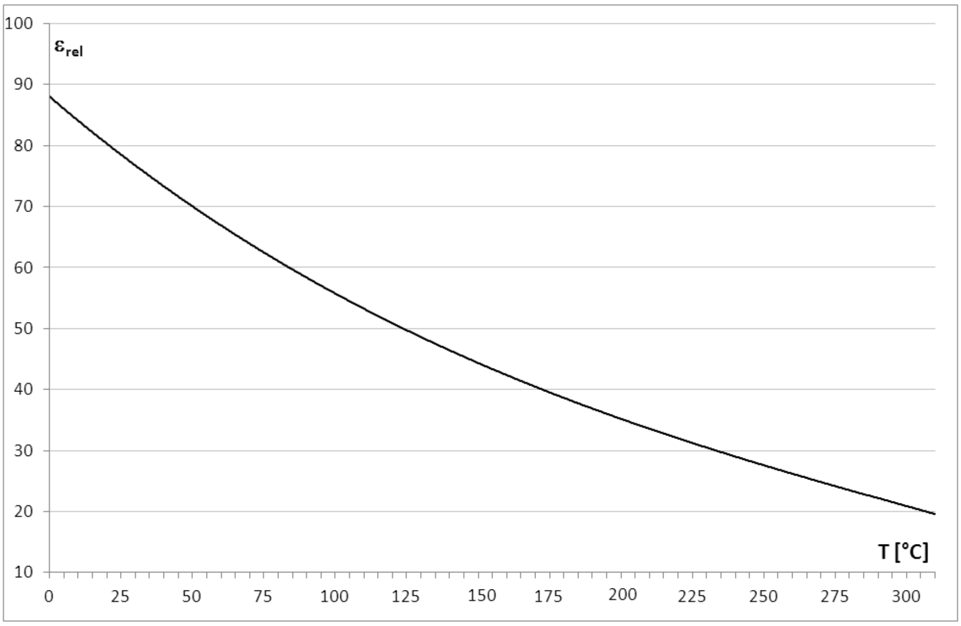


Figure II.1: Temperature dependence of the relative dielectric constant of water at a pressure of 20 MPa.[18]

Ionic Product

The ionic dissociation constant or ionic product of water is based on the following equation

$$2\ H_2O \rightleftharpoons H_3O^+ + OH^-.$$

At room temperature its equilibrium constant K_w (includes the activity of undissociated water) is about 10^{-14}, which results in the familiar value of pH 7 for neutral water.[11]

Initially the pK_w (the negative decadic logarithm of K_w) decreases with increasing temperature, thus accounting for an increased activity of both ionic species (compare figure II.2). Around 250°C, however, there is a minimum after which the pK_w increases again. Around the critical point, then, the ionic product varies strongly with temperature and pressure, providing a measure of fine-tuning the catalytic properties of the solvent.[17]

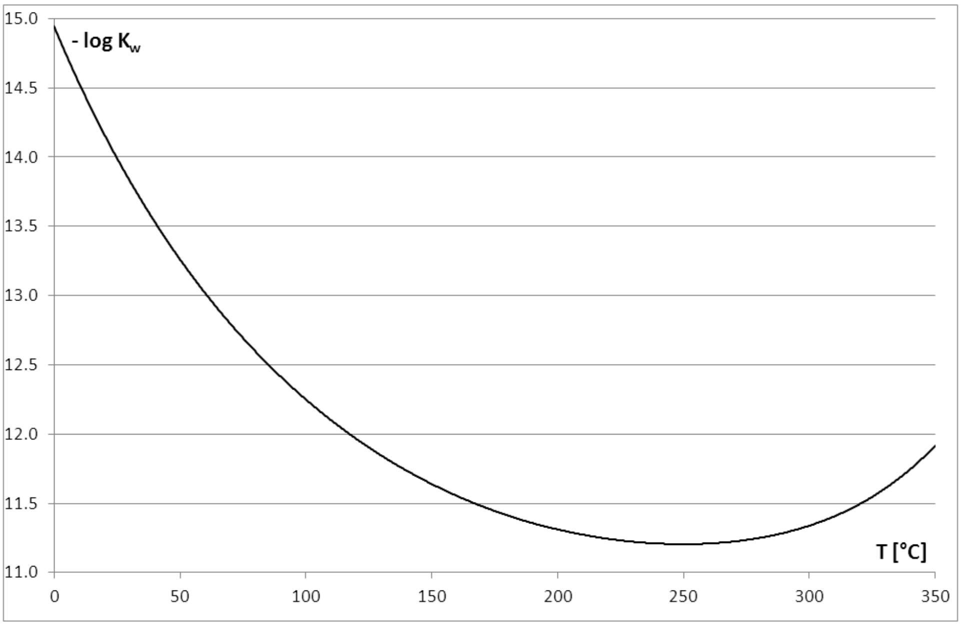


Figure II.2: Temperature dependence of the dissociation constant of water at 0.1 MPa at T < 100°C, or p_s (saturated liquid) at T > 100°C.[19]

Transport Characteristics

To react, molecules have to come in close contact first. In this context, important factors to change the rate constants of reactions are the transport characteristics of a solvent. They consist of parameters such as viscosity, heat capacity, diffusion coefficients and density.[20] In general they alleviate reactions with increasing temperature, for details the reader is referred to the corresponding literature.[12] Here shall only be mentioned that by controlling the density around the critical point, a lot of other variables can be controlled to a high extent.[20]

1.2 Reactions in HTW

The above mentioned physicochemical properties of high-temperature water make it an interesting medium for chemistry.

Historically, coming from geothermal science, it has been used first for inorganic synthesis.[21,22] A wide range of materials have been synthesized: microporous crystals (also called zeolites), ionic conductors, complex oxides and fluorides, low-dimensional aluminophosphates, inorganic–organic hybrid materials, and specially condensed materials such as diamond and inorganic helical chains.[23] Also, synthesis of nanocrystalline oxide materials has raised some interest.[20]

Natural occurring hydrothermal reactions of organics have been responsible for the formation of fossil fuels. And much sooner, as the formation of the first organic molecules on earth were placed in a hydrothermal environment.[24] Similar conditions are still found at hydrothermal vents in the deep sea (Figure II.3). Despite that, organic synthesis in high-temperature water grew popular not until the 1980ies. Numerous articles on different organic reactions have been published since, of whose Katritzky et al. give a good directory.[26] Some important examples have been reviewed by Galkin and Lunin,[20] or, more recently, Simsek Kus.[27]

In general, possible organic reactions include hydrolysis, hydration/dehydration, various rearrangements, elimination, formation and cleavage of carbon–carbon bonds, hydrogenation/dehydrogenation and oxidation. Some selected examples are shown in table II.2.

Whereas subcritical water gives a good environment for acid/base catalyzed reactions, supercritical water promotes mostly free-radical processes. The latter is based on the decomposition of water molecules and collision between the reagent and solvent molecules. What more, supercritical water offers a wide range of fine-tuning options of its solvent properties with density. And last but not least, there are some more additives increasing options for both

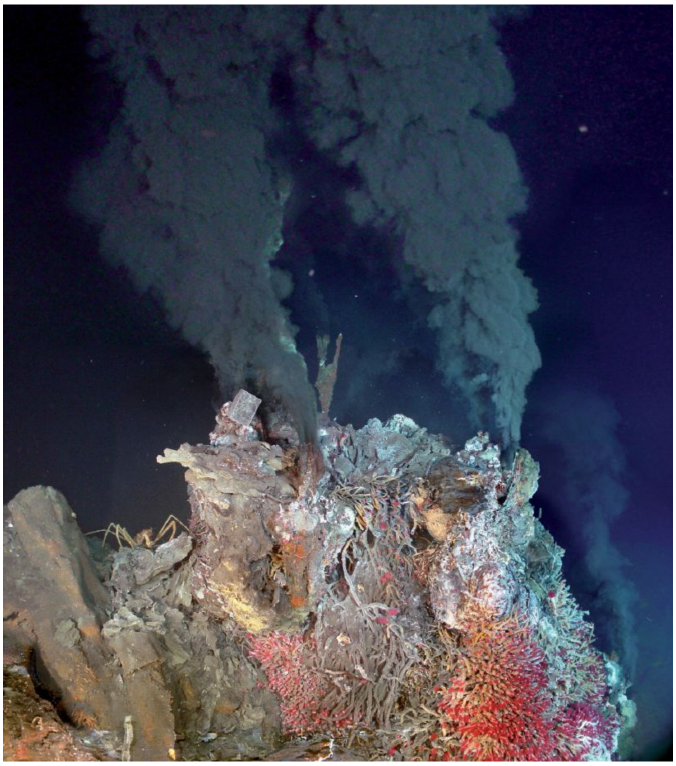


Figure II.3: A black smoker in the Main Endeavour Field, North Pacific. These hydrothermal vents are assumed to have created the first organic molecules and generated life on earth.[25]

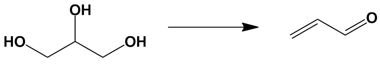
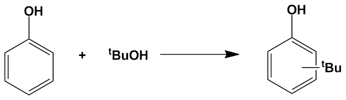
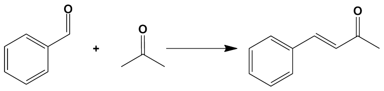
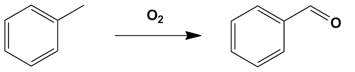
Reaction type	Example	Temp. (°C)	Yield (%)	Ref.
Dehydration		360	75	[28]
Friedel-Crafts alkylation		275	20	[29]
Aldol condensation		250	24	[30]
Oxidation		375	60	[27]

Table II.2: Some examples of organic reactions in SCW.

sub- and supercritical water reactions: Gases such as CO_2 and O_2, inorganic salts, HTW-stable catalysts, or an additional organic phase.

However, most of the above mentioned examples concentrate on the near critical or supercritical region, whereas the region between 100°C and 200°C has hardly been investigated. The implications of this will be discussed later in section II.4.

Finally, we have the aforementioned phenomenon of hydrothermal carbonization (HTC). Going all the way from complex biomass molecules to simple coal, most of the above mentioned reactions are supposed to take place simultaneously. For this transformation, no supercritical conditions are required. On the other hand, most experiments take place up to 200°C and the corresponding autogenous pressure.[31–33]

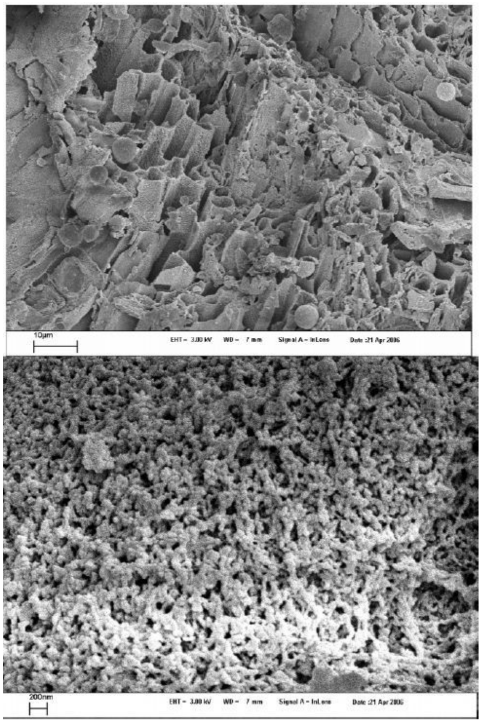


Figure II.4: SEM overview (above) and magnification of a HTC treated oak leaf.[3]

1.3 Technical Details

Challenges to the Reactor Material

Pressure, temperature, and corrosion impose certain demands on the vessels containing hydrothermal reactions. This section discusses the advantages and disadvantages of various standard laboratory materials. To the present knowledge there exists no universal material for sub- and supercritical water experiments.[34]

Glass is a risky material to use under high-pressure conditions, the risk of cracking and shattering makes it a safety risk. Furthermore, it is sensitive to high pH, with a sharp increase of reaction kinetics at temperatures over 100°C.

Steel and its alloys are the standard reactor material for autoclaves and high-pressure containers. With increasing temperature, though, corrosion of the material takes place. Due to the changes in the ionic product of water reactor walls are being dissolved, albeit slowly. This results in the appearance of iron ions in the solution, which often catalyzes reactions.[35]

Teflon is used e.g. for sealings and coatings of laboratory tools. Its virtue is its stability against chemicals. However, for HTW experiments it possesses a relative low melting point of about 300°C. At temperatures over 200°C its texture softens up and becomes butter-like. Then it also incorporates easily organic chemicals, to lose parts of it again at later heatings. Cleaning processes are rather ineffective, and contamination of the samples is the result.

Batch Mode versus Continuous Flow Reactor

The simplest setup for a hydrothermal reaction consists of a sealable vessel which is able to withstand high pressures. However, in industry most processes are carried out in flow. To mimic these reaction conditions, microreactors have been employed for laboratory purposes in various circumstances (compare figure II.5).

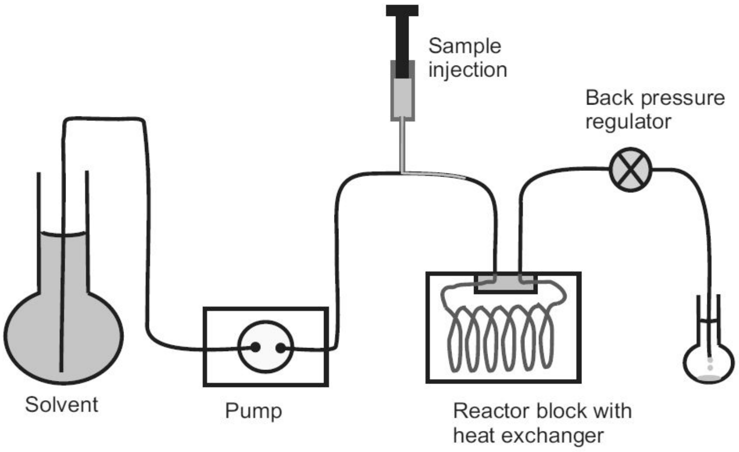


Figure II.5: Schematic overview of the essential part of a high pressure continuous flow reactor.[36]

Besides the easy upscaling of experiments to large quantities, other advantages include increased efficiency, control and safety.[37] With the addition of a pressure regulator, microreactors can also be used for HTW reactions. While D. Kopetzki employed a commercially available flow reactor with Hastelloy reaction tube from Thales Nano,[36] Ulbrich et al. used a microreactor built from two HLPC pumps connected to a stainless steel tube.[38]

Both workgroups started with materials coming from carbohydrates biomass conversion. A common problem in this area is the occurrence of unwanted side reactions of hydrothermal carbonization, also discussed in section II.4.3.

It leads to rapid blockage of the thin tubes. As countermeasure to this issue Ulbrich et al. proposed the addition of toluene to the reactor stream to dissolve the formed byproducts continually.

2 Salt Effects

2.1 General Salt Effects: The Brönsted-Bjerrum Equation

Many chemical reactions include ions or ionic intermediates. The activity coefficient of an ion γ_i depends on the ionic strength I:

$$I = \frac{1}{2} \sum c_i z_i^2 \tag{II.1}$$

with c_i being the concentration and z_i the electrovalency of every ion i in the solution. According to Debye and Hückel,[39] this correlation is, at low salt concentration,

$$\ln \gamma_i = -\frac{e^2}{2\epsilon kT} \left(\frac{8\pi N_0 e^2}{1,000\epsilon kT} \right) 0.5 \cdot z_i^2 \sqrt{I} \tag{II.2}$$

with ϵ being the permittivity of the medium, T the temperature, k the Boltzmann constant, e the elementary positive charge and N_0 the Avogadro constant.

Brönsted and Bjerrum formulated a reaction of two ions A and B in equilibrium with their initial collision complex C before continuing to the product(s) P

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \longrightarrow \mathrm{P} \tag{II.3}$$

with

$$c_c = K c_A c_B \left(\frac{\gamma_A \gamma_B}{\gamma_C} \right) \tag{II.4}$$

and K being the equilibrium constant. According to the postulates of Harned and Lewis, the rate of breakdown of the complex C into P, is proportional to its concentration, and not so fast as to disturb the equilibrium. Then the reaction velocity becomes

$$-\frac{dc_c}{dt} = +\frac{dc_p}{dt} = k'c_c = k'Kc_Ac_B\left(\frac{\gamma_A\gamma_B}{\gamma_C}\right) \tag{II.5}$$

and the bimolecular constant

$$k_2 = \frac{1}{c_Ac_B} * \frac{dc_p}{dt} = k'K\left(\frac{\gamma_A\gamma_B}{\gamma_C}\right) = k_2^0\frac{\gamma_A\gamma_B}{\gamma_C} \tag{II.6}$$

where k_2^0 is the bimolecular constant at infinite dilution.

Inserting the findings of Debye and Hückel, the Brönsted-Bjerrum theory arises

$$\log_{10}(k_2/k_2^0) = \frac{e^2}{2.303\epsilon kT}\left(\frac{8\pi N_0e^2}{1,000\epsilon kT}\right)0.5z_Az_B\sqrt{I} \tag{II.7}$$

Although this is calculated for a bimolecular reaction involving two ions, one can clearly see a general dependence of reaction rates on the ionic strength of a solution (as long as ions are involved). Unfortunately this equation works only well at concentrations up to one millimole per liter. At higher concentrations, effects like the formation of ion pairs disturb this simple view of reaction mechanisms.

2.2 Specific Salt Effects: The Hofmeister Effect

Not only the overall ionic strength of a solution characterizes its physical behaviour, there are also differences between ions. Father of this insight was the German Pharmacology professor Franz Hofmeister. He investigated the effect of different aqueous salt solutions on the precipitation of globulin from hen egg white, and also isinglass (a gelatine), colloidal ferric oxide and sodium oleate. According to the results he sorted the salts regarding to their "ability to absorb molecular water", an arrangement which today is widely known as the "Hofmeister Series".[40]

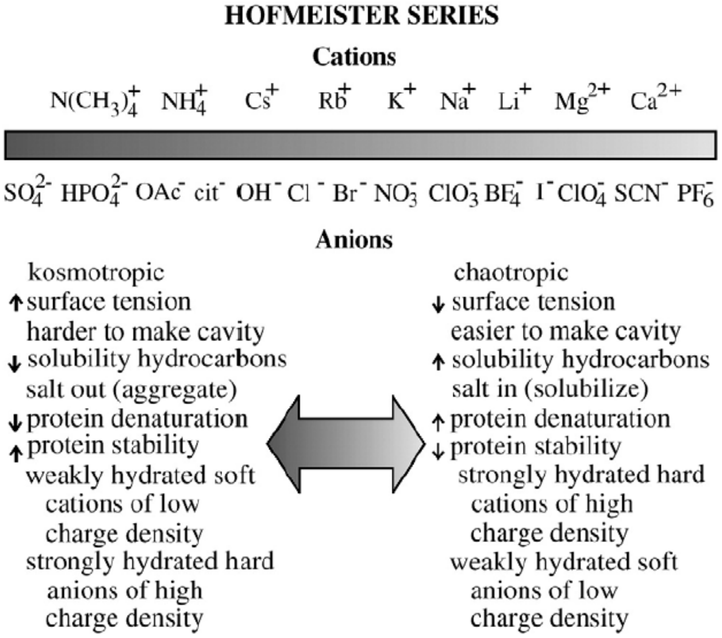


Figure II.6: Typical display of a Hofmeister Series.[41]

Since then the Hofmeister Series have been widened and many studies have been undertaken to understand this phenomenon. Commonly they are shown as array of ions (compare figure II.6), although one has to keep in mind that specific ion effects are strongly dependent on the experimental setup. They are not only affected by the counterion, but also on concentration, pH, or the design of interacting macromolecules and surfaces.[41]

An interesting concept to simplify this rather complex problem was introduced by Collins. Here ions are approximated as charged spheres. Small ions bind water tightly, making them 'hard' or 'kosmotropic', whereas 'soft' or

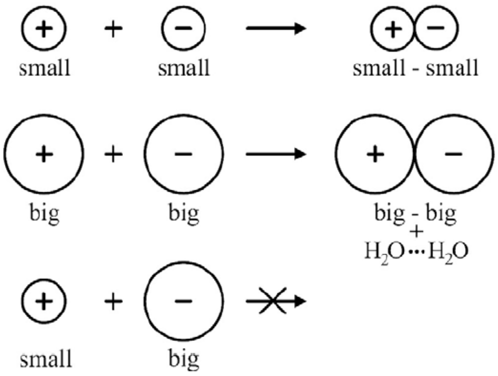


Figure II.7: Schematic interactions between ions according to Collins concept of matching water affinities.[42]

‘chaotropic’ ions are large compared to water. They possess only a loosely bound hydration sphere. Now when comparing the forces between water molecules, water and ions, and ions among themselves, the different interactions are being observed. Figure II.7 presents a sketch of the situation: Two small ions of opposing charges attract each other strongly and form direct contact pairs, excluding the hydration layer between them. Two large ions also form contact pairs, although they attract each other to a lesser extent. This is more than compensated by the weak interactions with their hydration shell, compared to water – water interactions. A combination of a soft and a hard ions, on the other hand, will always be separated by water because the attraction between ions is not strong enough to break the hydration shell of the smaller ion.[42] This concept of ‘like seeks like’ depicts a rather simplistic approximation towards the real situation, but as a rule of thumb it is useful not only for ions but also for polymers and other macromolecules.

2.3 Consequences

The above mentioned effects are generally described for aqueous systems at room temperature or slightly more, but not for hydrothermal environments. Up to date there are no known studies about specific salt effects at temperatures above 100°C. There are, however, some single studies on the effects of salt addition towards reactions yields in HTW. Among these studies sodium chloride solutions (also called brine) have been used preferentially due to their abundance in nature, but also experiments with lithium chloride, potassium chloride, potassium bromide, sodium sulfate, calcium chloride and iron chloride have been conducted.[43–50] These results have lead to different postulates and assumptions.

The publication of Oshima et al. referred the increased methanol conversion to a local density increase around ions in SCW.[47] This was also assumed by Huppert et al. concerning the hydrolysis reaction of guaiacol.[43]
The works of Torry et al. and Li et al. both were interpreted with a change of polarity of the transition state of the organic reaction with respect to product and starting material.[48,50] In addition, Torry's results showed a decrease of hydrolysis reaction yield at high NaCl concentrations. This was interpreted by phase separation and the succeeding decreased availability of water in the organic phase, shifting the equilibrium towards the side of the starting materials.
Another explanation based on the acid/base concentration of hydrothermal aqueous salt solutions and their catalytic activities.[45,46,49] Penninger et al. offered a simple explanation for the effect of NaCl to increase hydrolysis yields of diphenylether (reaction scheme in figure II.8). They postulated charge–transfer in HTW between Na^+ and the surrounding water cluster,

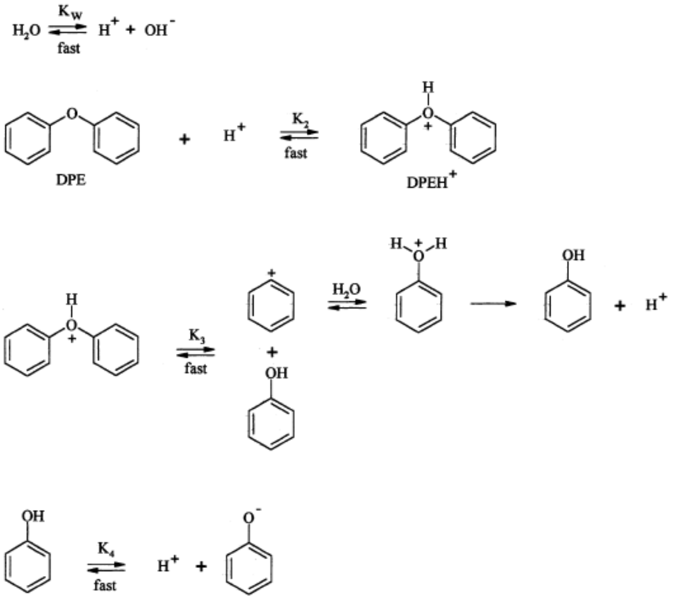


Figure II.8: S_N1 mechanism for hydrolysis of diphenylether in supercritical water.[46]

making it an effective Lewis acid comparable to Fe^{3+} and Al^{3+} at ambient temperatures. Cl^- reacts at high temperatures in a pretty much similar way as Lewis base (see figure II.9). On a simpler approach Ott et al. neglected the effect of sodium ions and calculated the effective increase of pH due to a basic behavior of the sulfate ions. This was used to explain the decrease in dehydration rate of several polyols.

However, up to date studies on the effects of inorganic salts in organic hydrothermal synthesis are sparse and almost exclusively confined to nearcritical and supercritical systems. Some theories have been voiced, but there still exists no hard proof through clear measurements due to the harsh conditions.

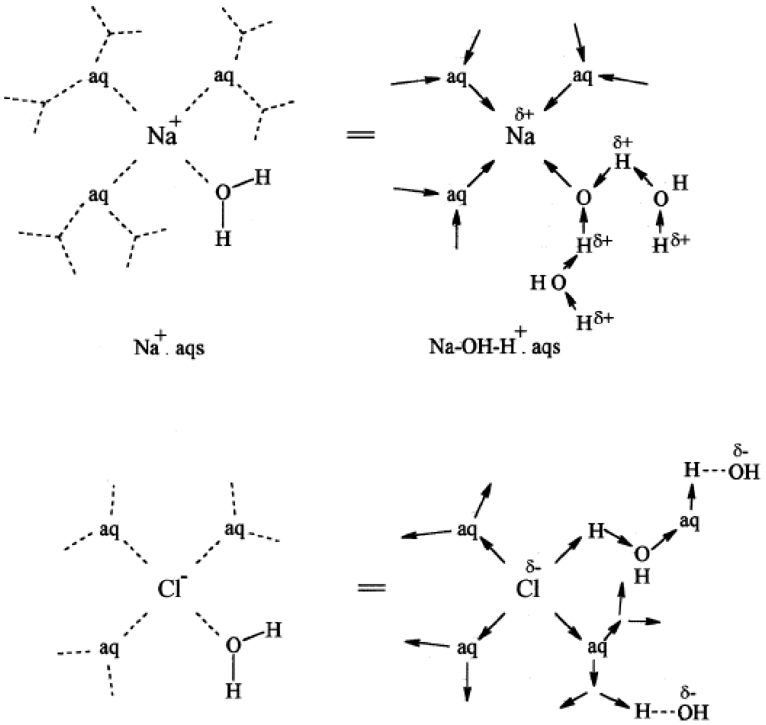
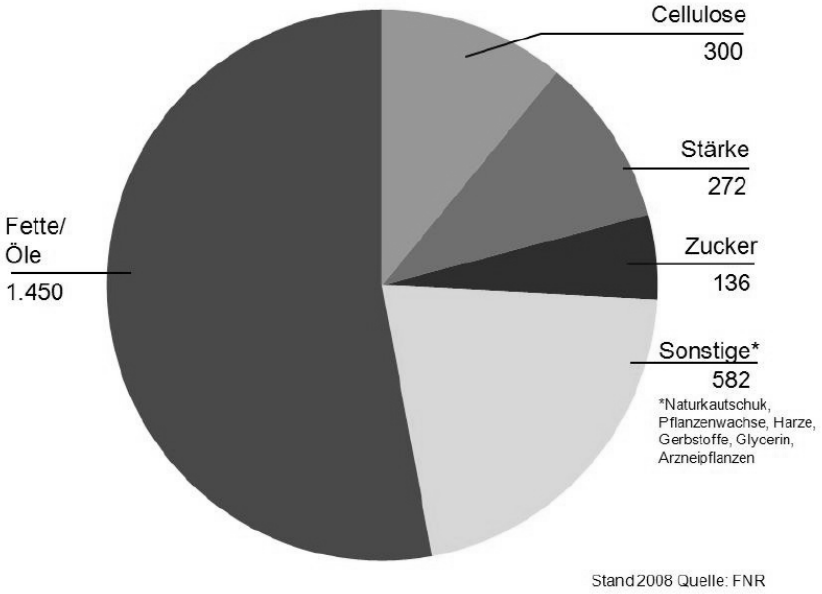


Figure II.9: Lewis acid and Lewis base character of Na^+ and Cl^- as central ions in water clusters.[46]

3 Biomass

According to the Biomass Energy Data Book of the U.S. Department of Energy, biomass is defined as “any organic matter that is available on a renewable or recurring basis. It includes all plants and plant derived materials, including agricultural crops and trees, wood and wood residues, grasses, aquatic plants, animal manure, municipal residues, and other residue materials.”[51] Plants store efficiently solar energy with conversion of water and carbon dioxide to carbohydrates, fats and proteins. Therefore, they provide us with energy as well as organic matter. While these have been used throughout history (food, medicine, fibers, tools, furniture, ...), the chemical industry provided us with a growing palette of alternatives made out of fossil resources.

However, in times of a growing population and limited petrochemical resources, biomass became a viable alternative as feedstock for both energy and chemicals again. In Germany, for example, the percentage of renewable resources in industry rose from 8% in 1991 to 13% in 2007,[52] and it is expected to increase even more rapidly in the coming years. Figure II.10 shows that presently oil and fats represent more than half of the total amount of used biomass, and carbohydrates (sugar, cellulose, starch) another quarter. The rest is divided into a lot of different substances like natural rubber, wax, resins, tanning agents, glycerin, and medicinal plants. That leaves a substantial amount of biomass unexploited, and new ways for filling this gap are being researched worldwide. An overall plan thereof is exhibited in figure II.11.



*Naturkautschuk, Pflanzenwachse, Harze, Gerbstoffe, Glycerin, Arzneipflanzen

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Figure II.10: Renewable resources input in German industry 2008 (1000 tons).[53]

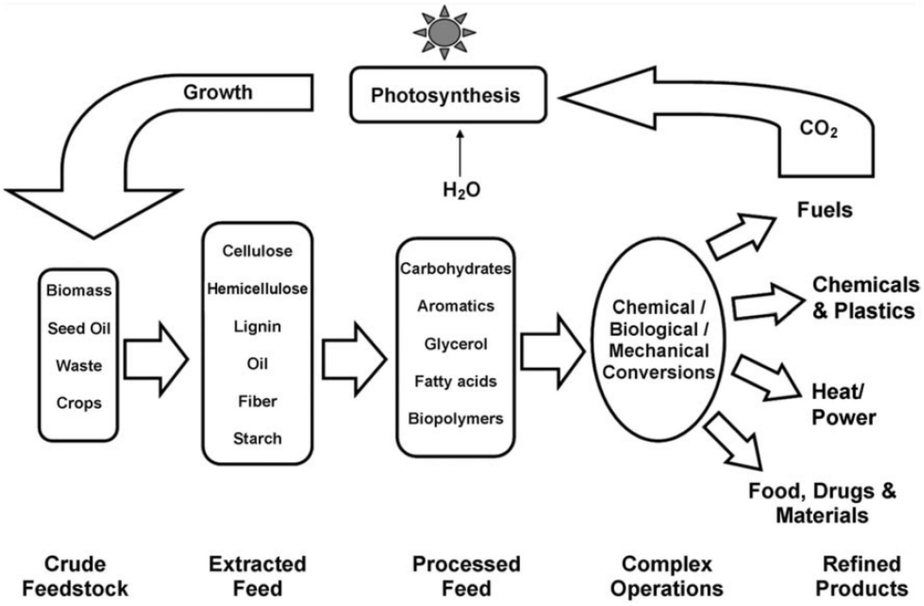


Figure II.11: Theoretical biomass cycle.[54]

3.1 Lignocellulosic Biomass and Lignin

Worldwide about 200 Gigatons of lignocellulosic biomass are generated every year, making it the most abundant renewable biological resource on earth.[55] It consists of three main components: Lignin, cellulose, and hemicellulose. Examples and their average compositions are shown in table II.3. These three components are cross-linked with each other, forming a stable, three-dimensional network. Thus pretreatment of lignocellulosic biomass for separation is an important part of directed biomass-to-chemicals conversion (compare figure II.12 and section 1 of chapter IV).

While cellulose and hemicellulose are polymers based on sugar units, lignin is a highly branched and irregular polyphenol. An exemplaric section of its native structure is displayed in figure II.13. Basically it consists of a network of C9 phenylpropenyl units, provided by the enzymatic dehydrogenation of

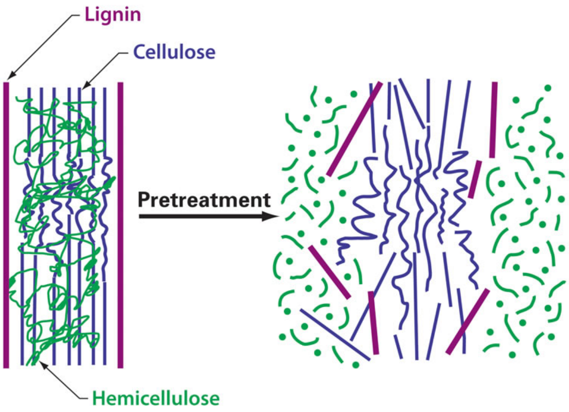


Figure II.12: Schematic composition of lignocellulosic material and pretreatment procedure.[56]

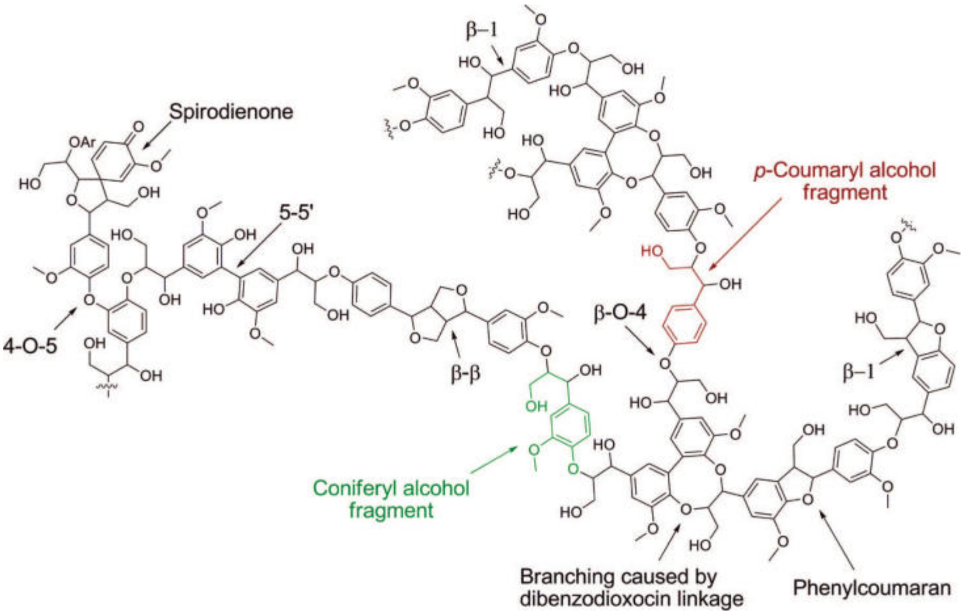


Figure II.13: Schematic representation of a softwood lignin polymer section. Reprinted with permission from Chemical Reviews Magazine.[57] Copyright (2010) American Chemical Society.

	Cellulose (%)	Hemi-cellulose (%)	Lignin (%)
Corn stover	30 - 38	19 - 25	17 - 21
Sweet sorghum	27	25	11
Sugarcane bagasse	32 - 43	19 - 25	23 - 28
Hardwood	45	30	20
Softwood	42	21	26
Hybrid poplar	39 - 46	17 - 23	21 - 8
Bamboo	41 - 49	24 - 28	24 - 26
Switchgrass	31 - 34	24 - 29	17 - 22
Miscanthus	44	24	17
Giant Reed	31	30	21

Table II.3: Characteristics of selected feedstocks.[51]

p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (see figure II.14). The relative abundance of these units differs with the lignin source, as well as the types and abundance of their linkages. Softwoods are made from roughly 90% coniferyl units, whereas in hardwoods both coniferyl and sinapyl units appear in equal quantities.

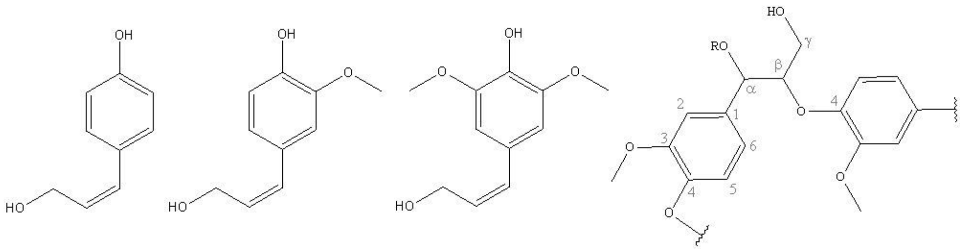


Figure II.14: From left to right: Coumaryl, Coniferyl and Sinapyl Alcohol, and an exemplaric $\beta - O - 4$-linkage.

The most common inter-linkage between monomers is β-O-4, but also β-1, β-β, β-5, 5-5, 4-O-5, spirodienones, dibenzodioxocin, and various crosslinks to the carbohydrate polymers occur.

While currently most of the lignin is burned for energy (Kraft lignin e.g. has about two-thirds of the fuel value of heating oil), there are several commercial lignin-based products available. Mostly they take place in sectors where

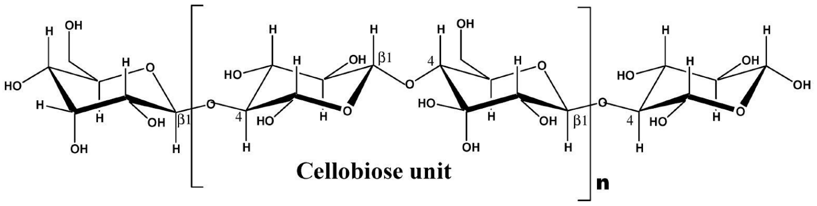


Figure II.15: Structure of Cellulose. Reprinted with permission from Energy & Fuels.[59] Copyright 2006 American Chemical Society.

lignin's color properties matter little and where they profit on lignin as low-cost substrate with low toxicity, improved heat resistance, water resistance, and biodegradability. These include additives for concrete, animal food, road binders, pesticides, resins, wallboards, dispersants, emulsifiers, chelants, and many others. Also production of fine chemicals such as phenol and vanillin has taken place in industry, but these processes strive to compete with current petroleum-based technologies.[58]

3.2 Carbohydrates and Sugars

The commonly known basic reaction of photosynthesis is

$$6\ CO_2 + 6\ H_2O + \text{sunlight} \longrightarrow C_6H_{12}O_6 + 6\ O_2$$

It is a means for plants to store the energy of the sun on a molecular level for later use. Glucose $C_6H_{12}O_6$ is either stored directly or transformed into other sugars such as fructose, xylose, ... or macromolecules consisting of sugars such as cellulose (figure II.15) and starch. These carbohydrates account for 75% of the total biomass production of nature (170 billion metric tons per year), yet only 3-4% of them are used for food.[60] Therefore it is an indispensable goal for research to improve the employment of these high-energy molecules in all fields of human demands.

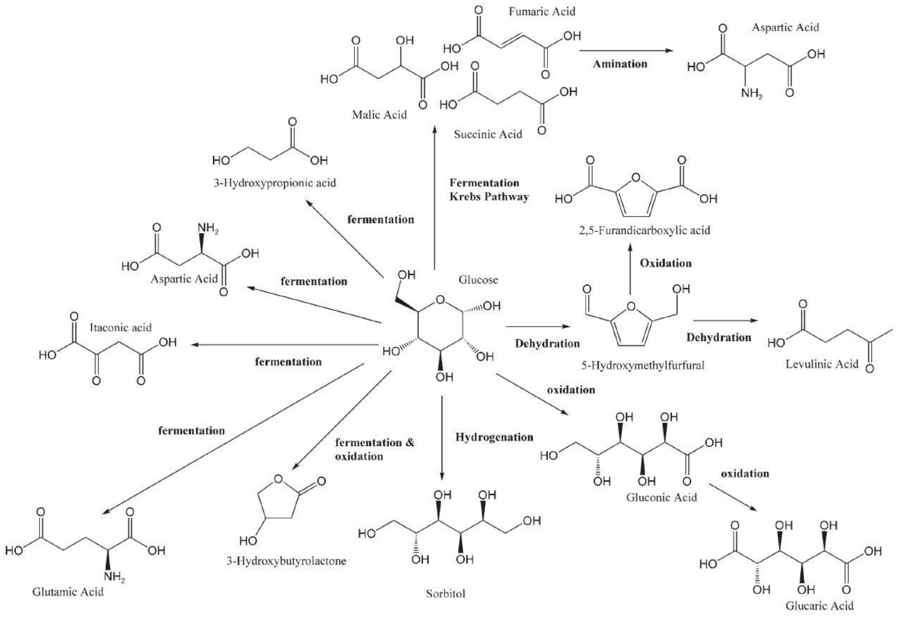


Figure II.16: Top-value added chemicals from glucose.[54]

When thinking of sugars as platform chemicals, the key difference to already existing processes of petrochemicals is the abundant functionality of carbohydrates. Selective removal of functional groups, particularly hydroxy groups in this case, is an important issue to address.

A more direct approach was attempted by the U.S. Department of Energy.[61] By identifying key chemicals to serve as building blocks for synthesis, research should be focused and directed towards meeting the current needs of industry. The most important reaction pathways are shown in figure II.16.

3.3 Oils, Fats and Glycerol

Another substantial part of biomass are the triglycerides, more commonly known as fats and oils. They are obtained from both vegetable and animal sources, and exhibit side chains of varying length and number of double

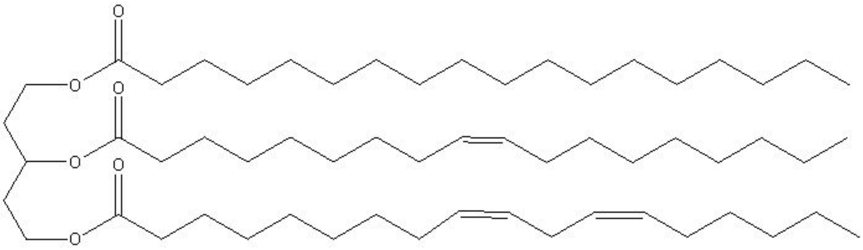


Figure II.17: Triglyceride with stearic acid, oleic acid, and linoleic acid (top to bottom)

bonds. Their applications are widespread and include surfactants, polymers, lubricants, emulsifiers, fragrances, pharmaceuticals, ...[60] Their properties are not as different from some petroleum fractions, which makes them a popular choice for fuels. Biodiesel is produced by transesterification of the fatty acids with methanol or ethanol, resulting in a large amount of aqueous glycerol solution as byproduct. So far the resulting glycerol production has not been put to use efficiently, making it a popular goal for research. Figure II.18 shows some possibilities for chemicals produced from glycerol as starting material.

3.4 Terpenes

Terpenes are vegetable hydrocarbons based on isoprene units. They are found in essential oils that are components of resins, steroids, and rubber. Since centuries they have been used for flavors and fragrances, and they have the highest energy content among all the biomass classes. However, terpene production is too low to consider it for energy production, so it should mainly be considered as a replacement for high-value products coming from petroleum.

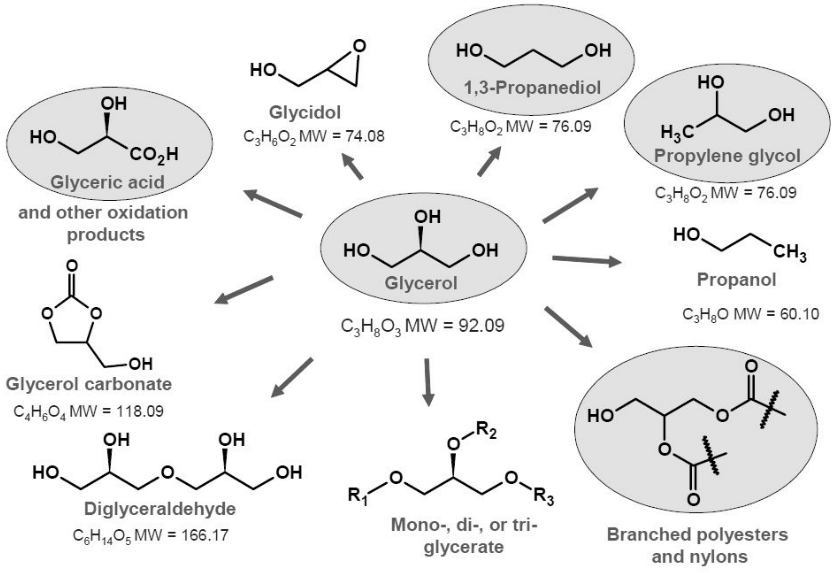


Figure II.18: Derivatives of Glycerol[61]

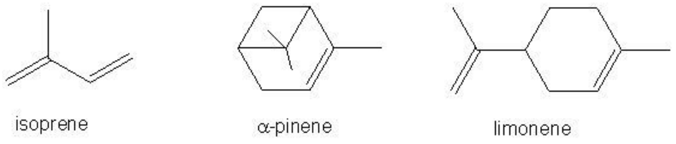


Figure II.19: Structure of Isoprene and some Monoterpenes.

4 Green Chemistry

Sustainability and environmentalism is a topic that has become more and more important in our modern times. Human population grows steadily, making the responsible use of resources an imperative. Information and education are core keys towards achieving a better awareness in all areas of this very complex issue. In Germany, e.g., the FNR (Agency for Renewable Resources) is funding about 300 projects every year, not only in research but also in demonstration. With these activities the hope is to foster a deeper understanding not only of the needs of sustainability, but also the operational

Figure II.20: Cover of a leaflet of the German Federal Ministry for Food, Agriculture and Consumer Protection, Agency for Renewable Resources. In comics children are informed of topics such as biodiesel, biogas, plastics from natural materials, natural dye, and many more).[62]

concepts and problems involved. Targets are all levels of population, from politicians and researchers to children (see figure II.20).

In Chemistry, “Green” and “Sustainability” are key words used in almost every context. Most researchers focus on only one aspect of the broader picture, though. Few are really aware of the true complexity of sustainability. Luckily there are numerous guidelines and essays covering that topic. The most prominent will be introduced in the following.

4.1 The Twelve Principles of Green Chemistry

The expression of “Green Chemistry” was formed in the beginning of the 1990 by Anastas et al. It is defined by them as “design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances.”[63] They also provided a set of guidelines which help to transfer the idea into actual research goals.

The Twelve Principles of Green Chemistry

cited from the review “Green Chemistry: Principles and Practice”[63]

1. **Prevention.**

   It is better to prevent waste than to treat or clean up waste after it is formed.

2. **Atom Economy.**

   Synthetic methods should be designed to maximize the incorporation of all materials used in process into the final product.

3. **Less Hazardous Chemical Synthesis.**

   Whenever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no toxicity to human health and the environment

4. **Designing Safer Chemicals.**

   Chemical products should be designed to preserve efficacy of the function while reducing toxicity.

5. **Safer Solvents and Auxiliaries.**

   The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.

6. **Design for Energy Efficiency.**

   Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. **Use of Renewable Feedstock.**

   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. **Reduce Derivatives.**

   Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. **Catalysis.**

   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. **Design for Degradation.**

    Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. **Real-Time Analysis for Pollution Prevention.**

    Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. **Inherently Safer Chemistry for Accident Prevention.**

    Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Anastas et al. also put an emphasis on the fact that these principles are not to be looked at separately, but taken as a whole. To achieve an improvement in sustainability, the best compromise to meet all of these conditions has to be found. Also, this concept addresses not only the research lab, but also industry, education, and other institutions.

4.2 Evaluation of Hydrothermal Reactions

In the following the concept of hydrothermal reactions will be discussed in comparison to classical reactions in organic solvents.

The points regarding Atom Economy, Design of safer Chemicals, Use of Renewable Feedstock, Derivatization, and Design for Degradation refer to the actual synthesis taking place. Therefore they cannot be discussed in this context, although they still have to be taken into account when designing processes. One of the major advantages of water and salt solutions is their low toxicity (depending on the salt, of course). Thinking of the vast abundances of sea water (approximately 3.6% salt content, or 0.6M, mostly NaCl),[64] a direct use could be advantageous to straining the dwindling fresh water reserves. To minimize waste and cleaning costs, this water could be reused through several cycles, improving the statistics concerning point 1 of the Green Chemistry Principles.

On the downside of this process are a comparatively high energy input and pressure (point 6 and 12 of the Green Chemistry Principles). Surely the economical gain has to be calculated in every specific case. After all, also energy comes at an environmental cost, depending on the source (see also section 4.3). Pressure, on the other hand, is significantly lower than at supercritical conditions. It can be handled industrially without too much effort.

4.3 Other Aspects Concerning Environment and Sustainability

In the last section hydrothermal reactions have been directly evaluated according to the rules of green chemistry. However, there are other aspects where HTW can be combined with new ideas or existing problems to improve general sustainability.

Power-Heat Cogeneration

Renewable energies like solar and wind power are environmentally benign, but presently they cannot cover the needs of industry and population alone. Another green energy source which can be explored hydrothermally is waste energy from electrical power plants. Huge cooling towers evaporating water are often a common element of a plant (see picture II.21). First, steam is gen-

Figure II.21: Coal power plant in Datteln (Germany) at the Dortmund-Ems-Kanal. Copyright Arnold Paul.[65]

erated from water through any means of heat (combustion, nuclear power). The steam generates electricity in a turbine and is being cooled down in the process. However, the initial temperatures are not being reached due to technical limitations. Therefore some of the heat is always lost to the environment. Theoretically this heat can be used, e.g. to heat up buildings and for industrial processes. The efficiency of this Heat Cogeneration is limited by fluctuating need of heating and the transport loss rates. In consequence, the fraction of cogenerated heat constitutes only a minor fraction of the total heat consumption (see also figure II.22).

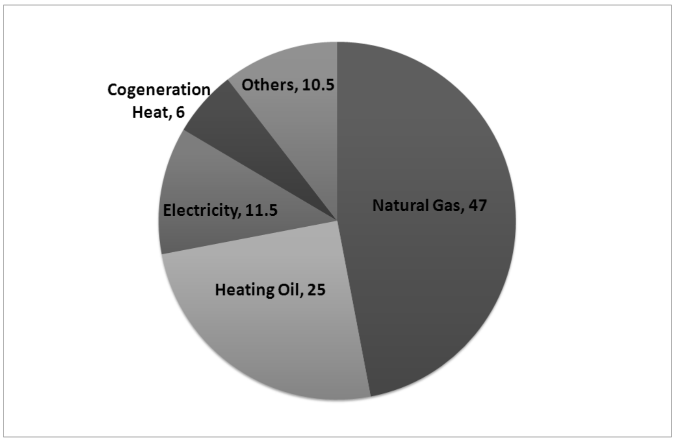


Figure II.22: Distribution of Heat Consumption in Germany 2004 in percent.[66]

Using the cooling water from power plants for hydrothermal means would be an alternative way to increase sustainability of this process. Synthesis on-site would minimize transport losses of the heat. The proposed reaction temperatures would mean a decrease in electricity production, but on the other hand the technical costs of operating on partial vacuum (to maximize vapor range) could be saved.

Carbon Dioxide Neutrality

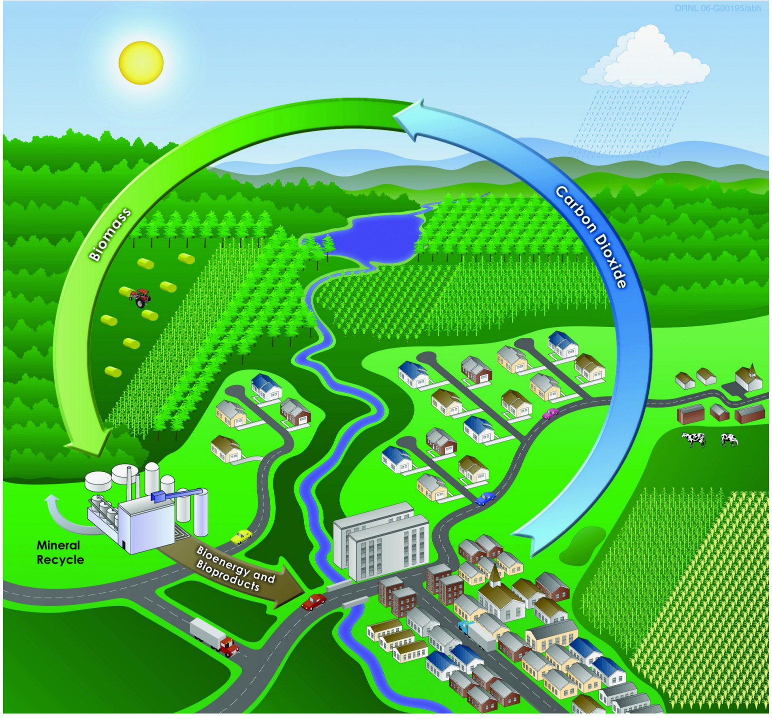


Figure II.23: Schematic Carbon Cycle.[67]

The carbon cycle, as shown in figure II.23, shows the natural movement of carbon through reuse and recycling as part of life on earth. But lately human's high output of carbon dioxide CO_2 induces a worldwide climate change.[68] It causes serious problems and initiates a new global thinking to reduce and remove the CO_2 emissions significantly.[69] But up to date there is no ultimate way to capture and store greenhouse gases efficiently.

In this context, hydrothermal treatment of biomass becomes yet again more interesting. As Antonietti et al. postulated 2007,[5] hydrothermal carbon is not only a good way to store CO_2. It can be used in a variety of functions, from soil fertilizer to high-performance catalytic materials. Also industry is interested in this concept, considering it e.g. for fast-growing algae carbonization.[70] In conclusion, even the side products normally considered as waste can be useful when seen in the light of carbon dumping.

Unwanted Hydrothermal Side Reactions in Biogas Generation

When submitting wet biomass to higher temperatures and pressures, hydrothermal carbonization processes occur. In the area of biogas generating plants this can cause a severe problem. Not only the yield will be diminished by this side reaction. What is worse, the carbon deposits primarily on the hot tube walls, which eventually leads to complete congestion.

As mentioned in section 1.3, an unpolar solvent is able to dissolve polymerization products under experimental conditions. In most cases this is not a sustainable solution, though. A clever mix of different biomass batches or also addition of cheap and non-toxic substances could improve these processes hugely, rendering them more effective and thus even greener. In consequence, better knowledge on hydrothermal (carbonization) reactions can help biogas generation plants, too.

III

Alcohol Dehydration

In this chapter basic parameters for hydrothermal reactions have been thoroughly tested on the model reaction of alcohol dehydration. These novel concepts have been applied onto other model reactions as well.

1 Background

For hydrothermal carbonization (HTC), the starting materials have high contents of carbohydrates. These contain multiple hydroxy groups, while the result is generally carbon rich and has reduced content of chemical functionalities. The predominant reactions, therefore, are assumed to be elimination reactions.

Elimination Reactions

As seen in figure III.1, eliminations can happen in α-, β-, 1,3-, or even 1,4-positions. The most common reaction, however, is the β-elimination. Concentrating on the latter, the free rotation of the σ-bond makes for more

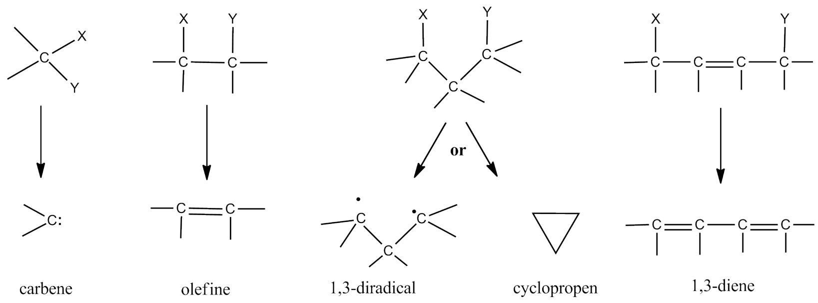


Figure III.1: Possible elimination reactions.[71]

differences. A result of the leaving groups being on the same side (*syn*), or on different sides (*anti*), groups connecting to the resulting double bond can be in *cis*- or *trans*-position (see picture III.2).

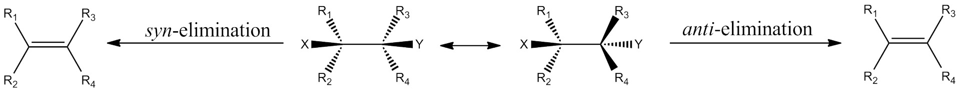


Figure III.2: Elimination with *syn* and *anti* geometry.

Also, if the leaving group is bound to a secondary or tertiary C-atom, the possibilities of the resulting products increase significantly (compare III.3).

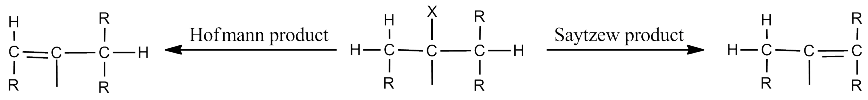


Figure III.3: Hofmann and Saytzew products.

The mechanism of a β-elimination (figure III.4) can be E2 (both groups leave at the same time), E1 or E1_{cb} (either the heterogroup or the hydrogen, respectively, leave the molecule first and create an ionic intermediate).

Clearly it has been shown that a simple elimination reaction can result in a variety of different products. And even more, having two hydroxy groups at neighbor carbon atoms, dehydration leads to formation of an aldehyde or

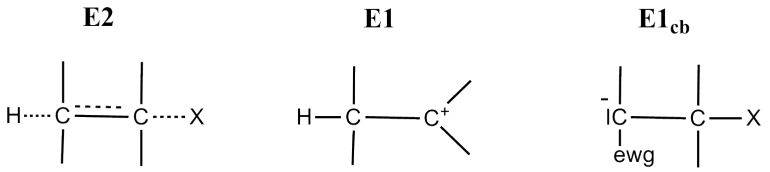
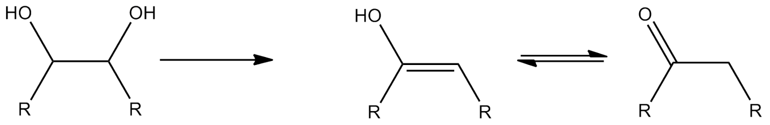


Figure III.4: Transition states of the different elimination mechanisms (ewg = electron withdrawing group, essential for the formation of a carbenium ion).

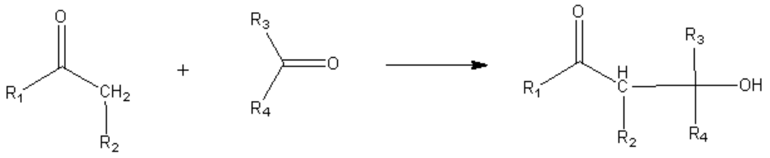
ketone.



This opens the window to the world of carbonyl chemistry with its manifold reaction paths. Carbonyl groups in biomass are numerous, being part proteins as well as carbohydrates. Also in this work, some of these reactions happened. One of them was examined further for its sensitivity to changes in the hydrothermal conditions. It is introduced shortly in the following.

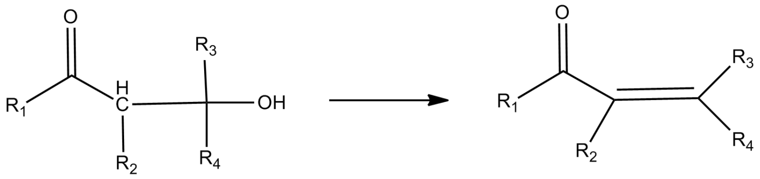
Aldol Condensation and Michael Addition

If hydrogen atoms are bound to the α-C atom next to the carbonly group, they react acidic. Therefore, such a molecule is also a good nucleophile. It can add at a second carbonyl group (inter- or also intramolecular).



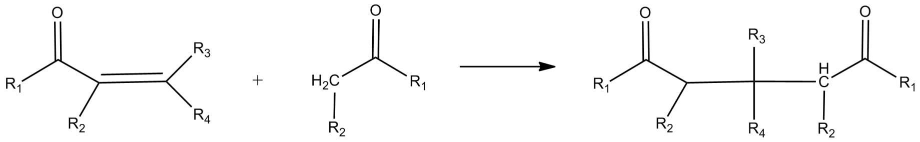
This aldol addition can be acid or base catalyzed. Generally it leads to a wide range of products, because the carbonyl groups of both substances can react with oneself and with each other. This results in four possible combinations alone. If one of the two components does not have an α-C atom or no hydrogen attached at this position, possibilities are reduced. Organic chemists also employ design bases such as organic lithium compound to improve yields toward the desired products.

The produced aldol molecule (a word composition from **ald**ehyde and alcoh**ol**) is not particularly stable and does often loose a water molecule, dependent on the reaction conditions.



The combination of these two reaction steps is then called aldol condensation. It produces an α,β-unsaturated carbonyl compound.

This type of chemical, in turn, has still a reactive carbonyl group. Consequently it can add a second carbonyl group. Due to the enlargened π system the attack of the nucleophile can also take place in β position.



This is called a Michael Addition.

As seen in the short overview above, elimination reactions without specific starting material and reaction conditions proceed in a versatile way. To get a better understanding of the mechanisms involved in this process, the basic dehydration reaction of an alcohol group under hydrothermal conditions was investigated instead of complex biomass molecules.

In literature, alcohol dehydration in hot water is already known. However, in general, temperatures above 300°C are being used to reach respectable yields. Alternatively some mineral catalyst is applied.[26] At lower temperatures and without additives simple alcohols do not react easily. Siskin et al.[44] found only 0.1% of decene after 1-decanol in water at 250°C for a time span of thirteen days. The following first experiments comfirmed the low reactivity of simple alcohols.

2 Preliminary Results on *n*-Heptanol

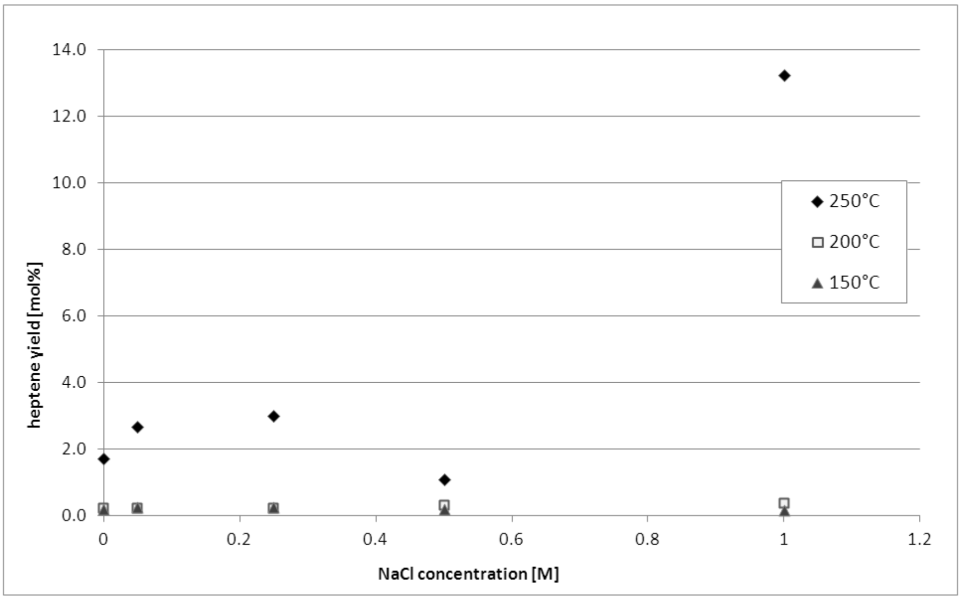


Figure III.5: Heptene yield from 1-heptanol at different temperatures and NaCl concentrations.

In the following diagram conversion rates of 1-heptanol into 1-heptene are shown. As expected, overall conversion is very low. At 250°C, the yield improves with rising NaCl concentration, although the quantity of these values are not satisfying (the lower the amount, the bigger the contribution of experimental fluctuations). At temperatures of 200°C and lower, only yields around 0.1% are being found. In consequence, heptanol can be regarded as unreactive under these conditions. To get a better reaction span a different alcohol was selected to continue with the salt studies.

3 Studies on 1-Phenyl-1-Propanol

As a secondary alcohol with a possibility to generate an extended π-system, 1-phenyl-1-propanol was selected for further studies.

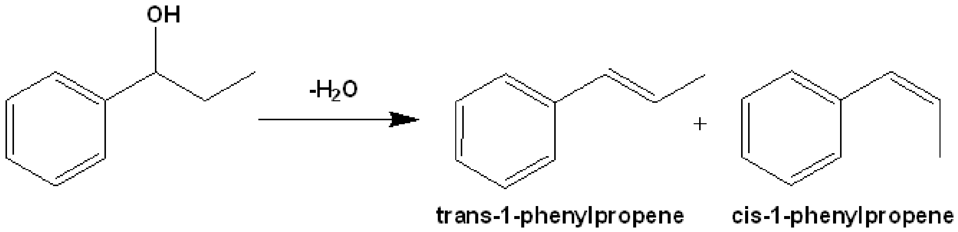


Figure III.6: Dehydration reaction of 1-phenyl-1-propanol

Main product is *trans*-phenylpropene as the thermodynamically more stable alkene, while the generation of the *cis* alkene not transcends 10% of the total amount of substance.

3.1 Time Dependence

Submitting 5mmol of this alcohol to hydrothermal treatment at 180°C, time dependence of *trans*-phenylpropene yield is shown in figure III.7. The large deviation of the value at 4 hours from the standard kinetics curve is assumed

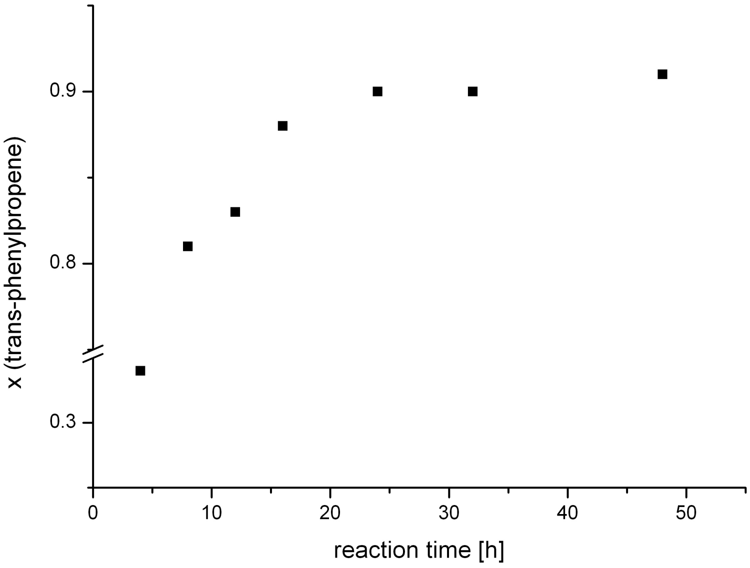


Figure III.7: Yield of trans-Phenylpropene as function of time at 180°C.

to be caused from heating lag. Unfortunately the experimental setup does not allow temperature measurement, therefore the oven temperature is stated in all diagrams. However, the Teflon inlet inside the steel mantle is known to be a good heat isolator, delaying the point where the contents of the autoclave reach reaction temperature. With the increase of total reaction time, this heating lag becomes negligible.

In the following experiments 16 hours was selected as the standard reaction time, with some tolerance to shift the total yield to both sides up and down.

3.2 Dependence on Salt Concentration

As can be seen in figure III.8, pure super heated water is able to give a reasonable conversion, but that conversion is improved by adding even "inert" salts. First an increase of the conversion rate with increasing salt concen-

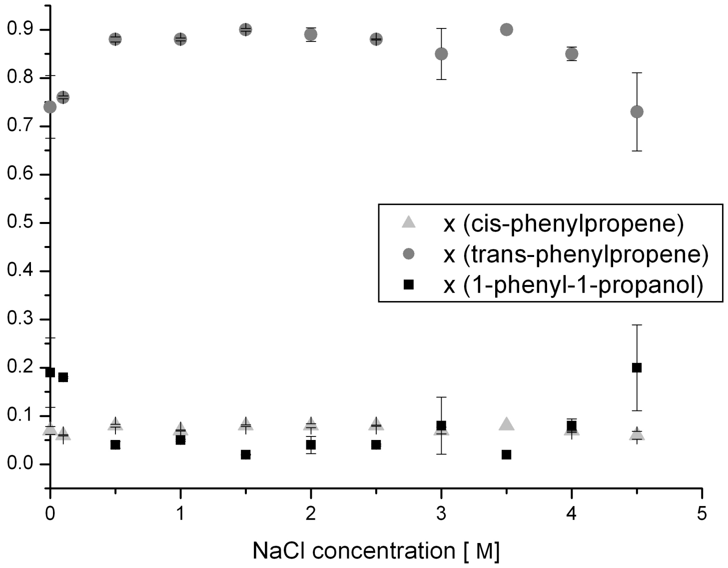


Figure III.8: Yield of 1-phenylpropanol as a function of NaCl concentration at 180°C.

tration was found, which leveled into a plateau, and then dropped again. This plateau presumely correlates with the total equilibrium concentrations of this reaction (also seen in figures III.7 and III.10).

Torry et al.[50] observed a similar phenomenon when investigating the rate of hydrolysis of dibenzyl ether and benzyl phenyl amine in near-critical water containing sodium chloride. The first increase in reaction rate was assigned to an initial increase in the polarity of the reaction medium favoring the polar transition state of the reaction (compare section II.2.1). The decrease of the reaction rate at higher salt concentration was explained by Torry et al. by a decrease in water availability for the reaction. This may be reasonable in their case, but seems less plausible in our case (where on the contrary water is generated).

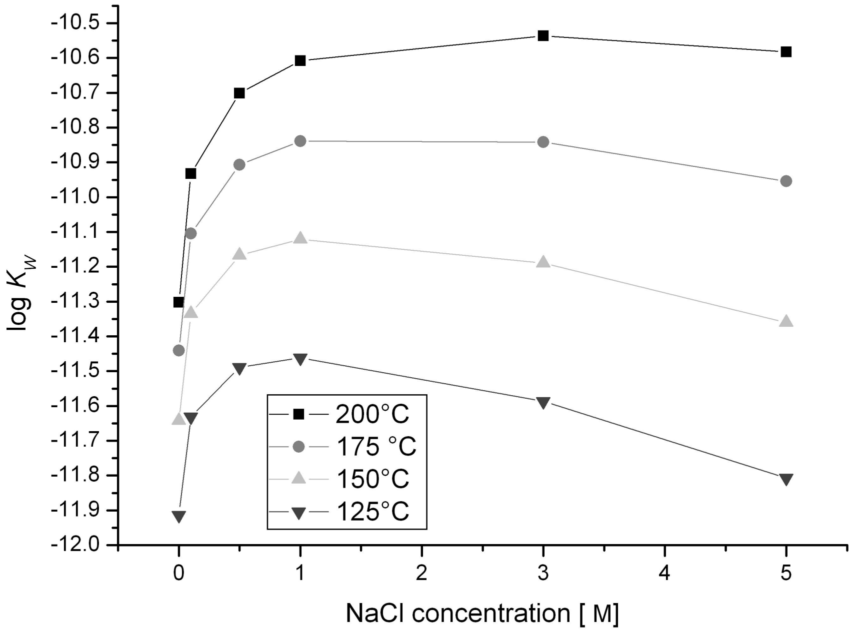


Figure III.9: Dependence of the water dissociation constant on temperature and NaCl concentration.[72]

Another, more plausible interpretation targets the pH values in situ. According to Busey and Mesmer,[72] the water dissociation constant varies with NaCl concentration (figure III.9), showing a broad maximum between 0.5 M (molar) and 3 M ionic strength. This provides an increased proton concentration in this range, leading to acceleration of the classically acid-catalyzed dehydration reaction. The influence of temperature on the outcome of the reaction was also tested. Figure III.10 shows the yield of 1-phenylpropene after 16 hours as a function of temperature and salt concentration. At 200°C the reaction proceeds so fast that no effect of the salt could be observed (equilibrium concentrations reached). On the opposite at 140°C the reaction is so slow that the salt effect is negligible. At intermediate temperatures a strong yield increase is observed which is consistent with the data reported

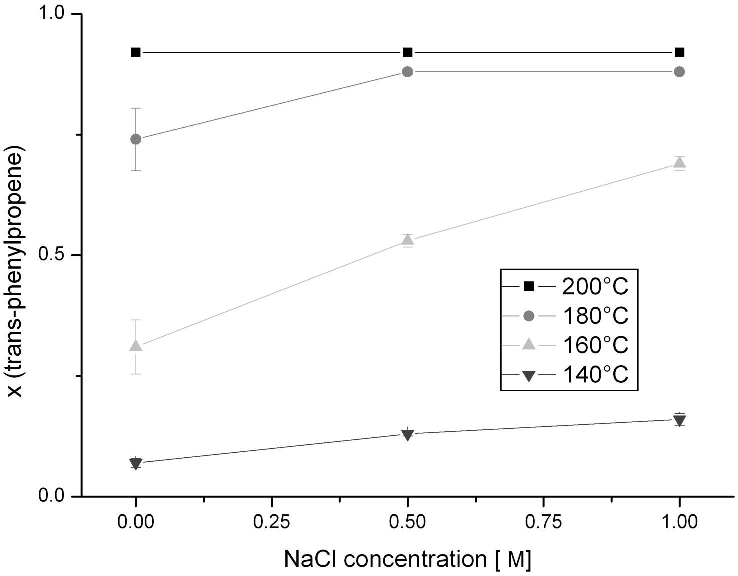


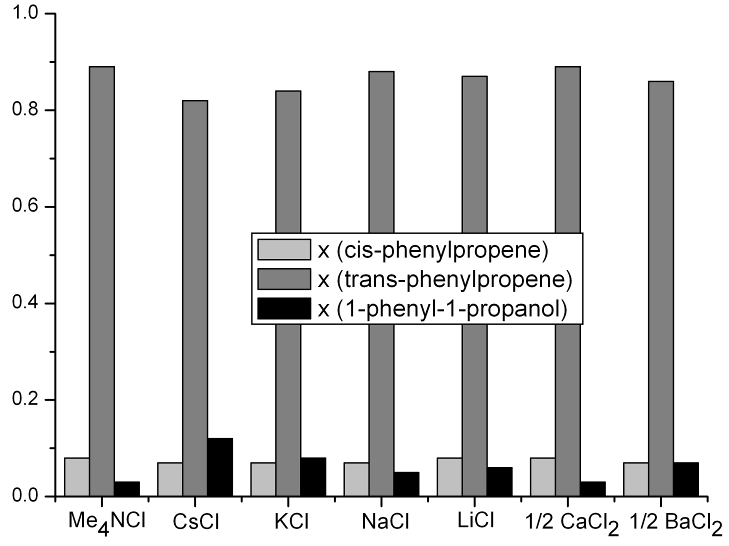
Figure III.10: Yield of 1-phenylpropanol as a function of NaCl concentration and temperature.

in figure III.9.

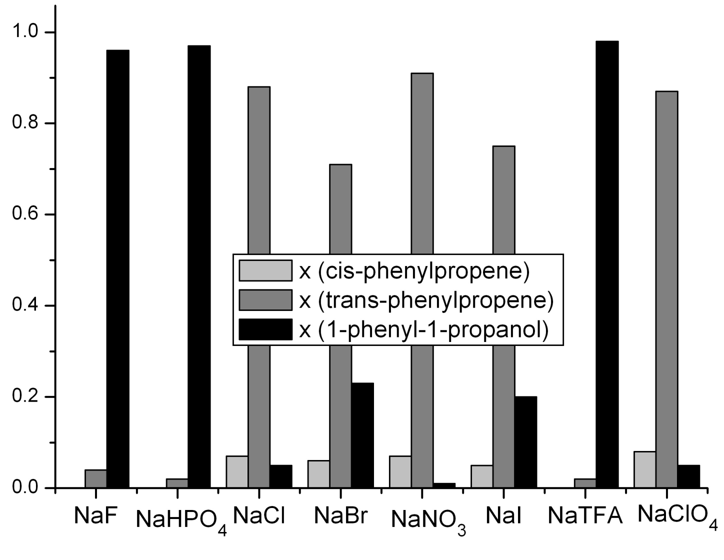
3.3 Salt Dependence

In addition to NaCl, various other salts at 1M anion concentration were also tested. Figure III.11 summarizes some of the results obtained. As can be seen, cation variation had only little impact on the 1-phenylpropene yield (between 85 and 95% of alkenes are obtained as long as chlorine is the anion), at least for the examples presented here. This is somewhat unexpected as catalytic behaviour is usually ascribed to the cations and more specifically to metals and their incomplete coordination sphere.

The nature of the used anions, on the other hand, has a pronounced impact on the phenylpropene yield. Interestingly, anions classically assumed to fea-



(a) 1M salt concentration with variations of the anion



(b) 1M chloride concentration with variations of the cation

Figure III.11: Molar fraction of *trans*-phenylpropene after dehydration at 180°C reaction temperature.

ture some activity (e.g. fluoride, phosphate, trifluoroacetate) show almost no conversion, while the highest conversion is found for nitrate. The observations at hand allow us to exclude that the anion effects on the reaction rate can be ordered according to a classical Hofmeister series.[73–75] This means that the influence of the anion on water structuration and direct ion-organic compound interactions are not the main driving force of the reaction.

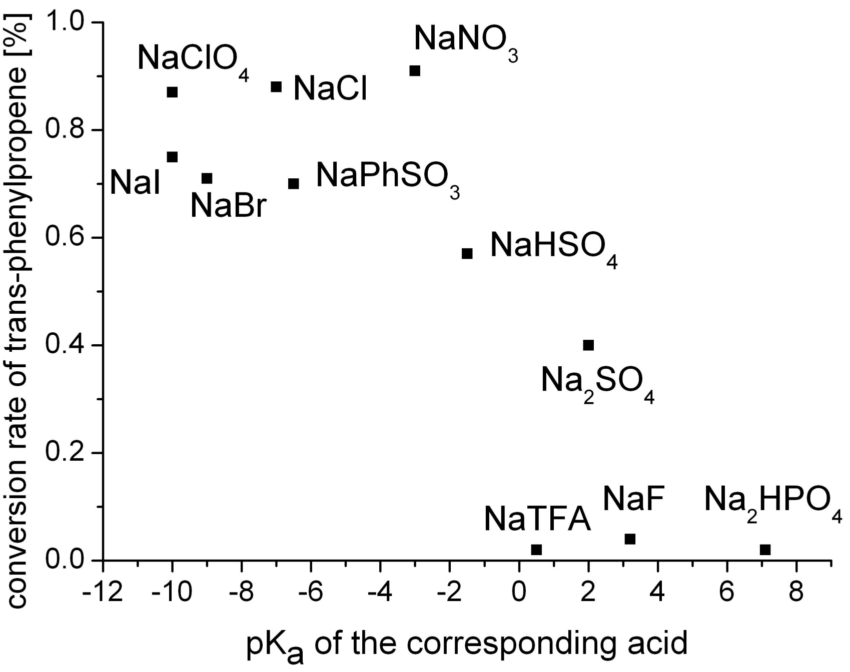


Figure III.12: Conversion ratio of 1-phenylpropanol to *trans*-phenylpropene vs. basicity of the added salt anion.

In contrast, ordering the anions according to their basicity at room temperature (via the pK_a of the corresponding acids, figure III.12) seems to be more coherent. This leads us again to the conclusion that the amount of free protons is the main reason for changes in the trans-phenylpropene yield.

According to the presented reaction yields, one can assume that, compared to pure H_2O, at 180°C NaCl acts as a mild acid, while Na_2SO_4 takes up the place of a base catalyst. While the role of the anions as bases has been discussed already, acidic reaction of the cations have been neglected so far. Indeed, in this case the proton derives from the metal aquo complex, a reaction well known for transition metal ions such as iron. In case of the sodium ion (equation III.1), at ambient temperature this reaction is overshadowed by the autoprotolysis of water itself (pK=14.18).[76]

$$\mathrm{Na(OH_2)_6^+} \rightleftharpoons \mathrm{Na(OH_2)_5(OH)} + \mathrm{H^+} \tag{III.1}$$

For the determination of the temperature dependence of the acid constant, calculations similar to the work of Kopetzki and Antonietti have been done, who also claimed the role of sodium sulfate as a basic catalyst in hydrothermal reactions.[8]

$$R\,\ln K_P(T) = -\frac{\Delta G^0}{T^0} + \Delta H^0\left(\frac{1}{T^0} - \frac{1}{T}\right) + \Delta c_P^0\left(\frac{T^0}{T} - 1 + ln\left(\frac{T}{T^0}\right)\right) \tag{III.2}$$

Equation III.2 includes neglect of the temperature dependence of the heat capacity change c_P, and relates only to reactions at constant pressure (compare original work of Clarke and Glew).[77] With T^0 being the reference temperature (298.15 K), and data for protolysis of HSO_4^- (G^0 = 11.342 kJ/mol, H^0 = -22.4 kJ/mol, c_P^0 = -258 J/molK)[8] and $Na(H_2O)_6^+$ (H^0 = 56.1 kJ/mol, S^0 = -83.2 J/molK, c_P^0=0 J/molK),[76] the graphs shown in figure III.13 are achieved.

Dissociation constants from Busey and Mesmer (H_2O, experimental data)[72] and Helgeson (HCl, fit from experimental data)[78] have been included for a

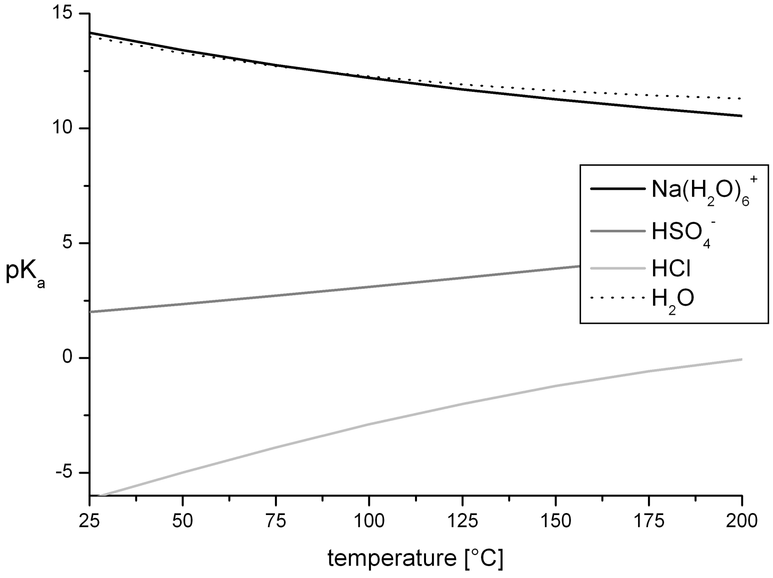


Figure III.13: Temperature dependence of the dissociation constants of $Na(H_2O)_6^+$, HSO_4^-, H_2O, and HCl.

better comparison. As can be seen, at high temperatures the acidity of the sodium complex increases even more than that of pure water, although at 200°C the difference is not very pronounced. However, it is still enough to better promote acid catalyzed reactions, as seen in figure III.10. On the other hand, the used anions increase both their basicity. However, the main quantity of chloride remains dissociated at 200°C. The sulfate, on the other hand, is protonated to a substantial extent. This is likely to shift the overall pH to a strong basic medium.

As a result, the temperature dependent pK$_a$ values are in line with the observed reactivities and suggest that the salt modified proton concentration may be the most important salt effect. Anyhow, one has to have in mind that the used theoretical calculations refer only to the temperature dependence at constant pressure, so the actual values may still differ from these curves.

4 Comparison with other Alcohols

With this background, we tested the reactivity of some alcohols at 180°C in water as well as aqueous 1M NaCl and 1M Na_2SO_4 solutions. Figures III.14 to III.17 display the corresponding results.

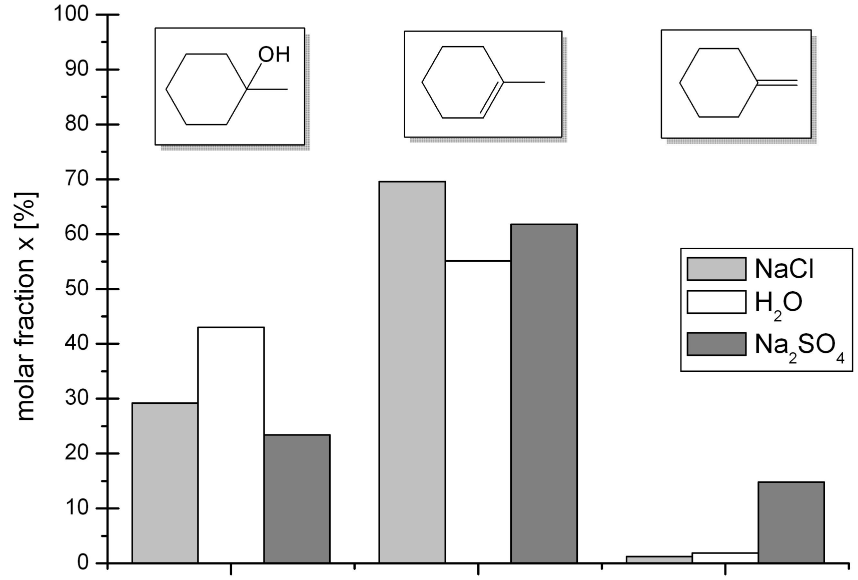


Figure III.14: Composition of the hydrothermal reaction of 1-methyl-1-cyclohexanol at 180°C for 16 hours, respectively with 1M NaCl, pure water, and 1M Na_2SO_4

In contrast to the aforementioned decrease in reaction rate with increasing basicity of the medium of phenylpropanol, methylcyclohexanol was accelerated by both NaCl and Na_2SO_4 addition (figure III.14). Looking at the distribution of the products, sulfate promoted a significant amount of the

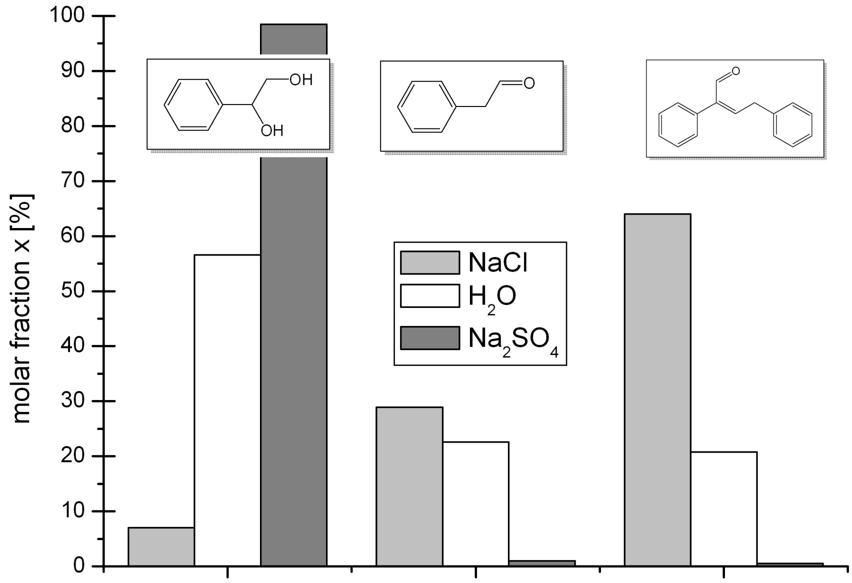


Figure III.15: Composition of the hydrothermal reaction of 1-phenyl-1,2-ethanediol at 180°C for 16 hours, respectively with 1M NaCl, pure water, and 1M Na_2SO_4

terminal alkene. This could be explained according to the rules of Hofmann and Saytzew, where a bulkier base raises the yield of the kinetically favoured product (compare section 1.

The dehydration of phenylethandiol in figure III.15led to 2-phenylethanal (via a keto-enol tautomerism) with the expected decrease in yield with raised basicity. This aldehyde, in turn, reacted partially with itself through aldol condensation, which can be acid or base catalyzed. Indeed, even at a very low yield of intermediate the condensation product still appeared on the GC chromatogram. In consequence, HTW seems to be a good medium promoting aldol reactions even at low quantities. A thigher temperatures, and/or addition of hydrochloric acid in can even react to 2-phenylnaphthene.[79]

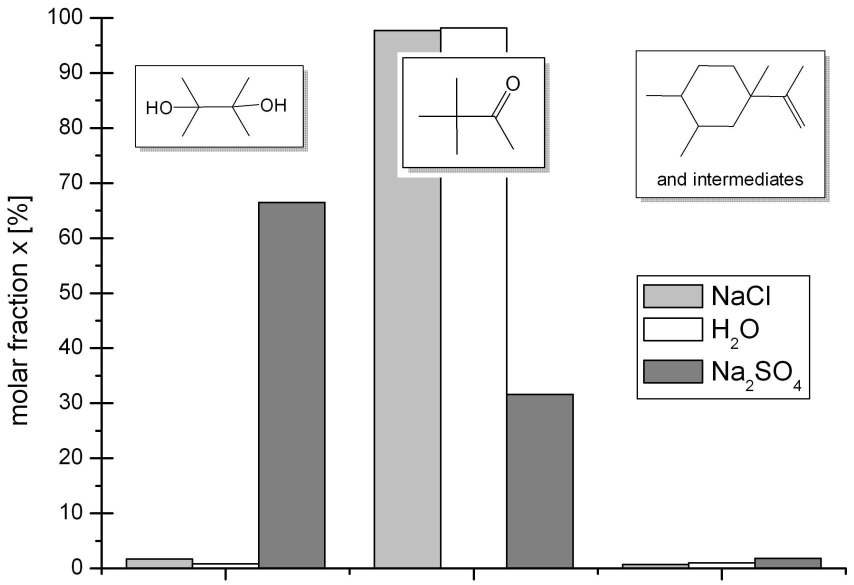


Figure III.16: Composition of the hydrothermal reaction of pinacol at 180°C for 16 hours, respectively with 1M NaCl, pure water, and 1M Na_2SO_4

Hydrobenzoin and pinacol are alcohols capable of a pinacol rearrangement reaction (figures III.16 and III.17), which is in both cases also the favoured product, with only minor differences between NaCl addition and pure water. Double dehydration in the case of pinacol led to the formation of traces of a Diels-Alder condensation product (figure III.18). Interestingly, this reaction pathway seems to be encouraged relative to the rearrangement pathway on addition of Na_2SO_4, although the overall conversion is much lower than in the other cases. The same dehydration/Diels-Alder product was found by Ikushima et al,[80] who used supercritical and near-critical water as a reaction medium.

Glycerol was tested as well, but this highly hydrophilic alcohol could not

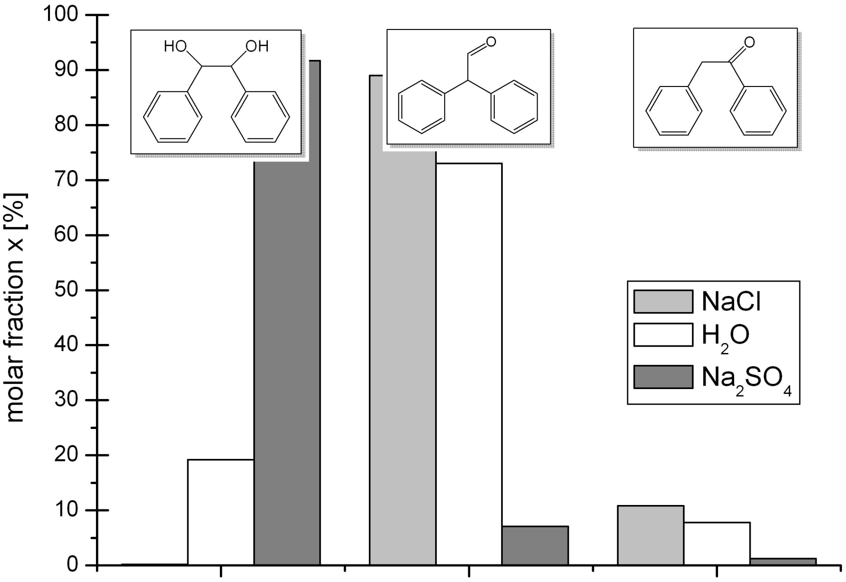


Figure III.17: Composition of the hydrothermal reaction of meso-hydrobenzoin at 180°C for 16 hours, respectively with 1M NaCl, pure water, and 1M Na_2SO_4

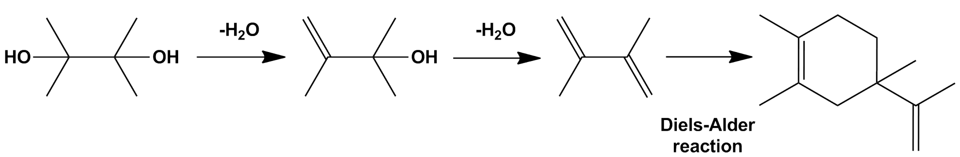


Figure III.18: Mechanism of the dehydration/Diels-Alder reaction of pinacol.

be detected with the chosen extraction and analysis method, neither were possible dehydratation products visible.

5 Studies on Non-alcoholic Substances with Similar Reactions

In order to gain a deeper insight into the secondary reactions from the more complex alcohol reactions, other model substances were investigated.

5.1 Comparison of Dehydration Reactions of Alcohol Groups with Thiol Groups

Substituting the oxygen atom of the alcohol group with a sulphur atom, the resulting molecule is called thiol. Their reactivity is quite similar to an alcohol's. Thiols are stronger acids due to their weaker bond between heteroatom and hydrogen. Also unique for thiols is their ability to form dimers containing a stable S-S bond.

For comparison with the hydrothermal reactivity of a simple alcohol, heptanthiol was tested at 200°C and 30 hours. Traces of heptene formation was only observed in a 3M sodium chloride solution. At lower concentrations only a little amount of heptanol was found (compare table III.1).

solvent	heptene	2-heptanol	1-heptanol	heptanthiole
NaCl 1M	0%	1%	1%	98%
NaCl 3M	3%	1%	1%	95%

Table III.1: Molar ratio of HTW heptanthiol conversion.

On the steel autoclaves, however, thiols and their reaction products proved to be a rather aggressive substance, for which reason these experiments were not deepened.

5.2 Aldol Condensation Reaction

Another approach was to investigate further the aldol reaction under hydrothermal conditions, as found after dehydration of phenylethandiol. For this benzaldehyde (BA) and acetophenone (AP) were selected as model molecules. The aldol condensation reaction is shown in figure III.19.

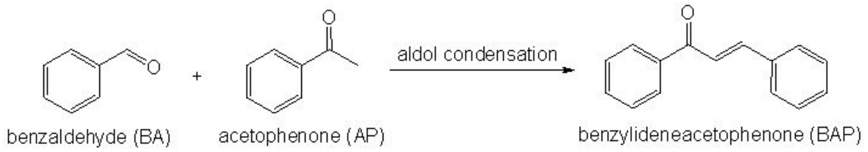


Figure III.19: Aldol condensation of benzaldehyde and acetophenone.

First experiments yielded not only the expected benzylideneacetophenone (BAP) in the gas chromatogram, but also a defined peak at much higher retention times. GC-MS analysis (see supporting information B.2 and B.3 in the Appendix) revealed it to be the product of a Michael addition of a second molecule AP on the produced BAP (as shown in figure III.20).

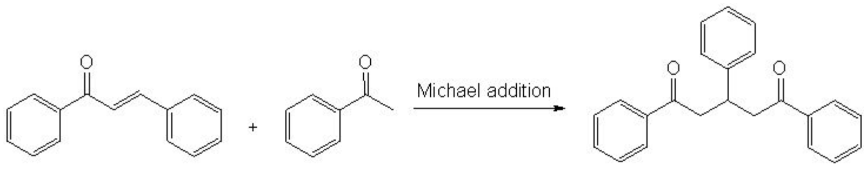


Figure III.20: Michael addition of acetophenone to benzylideneacetophenone.

Product yield at 180°C and 16 hours was very low, so the reaction time was increased to 30 hours. Figure III.21 shows the yields after summitting 5mmol of each starting material.

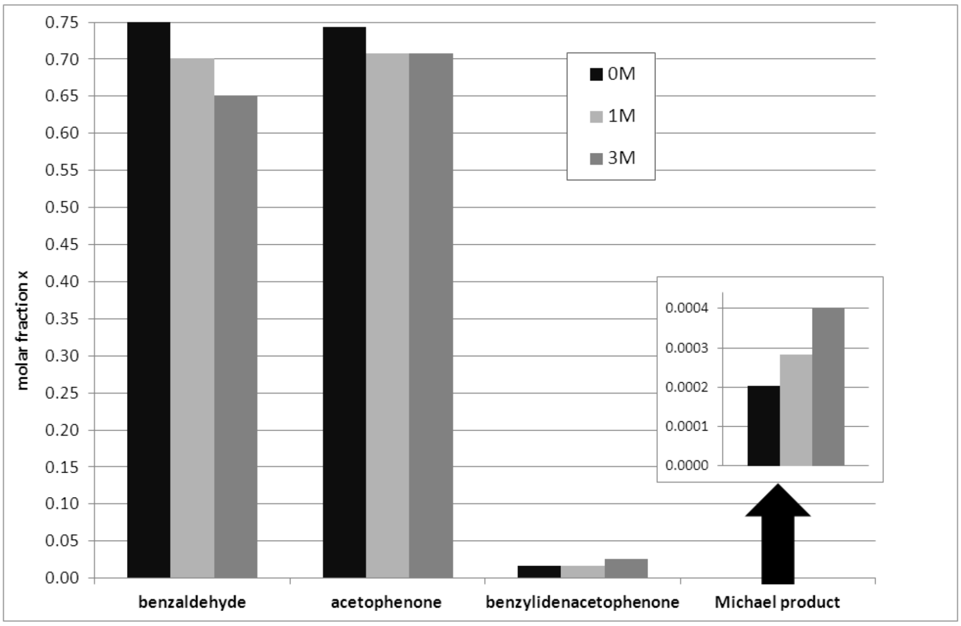


Figure III.21: Molar fractions of the reaction mixture in NaCl solution after 30 hours at 180°C.

Combined with a low initial pH even before the reaction, the still not satisfying conversion rates hint at a preferably base catalyzed mechanism in HTW. A side reaction of the used benzaldehyde, namely its disproportion into benzyl alcohol and benzidic acid, was the reason for the high proton concentration in the experiment. At the highest tested NaCl concentration, however, both product peaks rise significantly. The Michael product yield even doubled when comparing with the reaction in pure water only. Apparently on this case the proton concentration was sufficiently high for acid catalysis.

The second step was to compare the yields of acidic, neutral, and basic conditions of the reaction environment. The amount of starting material was also raised, to 15 mmol in total. This led to an accelerated reaction kinetics, increased the reaction yield again. While the starting pHs of 3 M

NaCl solutions settled around 3, a sodium acetate solution of 1M (pK_b = 9.25)[81] showed neutral to slightly basic pH values (around 7.5). Disodium hydrogen phosphate (pK_b = 6.80)[81] was used as an alkaline salt, giving pH values around 9 at 3 M concentration. Results are shown in figure III.22.

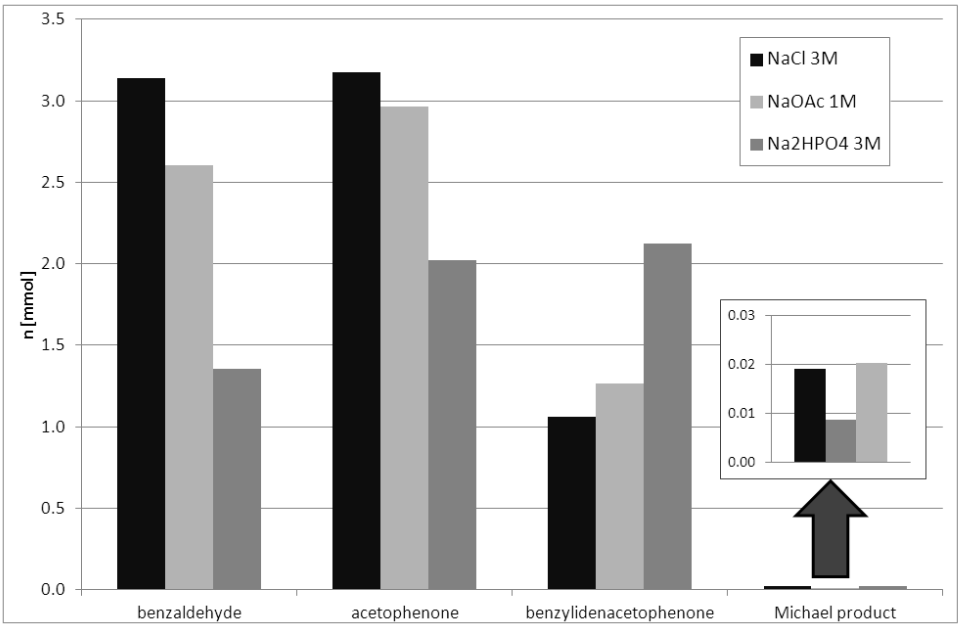


Figure III.22: BA and AP with a starting amount of 7.5 mmol each, at 180°C and 30 hours.

After the reaction pH values decreased about 0.3 units in all cases. Under all conditions the conversion rate was more than 60%, although lower at acidic and neutral conditions. Remarkably in this context, however, seems again the comparatively high yield of the Michael product in NaCl 3M. Apparently it benefits highly from acidic catalysis. Basic conditions give an even higher amount, although this does not seem surprising compared to the overall high yield and high BAP concentration.

But what about the stochiometry with regard to the Michael addition? Is the concentration of acetophenone the limiting factor? Figure III.23 shows a second set of reactions, with the same total amount of BA and AP, but at a stochiometric ratio of 1:2.

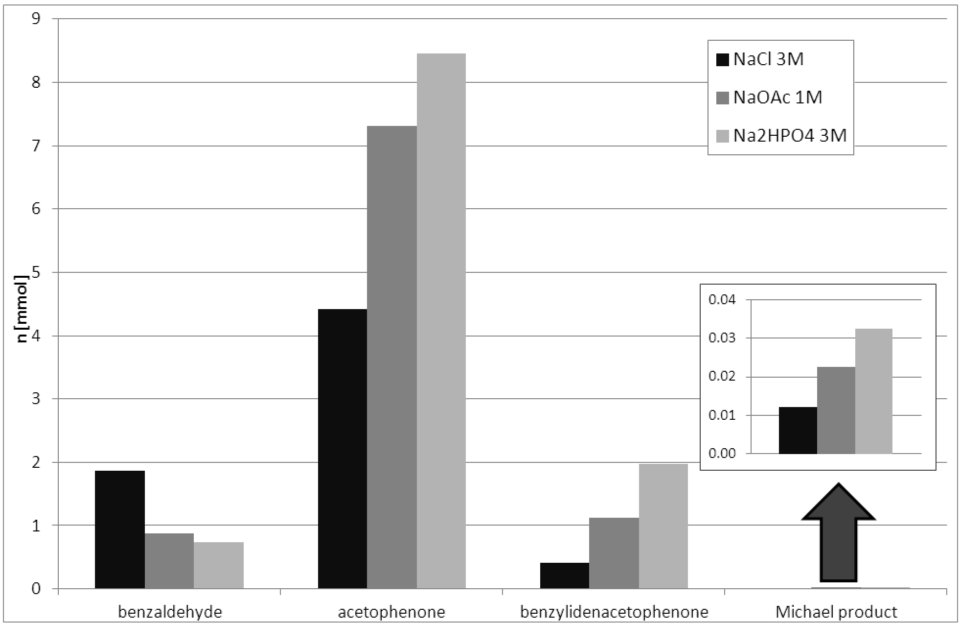


Figure III.23: 5 mmol BA and 10 mmol AP, at 180°C and 30 hours.

The pH values were similar to the other experiment, before and after the reactions. BAP yields were of similar magnitude, except in the case of NaCl solution. Acidic environment showed surprisingly low concentration of both BAP and of the Michael product. Apparently the acetophenone concentration does not limit the velocity of the aldol reaction, but the available amount of benzaldehyde.

On the other hand traces of various side reactions have been found on the GC chromatogram, although not enough for a proper analysis. Neutral conditions profited a little from the new proportions of the starting materials, but not in a significant way. Again, addition of a basic salt proved to be the most efficient environment for aldol reaction under hydrothermal conditions.

Last of all the BAP was directly employed as starting material, to investigate

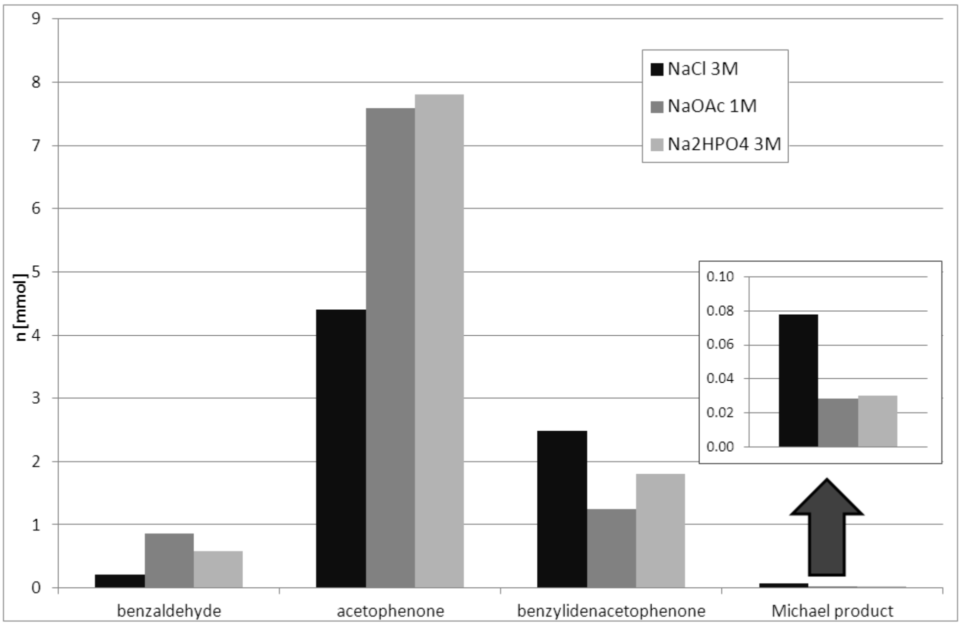


Figure III.24: BAP + AP, with a starting amount 5 mmol each, at 180°C and 30 hours.

about its stability and a more direct evaluation of the subsequent Michael addition. Results are shown in figure III.24.

As expected, acidic conditions promoted the Michael addition best. It also had the lowest back reaction yields of BA and AP. Neutral and basic environments were both quite similar in promoting both retro aldol reaction and Michael addition.

6 Summary

The addition of NaCl is able to promote the hydrothermal dehydration of 1-phenyl-1-propanol at moderate temperature (<200°C). The efficiency of salt addition decreases with increasing temperature, although the overall yield of trans-phenylpropene increases. Salt concentrations comparable to sea water show a promising improvement of hydrothermal conditions.

Remarkably, the chemical nature of the salt also makes a substantial difference. Indeed, the used cations do not influence the outcome of the reaction, while the anions - contrary to simple expectations - seem to be decisive for the alkene generation rate. It is assumed that this behaviour correlates with the intrinsic pH value at the corresponding temperature, pressure, and salt concentration.

Other organic reactions could also be observed in the following of dehydration reactions. Diels-Alder reaction, aldol condensations and others are able to form industrially relevant C-C bonds.

A closer look into the aldol condensation reaction showed that high salt concentrations of both acidic and basic natures improve the yield. Michael addition proceeds best in acidic environment, which could be another step in fine-tuning that reaction sequence.

Together with dehydratation, all these reactions raise the carbon to hydrogen ratio in biomass, making thus more valuable products in terms of energy storage and carbon trapping.

IV

Lignin Treatment

1 Background

Section 3.1 of the Fundamentals dealt with the general structure and properties of lignin in plants. But not only the nature of the lignin source, but also the pretreatment is fundamental for its actual molecular structure. Different processes used to disengage the lignin from the carbohydrates result not only in fragmentation and functionalization, but also in changing the linkages in the lignin polymer chains.[57]

The most common pretreatment process is used by the paper industry during pulping. **Kraft pulping** employs aqueous solutions of high pH containing sodium sulfide. At temperatures between 150°C and 180°C and reaction times around 2 hours the lignin degrades in a stepwise process, while the desired cellulose fibers stay intact for further use in papermaking. The lignin-containing remains, the so-called "black liquor", are subsequently burned for heating value and recovery of the sulphur. Kraft lignin fragments usually possess 1–2 % sulphur in form of thiol groups.

Another relatively common process is the **Lignosulphonate** or **Sulfite** process. Here calcium or magnesium sulfite is used, and the resulting lignin fragments possess sulfonate groups instead (3–8 % sulphur content) and a higher molecular weight. It is only applicable to softwood lignocellulose.[58]

The **Organosolv** process is a general term for using organic solvents for lignocellulose pretreatment. It results in separate product streams and clean but water-insoluble lignin. Handling and recovery of the solvent, however, makes the method expensive and thus unproductive.[57,58]

Other techniques for treatment of lignocellulosic biomass include **pyrolysis**, **steam explosion**, **alkaline oxidation**, **dilute acid hydrolysis**[58] and, more recently, **dissolution in ionic liquids**.[57] They are not commonly employed in industry mostly because of high costs and/or low quality of the resulting cellulose pulp.

So the aim of research is divided into three areas:

- Development of new, alternative processes of lignocellulosic biomass treatment to replace the existing ones.
- Improvement of the existing processes of lignocellulosic biomass treatment.
- Alternative recycling or reutilization of lignin waste products, mainly Kraft lignin.

The first topic is subject of numerous research projects and reviews,[60,82,83] often combined with hydrothermal conditions.[35,84] The innate moisture of most biomass loads make HTW an obvious choice for solvent, and the lack of toxicity enables waste to be simply deposited for carbon removal (compare section 4.3). However, due to its complexity it is not the scope of this work.

The influence of salts on existing processes like the Kraft cooking might be a field where improvement could still be essential. This subject is mentioned already in the work of Bogren et al.,[85] who even assumed a Hofmeister effect influencing Kraft lignin dissolution. But also these processes are governed by a lot of conflicting influences, not only solvation and reaction, but also the presence of organic anions, formation of complexes, influence of cell walls, and so on.

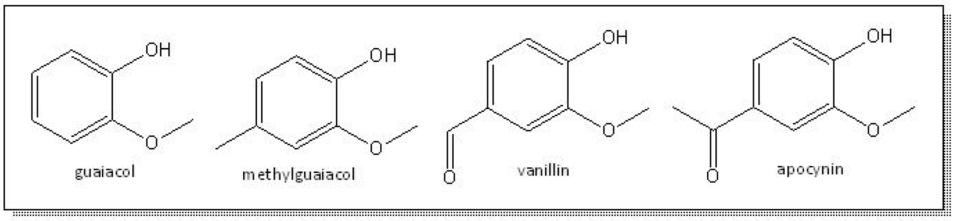


Figure IV.1: Aromatic substances obtained from Kraft lignin

This work mainly concentrated on the exploitation of Kraft lignin as common waste product for depolymerization and recovery of aromatic substances from the lignin scaffold. An emphasis was placed on obtaining the aromatic compounds of figure IV.1. These monomers are currently in demand for the production of pharmaceuticals, perfumes and food flavouring. They also play a huge role in future supply of aromatics for the chemical industry which are CO_2 neutral.

2 Dependence on Additives

For the experiment commercially available Kraft-Lignin from Sigma-Aldrich was selected.

Due to the technical problems with the Teflon material (see chapter A.2) and the well-known inhomogenity of the starting material, a high initial autoclave load of 0.5 g was chosen to reduce scattering of the data. The downside of high concentrations of biomass, as explained in the review of Schröder et al.,[35] is the higher extent of side reactions. In this case this refers mostly to the repolymerization reaction of monomers to the macromolecules.

After hydrothermal treatment the dark brown liquid was acidified with hydrochloric acid of about 10 mass% concentration. This was done to guarantee that all no hydroxy groups of the products were deprotonated. In consequence, the products were better soluble in diethyl ether than in water. This step affected also the remaining lignin polymer groups, which were now clouding the solution. During the first extraction step, the polymeric strands became a highly viscous, dark brown mass swimming between the aqueous and the organic phase. Though this waste product may have been interesting in itself, it was not investigated further in the scope of this work. The organic phase was then examined via GC-FID.

2.1 Sodium Hydroxide Solution NaOH

While slightly acidic (0.2 M HCl and 0.2 M NaCl) conditions seemed to have no visible monomer production, pure water yielded about 3mg guaiacol. Addition of NaOH promoted the ether cleavage of the guaiacyl units, almost tripling (compare figure IV.2). Methylguaiacol, vanillin and apocynin were also found, plus lots of other trace substances below the quantification limit.

Scattering of the data made a vigorous analysis difficult, yet a mysterious maximum at around 0.3 M NaOH concentration can be seen in the graph. The same maximum was also found in a student report by S.Constant.[86] A possible explanation for this could lie in the competing reactions of depolymerization and repolymerization on the lignin matrix.

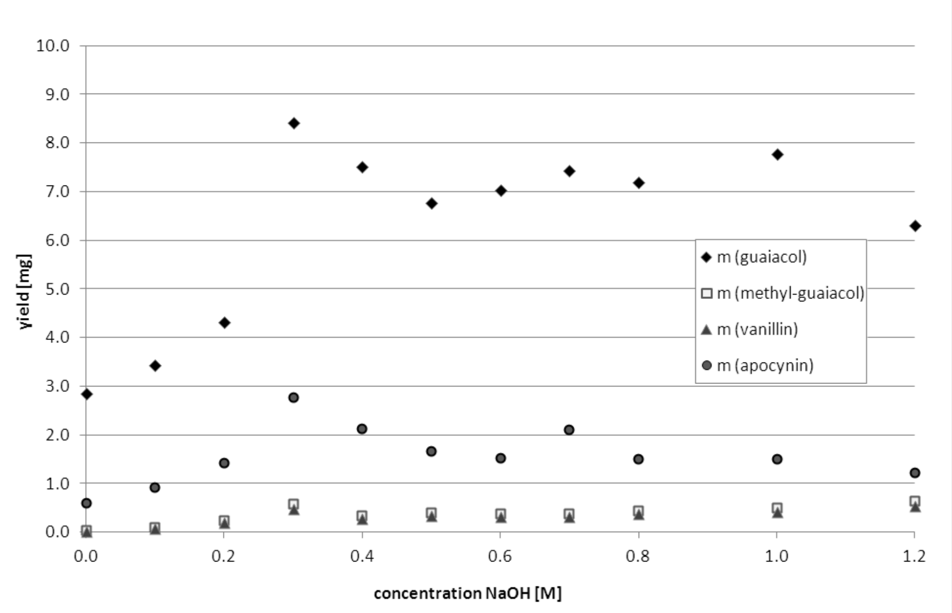
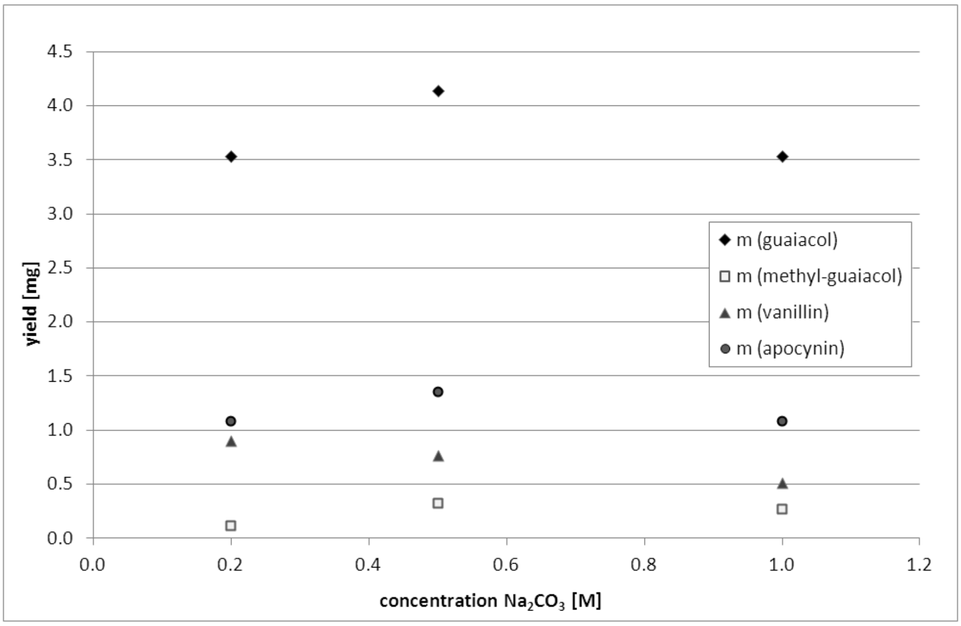


Figure IV.2: Yield of aromatic monomers as function of NaOH concentration at 200°C and 16 hours.

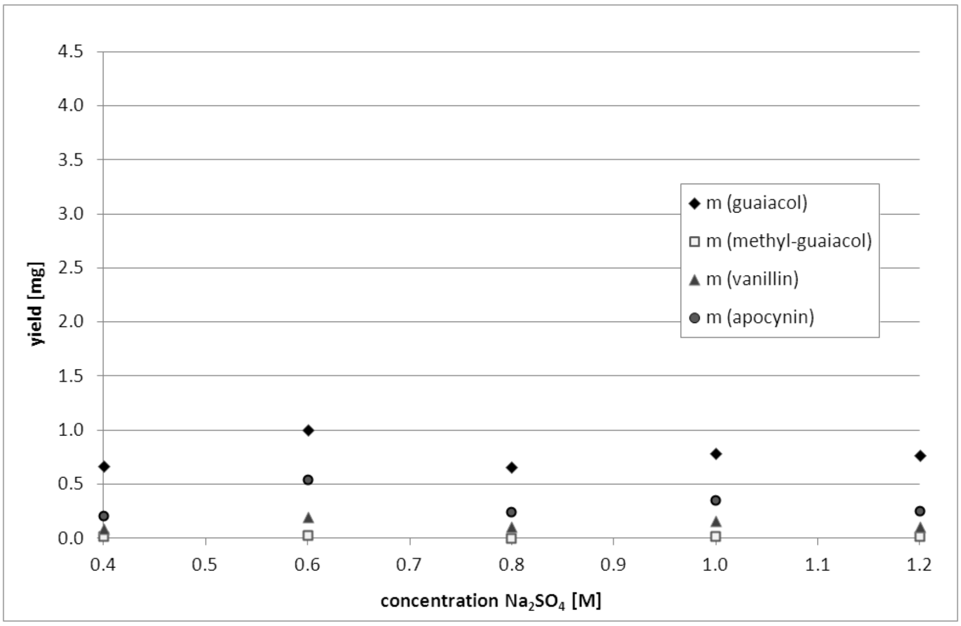
2.2 Alkaline Inorganic Salts

Some basic salts were tested next. Figure IV.3 shows the impact of Na_2CO_3 and Na_2SO_4 on the yield. Both salts did not reach conversion in the range of NaOH, despite their basic nature in prior results. Contrary to the expected increase in yield, Na_2SO_4 even seemed to inhibit the reaction. Also a short test of did not show any positive effects, the conversion range was even below the limit of analysis. Overall this hints to more complex side reactions of the used ions with the lignin matrix, instead of simple pH effects.

Na_2CO_3 had the additional complication of foaming during the extraction process, which made handling more difficult.



(a) CO_3



(b) SO_4

Figure IV.3: Aromatic compounds obtained of lignin treatment with Na_2CO_3 and Na_2SO_4.

2.3 Boric Acid H_3BO_3 and Aluminium Hydroxide $Al(OH)_3$

Inspired by the PhD thesis of V.Roberts,[87] the possibility of adding complexing agents to improve guaiacol yield was also tested. Boric acid is known to form esters with organic diols according to figure IV.4.

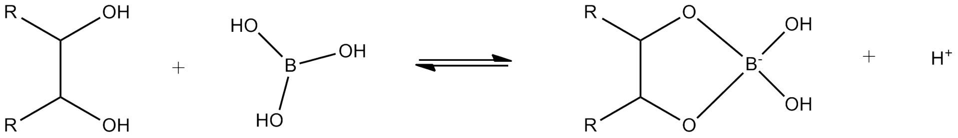


Figure IV.4: Formation of boric acid esters with cis diols.

The first diagram IV.5 shows the obtained aromatics after hydrothermal treatment with varying amounts of H_3BO_3 in 1M NaOH. Also in this context

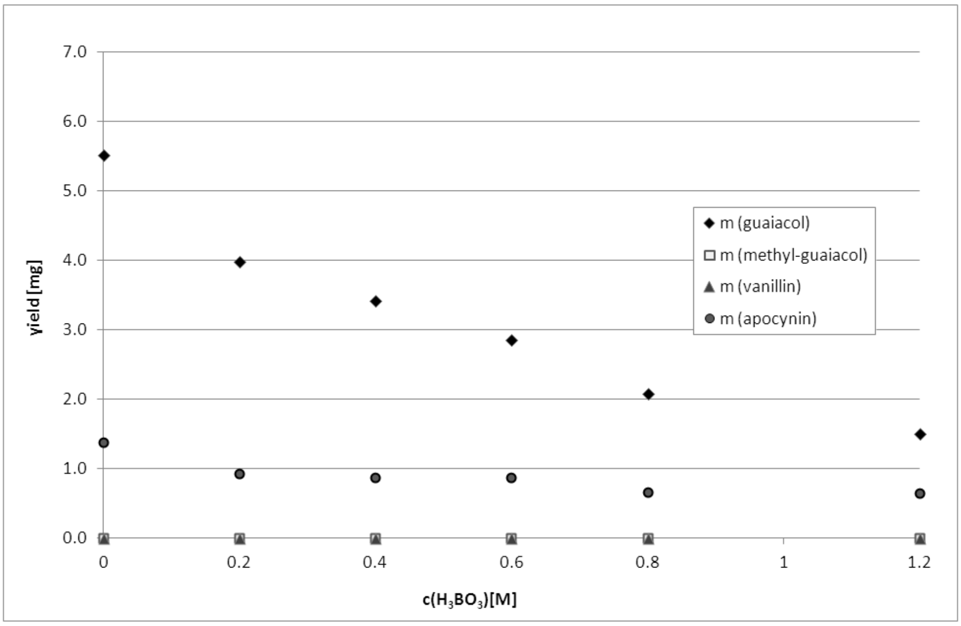


Figure IV.5: Aromatic yields with increasing concentration of boric acid in 1M NaOH.

$Al(OH)_3$ was tested for its similar build (graph IV.6).

Compared to pure NaOH, the yields decrease substantially, in contrast to

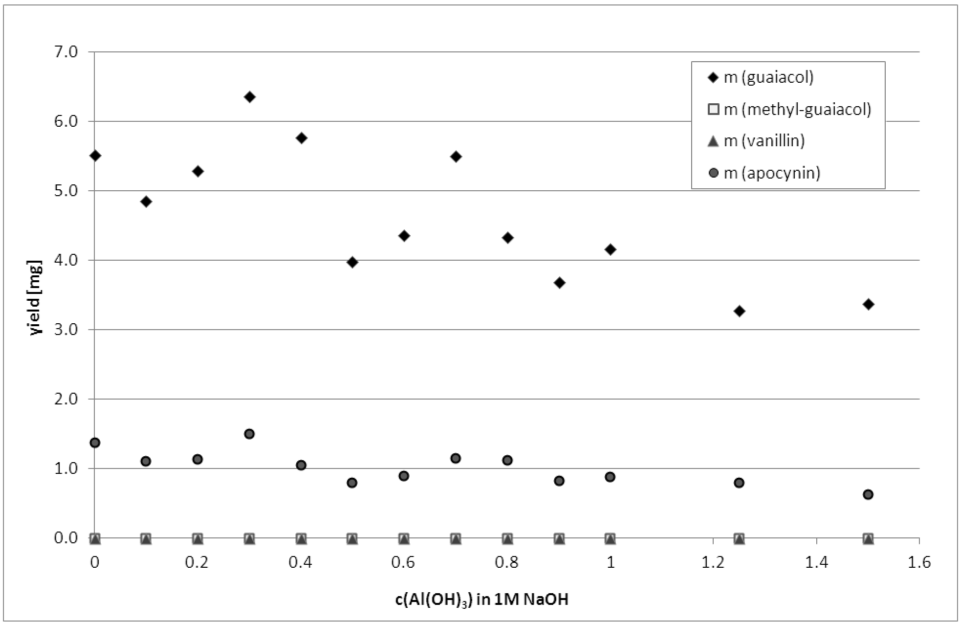


Figure IV.6: Aromatic yields with increasing concentration of aluminium hydroxide in 1M NaOH.

the expected effect. The reason for this could be the relative high reaction time compared to the other work, which was conducted at conditions close to the supercritial state. Subtracting the positive complexing effect of the boric acid, a relative reduction of hydroxy anions occurs due to the equilibrium $H_3BO_3 + OH^- \longleftrightarrow H_4BO_4^-$. This may apply to the aluminium hydroxide as well.

To counter this effect, H_3BO_3 was mixed with equal amount of NaOH. Graph IV.7 shows the result of an increasing concentration of BO_4^- -ions in 1M NaOH. Also there scattering of the data prohibits exact evaluation. Yet the borate does not seem to have any impact on the yields beyond reduction of the available OH^- in solution.

Note: *During the lignin experiments a break of about two years occurred. In this time the Kraft Lignin seemed to have undergone a substantial age-*

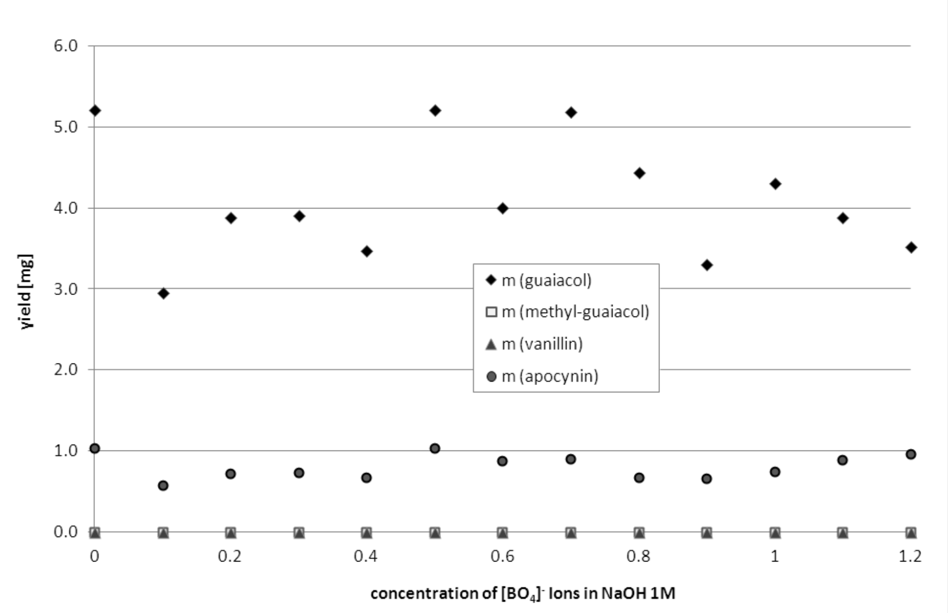


Figure IV.7: Aromatic yields with increasing concentration of borate ions in 1M NaOH.

ing process, although stored in a closed box without light. This discovery occurred relatively late into the new experimental series; as these were quite time-consuming, it was decided to continue with the lignin batch on hand. Inside a series the values were consistent and compatible for comparisons.

A closer look of the first two sections of this chapter reveals therefore incompatibilities of the results with the third section.

3 Summary

In this section the focus lay on applying the insights of the last chapter to the retrieval of aromatics from Kraft lignin. This type of lignin is being produced as waste product in paper mills and generally burned for lack of a better use. The Kraft process itself is conduced under hydrothermal conditions. Also there ion effects are playing a role,[85] making this topic an interesting but complex field to study.

Main molecules to recover were guaiacol and apocynin, also some vanillin and methylguaiacol could be found. These are valuable raw materials for industry.

additive		guaiacol amount
none		2.9 mg
HCl	0.2 M	below limit of detection
NaCl	0.2 M	below limit of detection
Na_2HPO_4	0.2 M	below limit of detection
Na_2SO_4	0.2 M	below limit of detection
Na_2CO_3	0.2 M	3.5 mg
NaOH	0.2 M	4.3 mg

Table IV.1: Comparison of the impact of different additives on guaiacol yield.

On neutral to slightly acidic conditions conversion was low. Salts had no major impact on the aromatics yield as well, but NaOH increased it fairly (see also table IV.1). A mysterious local maximum yield at about 0.3M concentration marked the border of competing depolymerization and repolymerization reactions; there the monomer yield was about 20% higher as the average yield at higher base concentrations.

Overall the numbers stayed pretty low, but comparable to the experiments of Zakzeski and Weckhuysen, who treated Kraft lignin hydrothermally with a Pt/Al_2O_3 catalyst.

Another interesting concept for further investigation was the idea of complexation of the generated phenolic substances (in the present studies with borate ions). Blocking of the reactive groups should hinder repolymerization of the monomers onto the lignin scaffold. A similar idea for blocking the reactive centers a solvothermal reaction was suggested by Okuda et al.[88] Unfortunately none of these methods worked well in the present study. The complex nature of the lignin material suggests further studies with model molecules, though.

All in all there is still much to do concerning the exploitation methods of lignin. The here presented experiments might help to improve current Kraft processes, which are quite similar in their conditions. Efforts should be made to incorporate the recovery of already produced aromatics into the existing process. Also, a second continuative hydrothermal treatment to recover lignin monomers is thinkable.
The resulting waste liquor could still be burned as usual, or reused as concrete admixture, road binder, low cost surfactants, and many other applications.[58]

V

MICROWAVE ASSISTED ORGANIC SYNTHESIS

In organic synthesis the activation barrier of a chemical reaction (and also sustenance of an endothermic process) is classically crossed by the means of thermal heating. Normal devices, like isomantle or oil bath, are slow and ineffective means to convey thermal energy. After introducing the microwave oven in the kitchen, the groups of Gedye and Giguere/Majetich used it in 1986[89,90] successfully for organic synthesis. However, it was a risky and insecure procedure prone to explosions until the turn of the century. There the construction of specially designed ovens for chemistry lab procedures opened a doorway for microwave assisted organic synthesis (MAOS).
A promising new field for efficient conversion of materials, it is not only known to reduce reaction times, but also to lower side reactions and increase yields. Numerous reviews[91–96] and books[97–99] summarize research results of the last years and provide advice for transforming ordinary procedures into the MAOS realm. The underlying mechanisms of this revolutionary method

will be discussed in the following section.

1 Background

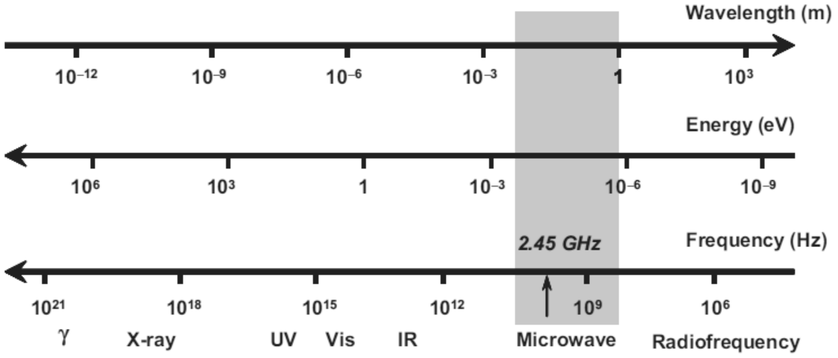


Figure V.1: Microwave frequency in the electromagnetic spectrum.[97]

Microwave irradiation takes place in the frequency range of 0.3 to 300 GHz, corresponding to wavelengths of 1 cm to 1 m (see figure V.1). All of the commercially available microwave oven (both domestic and lab equipment), though, operate exclusively at a frequency of 2.45 GHz. This is fixed so that they do not interfere with telecommunication and cellular phone frequencies.[97]

Unlike ultraviolet and visible radiation, its energy is too low to break chemical bonds. Some liquids and solids, however, absorb microwave energy and convert it into heat. This is called “dielectric loss” or “microwave dielectric heating effect”. It is commonly divided into two major phenomena: dipolar polarization and ionic conduction (see figure V.2).

One of the key factors to generate heat from microwave irradiation is a substance’s possession of a dipole moment. The dipoles try to align themselves in the oscillating electric field, and loose energy in the process. In consequence,

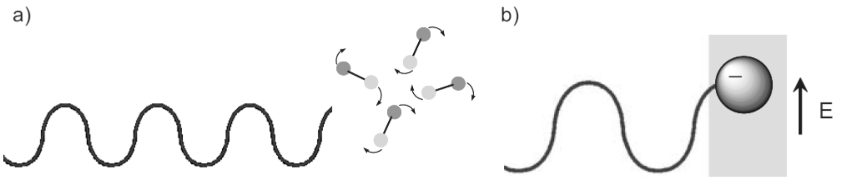


Figure V.2: (a) Dipolar polarization mechanism. (b) Ionic conduction mechanism.[97]

the aforementioned dielectric constant is actually frequency-dependent in the range of microwave irradiation, and the values given in table II.1 of chapter 1.1 are static ones. The magnitude of dielectric loss is best compared by the loss tangent values tan $\delta = \epsilon''/\epsilon'$, with the dielectric constant ϵ'' and the loss factor ϵ' (efficiency of energy-to-heat conversion). It has to be mentioned that the maximum of tan δ of a substance seldom is exactly at the selected frequency of 2.45GHz, which diminishes the efficiency of microwave heating somewhat. In exchange, the microwave radiation penetrates deeper into the mixture and heats more homogeneously. Loss tangent values for some common solvents are given in table V.1.

A way to improve the tangent loss at a given temperature and frequency is

Ethanol	0.941
Benzyl alcohol	0.667
Glycerol	0.651
Hexanol	0.341
Water	0.123
Chloroform	0.091
Ethyl acetate	0.059

Table V.1: Loss tangents of various solvents at 2.45 GHz and 20°C.[100]

to add ions (salts, ionic liquids, etc.). These provide an increased dielectric loss of a medium by moving in the electric field themselves.

The efficiency of microwave heating compared to normal external heating shows figure V.3. As the heat is generated directly inside the reaction vessel,

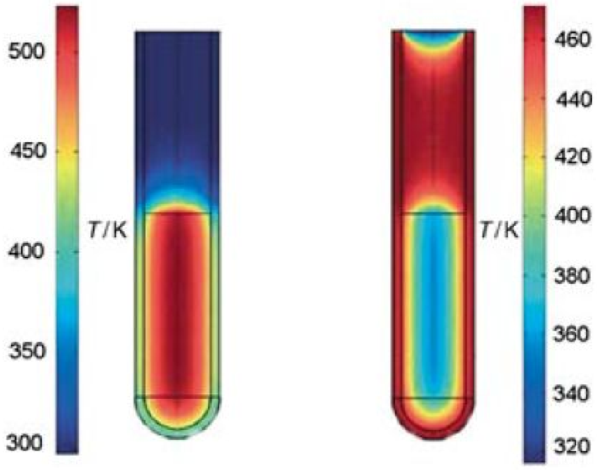


Figure V.3: Inverted temperature gradients in microwave versus oil bath heating after 1 minute: while microwave irradiation (left) results in an increased temperature of the whole volume, the oil-heated reaction mixture in contact with the vessel wall is heated first.[93]

high temperatures are achieved in a very short time and highly homogeneous distribution. This decreases reaction times, and thus, saves energy. What's more, side reactions will be minimized due to lack of overheating at the vessel walls.

In some cases, the efficiency of microwave synthesis goes beyond the simple heating advantages described above. While the overall thermal effects were essentially explained in the last section, there are thermal effects specific to the nature of microwave heating mechanism.
In this category falls overheating of a solvent: Classically boiling occurs at nucleation points on the hot reactor surface. Since microwave radiation heats from within, a liquid can be brought up to a temperature 100°C higher than its commonly known boiling point. Stirring or the use of boiling stones, however, cancel this effect.

In the sample, researchers have also detected the presence of so-called “Hot Spots” – small regions within the sample exhibiting a much higher temperature than the bulk. This phenomenon arises as a consequence of the inhomogeneity of the applied field.[101]

A reaction mixture with components having different dielectric loss factors shows selective heating. This can be of interest in phase transfer reactions or for heterogeneous catalysis, in cases where reactants would decompose otherwise.

Non-thermal microwave effects have been defined as a result of direct interaction of the electric field with specific molecules in the reaction vessel. Examples may be dipolar orientation effects prior to the reaction or a different polarity of the transition state. They are still a matter of controversial discussion, as it is not clear whether observations regarding that matter may be ascribed to inexactness in temperature measurement, for example. Yet it has lead to the new option of microwave synthesis with simultaneous external cooling.

2 Microwave Heating in HTW Reactions

2.1 Variation of Time

As shown in the last section, microwave heating has many advantages. Also reactions in HTW can be done under these circumstances, as several research groups show. Some of the experiments from chapter III were repeated in a commercially available microwave synthesis oven, to investigate about differences especially concerning the salt effect.

First a simple combination of water and phenylpropanol at 180°C and different time spans was done, the results are shown in figure V.4.

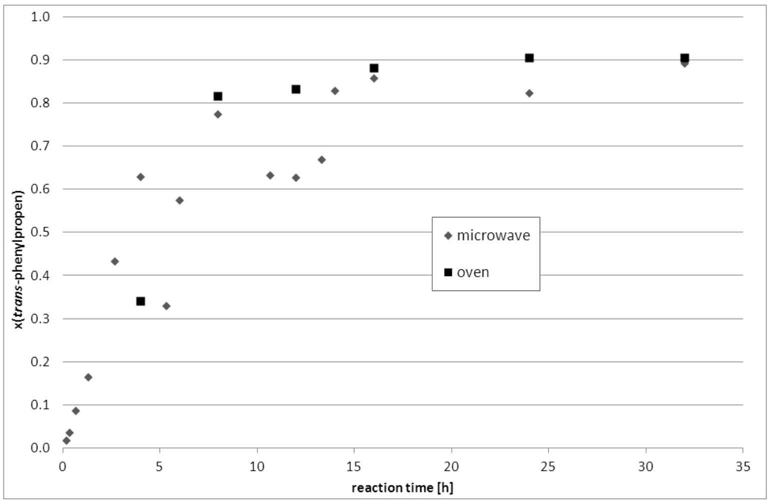


Figure V.4: Comparison of conventional heating vs. microwave heating at 180°C.

It can be clearly seen that there is no specific microwave effect increasing reaction kinetics in this case. On the contrary, the kinetics curve seems less steep, indicating a decrease in reactivity. However, this plot is not really suitable for good comparison of the two heating methods. Therefore, in the next step we assume that

- the dehydratation progresses only via protonation of the alcohol group,
- that this step is the slowest and therefore rate-determining step in the reaction path and
- that due to the comparatively high concentration of protons a pseudo-first order can be applied.

Consecutively, the revised rate constant k

$$-\frac{dc_{php}}{dt} = k \cdot c_{php} \tag{V.1}$$

can be calculated with a linear plot:

$$ln\frac{c^0_{php}}{c_{php}} = k \cdot t \tag{V.2}$$

with c^0_{php} the concentration of phenylpropanol at the beginning of the reaction, and c_{php} the concentration at time t.

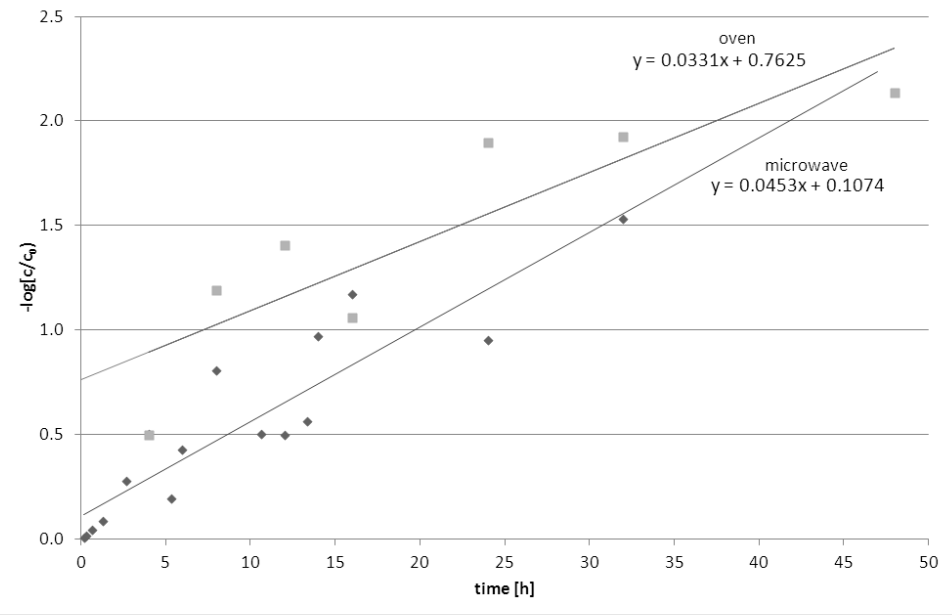


Figure V.5: Logarithmic plot of the two different yield vs. time curves.

Figure V.5 shows that indeed the reaction in the microwave proceeds at a slower rate than one heated by a conventional oven. Thus a search was done for other experimental differences than the heating method. These include:

- Cool off time spans: Teflon is a good heat isolator, which extends to a cooling off time of several hours instead of minutes as in the microwave oven. This difference is still regarded as of little importance, because phenylpropene yield at 160°C and 16 hours is already quite low.
- The glass vials are transparent, while the autoclave reactions proceed

in darkness. However, if this should make any difference it should be an increase of microwave reaction yields rather than a decrease.

- Container material: In the autoclave, direct contact is only with the Teflon, while microwave vials consist of borosilicate glass and the IntelliVent lid (made of Teflon). The implication of this difference will be discussed in detail in section VI.3.
- Stirring of the microwave reaction.
- Different ratio of starting material to solvent.

The last item could indeed make a substantial difference, although the water volume is still about 100 times bigger than that of phenylpropanol. Because microwave vials have a total volume of 10 milliliters, the solvent volume had to be cut down from 10 to 5 mL for the experiments (see appendix for experimental details). Considering the low solubility of phenylpropanol in water this could make for a lower yield. This, of course, implies that the catalytic effect is carried out only in the aqueous phase.

2.2 1-Phenyl-1-propanol

For this reason the next experiments were carried out with the initial amount of phenylpropanol as well as half the amount. Results are shown in table V.2.

Compared to the experiments with 5mmol phenylpropanol, reaction yields of half the amount did not increase in all cases. This finding questions the explanation of a decreased yield when heating with microwave radiation due to solubility effects. It might still play a role, but not a crucial one. Between the oven and the microwave results there is no general trend anymore. While

	NaCl	H_2O	Na_2SO_4	160°C
oven	88.0 (7.3)	73.9 (6.8)	39.9 (3.5)	30.7 (2.4)
MW	85.6 (7.7)	28.2 (2.6)	1.8 (0.2)	22.1 (2.0)
MW_half	43.5 (3.9)	65.8 (6.5)	5.0 (0.7)	42.8 (4.0)

Table V.2: Product yields of *trans*-phenylpropene HTW reactions in percent. The figures in brackets relate to the molar fraction of *cis*-phenylpropene. The amount in the second set of microwave experiments was adapted to match the oven experiments proportionally rather than in total amount.

the yields of water and sodium chloride increased, those of sodium sulfate and water at 160°C decreased. Interesting in particular is the comparison of microwave to oven without additives at different temperatures. One expects that both values either increase or decrease. The discussion of this phenomenon will be continued later in chapter VI, when a closer look into wall effects is being taken.

Calculation of the *trans*-to-*cis* ratio (table V.3) of phenylpropanol dehydration gave fairly constant values, with the only exception of the sodium sulfate additive. Due to its low reaction yields the deviation is still within error margins. Consequently, neither temperature, nor salt addition of different kinds, nor microwave radiation was able to shift the ratio of main product to side products closer towards one of the isomers.

	NaCl	H_2O	Na_2SO_4	160°C
oven	12.1	10.9	11.4	12.8
MW	11.1	10.8	9.0	11.1
MW_half	11.2	10.1	7.1	10.7

Table V.3: *trans* to *cis* ratio of phenylpropene yield.

2.3 1-methyl-1-cyclohexanol

On the other hand, in the dehydration reaction of 1-methyl-1-cyclohexanol (table V.4) the microwave increased the yield in all cases. The combination of microwave and pure water gave even a total conversion of 97% towards the reaction products, while the oven heated experiment yields were below that of both salt additives. The highest yield of methylenecyclohexane, however, was achieved in the microwave in a 1M Na_2SO_4 solution.

	NaCl	H_2O	Na_2SO_4	160°C
oven	69.6 (1.2)	55.1 (1.9)	61.8 (14.8)	64.9 (3.8)
MW	76.3 (16.0)	94.0 (2.8)	74.6 (22.0)	80.4 (5.3)

Table V.4: 1-Methyl-1-cyclohexene yield of HTW reactions at 180°C. Figures in brackets stand for methylenecyclohexane yield.

The ratios of methylcyclohexene (the Saytzew product) to methylenecyclohexane (the Hoffmann product) decreased in most cases with the exception of pure water as solvent, as table V.5 shows. This means that generally the microwave generates more of the kinetically stable isomer, which corresponds well with the heating profile and cool down rate of that equipment.

	NaCl	H_2O	Na_2SO_4	160°C
oven	58.0	29.0	4.2	17.1
MW	4.8	33.6	3.4	15.2

Table V.5: Methylcyclohexene to methylenecyclohexane ratio of table V.4.

2.4 Pinacol

For further comparison, the pinacol rearrangement was tested as well. Results in table V.6 show the same trend in decreased reaction rates as phenylpropanol, only even more pronounced. This time, water solubility should not be a problem, since pinacol is completely soluble in hot water. Results were exceptionally low, compared to the autoclave experiments.

	NaCl	H_2O	Na_2SO_4	160°C
oven	97.7 (0.2/0.3/0.1)	98.2 (0.6/0.3/0.1)	31.6 (1.3/0.4/0.1)	78.4 (2.9/1.2/4.5)
MW	13.8 (2.8/0.4/1.7)	7.0 (1.5/0.1/2.6)	4.2 (1.5/0.1/0.9)	3.6 (0.7/0.0/5.5)

Table V.6: Product yields of pinacol HTW reactions in percent. The top figure is the molar fraction of pinacolon, while the bottom figures in brackets relate to 1,2-dimethylbuten-3-ol, dimethylbutadien, and the Diels-Alder product, respectively.

Those from the microwave showed almost no rearrangement reaction to pinacolon (table V.7). The dehydration products, on the other hand, increased substantially. This can also be explained fairly well with the heating profile. The less stable transition products on the way to the Diels-Alder ring closure profit from the absence of hot walls and heat which is generated directly inside the solvent.

	NaCl	H_2O	Na_2SO_4	160°C
oven	139.6	89.3	16.6	6.0
MW	2.1	1.0	1.2	0.3

Table V.7: Ratio of rearrangement product to dehydration products of pinacol. The Diels-Alder product was counted twice, for two equivalents of pinacol participating.

Influences of the nature of salts cannot be ruled out, but at least they do not overrule or counter the general trend of a kinetics decrease of microwave reactions.

3 Summary

Some selected experiments from chapter III were repeated in a microwave synthesis oven.
Microwave ovens as heating sources generate heat directly inside the vial by exciting dipoles such as water molecules. This method has generally the advantage of lower reaction times, low side products and efficient synthesis.

However, in these experiments the microwave was not able to increase reaction yields in all cases. A possible explanation could be the different reactor material (compare section VI.3 for a deeper discussion).

While ratios of *cis* to *trans* isomers stayed constant, the study of selected model reactions showed that microwave increased the yield of Hoffmann alkenes, compared to the Saytzew type. Also the Diels Alder ring closure reaction worked way better due to the special heating profile of a microwave oven.

Regarding the salt effects no change in behaviour could be detected when switching to microwave heating. This does not naturally mean that there is no microwave salt effect, but it was low compared to other experimental factors.

VI

TEMPERATURE-SWITCHABLE PHASE SYSTEMS

Earlier chapters have shown that fine-tuning of the solvent properties of HTW is not as easy at moderate temperatures as it would be in the supercritical state. Another method which is employed yet for ages is mixing two different substances to achieve solvent properties that normally are in between the two pure components. A classical example thereof are water-ethanol mixtures, being cheap, non-toxic and popular e.g. for pharmaceutical extraction processes.

1 Background - Solubility Parameters

Historically the solubility of one component in a solvent had to be determined experimentally. Physical chemists have worked to improve and aid with this search of the perfect solvents by applying common thermodynamical concepts. One approach is to assign solubility parameters, with similar solubilization properties at similar values.

The Hansen solubility parameters HSP are an extension of the earlier Hildebrand parameter,

$$\delta = (E/V)^{1/2}, \tag{VI.1}$$

where E is the (measurable) energy of vaporization and V the molar volume of the pure solvent (both at 25°C). Its SI unit is MPa$^{1/2}$, US publication also apply quite often the cgs unit (cal/cc)$^{1/2}$ = 0.489 MPa$^{1/2}$. Hansen divided the forces responsible for the cohesive bonding into three parts: Dispersion forces D, permanent dipole-dipole forces P, and hydrogen bonding H. This cohesive energy must be overcome when evaporating the liquid, and it arises from interactions of a solvent molecule with its neighbour. Consequently, the Hansen Solubility Parameters are calculated as

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{VI.2}$$

with $\delta^2 = E/V$ of the respective energy. The distance R_a between the solubility parameters of a sample (1) and a test chemical (2) is calculated as

$$(R_a)^2 = 4(\delta_{D2}^2 - \delta_{D1}^2) + (\delta_{P2}^2 - \delta_{P1}^2) + (\delta_{H2}^2 - \delta_{H1}^2) \tag{VI.3}$$

where the constant 4 was introduced by Hansen et al. based on a set of experimental data.

The HSP of a solvent is generally depicted as a sphere in a three-dimensional diagram, with the additional parameter R_0 as radius of the sphere. R_0 is an experimentally determined value and shows the maximum difference in affinity tolerable for a good interaction between solvent and solute. In consequence, the quality of a solvent has been defined by the Relative Energy

Difference RED as

$$\mathrm{RED} = R/R_0. \tag{VI.4}$$

A good solvent has a value less than 1, while higher numbers stand for poor solubility. Additionally, Hansen mentioned that smaller molecular volumes result in a smaller free energy of mixing. Therefore the solubility also depends on the size of molecules. He chose to add the molar volume V_M as a forth parameter instead of multiplying the initial well-defined parameters.[102] Some HSP values of common solvents are given in table VI.1.

solvent	δ_D	δ_P	δ_H	V_M	δ
water[1]	15.5	16.0	42.3	18.0	47.8
glycerol	17.4	12.1	29.3	73.3	36.2
ethanol	15.8	8.8	19.4	58.5	26.5
dimethylformamide	17.4	13.7	11.3	77.0	24.9
1-octanol	17.0	3.3	11.9	157.7	21.0
acetone	15.5	10.4	7.0	74.0	19.9
toluene	18.0	1.4	2.0	106.8	18.2
diethyl ether	14.4	2.9	5.1	104.8	15.5
hexane	14.9	0.0	0.0	131.6	14.9

Table VI.1: Hansen Solubility Parameters for selected solvents in SI units.[102]

Naturally, these solubility parameters are temperature dependent. Often it is assumed that the HSP all show the same temperature dependence and don't need to be recalculated. Exceptions are usually substances with extended hydrogen bonding. Water takes a special place among these more complicated cases. Comparison with experimental values suggests an association of about six water molecules into a cluster. This corresponds fairly well with other studies.[13] The temperature dependence of the HSP of water as proposed by Srinivas et al. is shown in figure VI.1.

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[1] Values for a single molecule of water, calculated from the energy of vaporization.

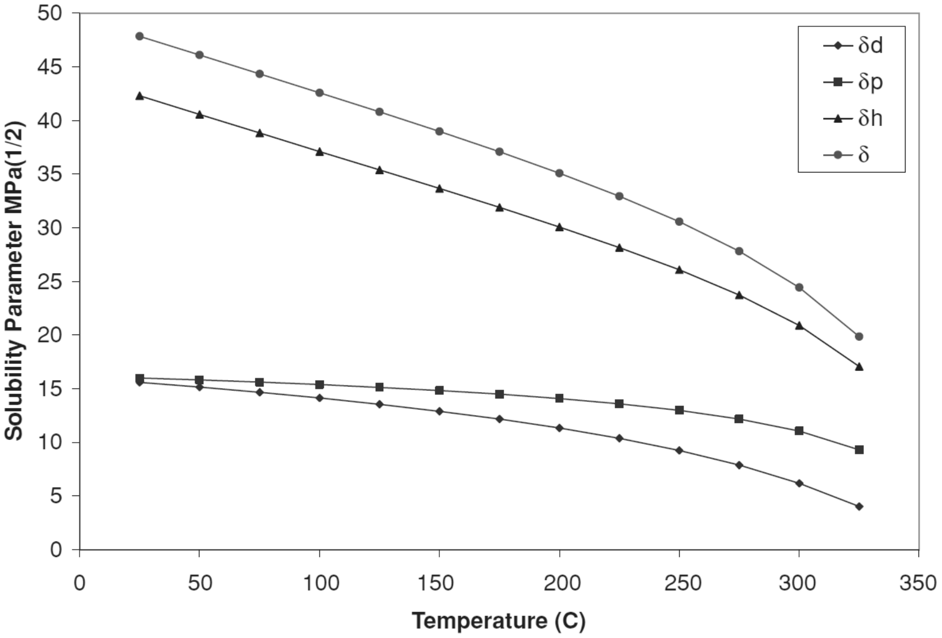


Figure VI.1: Variation of the Hansen solubility Parameters HSP of water with temperature.[103]

It can be seen that the solubility parameters of water decrease rather slowly at temperatures below 200°C. At 180°C they can be compared to these of glycerol (compare table VI.1), but they are still way above those of apolar solvents. One has to have in mind, however, that a temperature increase does not only change the HSP. It also increases the radius of the solubility sphere R_0, making solubilization thus more probable.

Since the determination of solubility parameters, different workgroups have tried to develop a predictive model. The most popular approach was the Group Contribution Method. It is based on the assumption that any physicochemical property of an unknown molecule can be added up from the values of its separate functional groups.

The here presented approach origins in the framework of Mavrovouniotis:[104]

Each compound is seen as a hybrid of conjugates. The property of a compound is then evolved from the properties of each single conjugate. This is called the ABC technique (contribution of **A**toms and **B**onds to the properties of **C**onjugates). Constantinou and Gani based on this their separation of first-order groups (representing the covalent or dominate conjugate) and second-order groups (representing the recessive or ionic conjugates).[105] A schematic example of this technique is shown in figure VI.2. The recessive conjugates are generated from the dominant form by a conjugate operator, for a more detailed explanation the interested reader is encouraged to read the corresponding articles.[104–109]

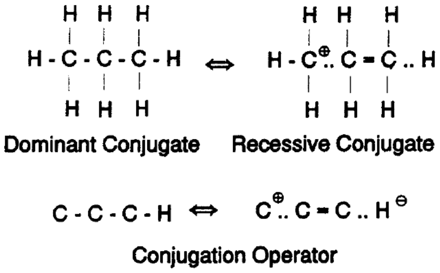


Figure VI.2: Example of a dominant conjugate, a recessive form, and the corresponding operator.[105]

Stefanis et al. established the following equations for calculating Hansen Solubility Parameters via first order and second order contributions (updated version of 2012):[109]

$$\delta_D = \left(\sum_i N_i C_i + \sum_j M_j D_j + 959.11 \right)^{0.4126} \quad \mathrm{MPa}^{1/2} \tag{VI.5}$$

$$\delta_P = \left(\sum_i N_i C_i + \sum_j M_j D_j + 7.6134 \right) \mathrm{MPa}^{1/2} \tag{VI.6}$$

$$\delta_H = \left(\sum_i N_i C_i + \sum_j M_j D_j + 7.7003 \right) \mathrm{MPa}^{1/2} \tag{VI.7}$$

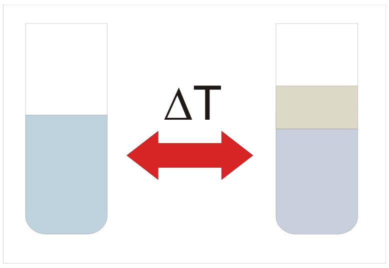
with C_i and D_j being the group contribution of first-order and second-order groups, respectively (for a complete list see appendix). N_i and M_j are the number of times of the said group. Equations VI.6 and VI.7 are only applicable for HSP $< 3MPa^{1/2}$, the corresponding information for smaller values can be found in literature.[109]

Still another improvement of comparing solubilities could be the splitting of the hydrogen bonding parameter into acidic and basic components. This can be done using the sigma profiles calculated by the COSMO-RS theory. This method was also recently published by Stefanis and Panayiotou[109] and will not be discussed in detail within this work.

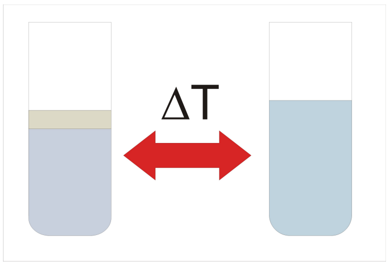
2 Search of Suitable Phase Combinations

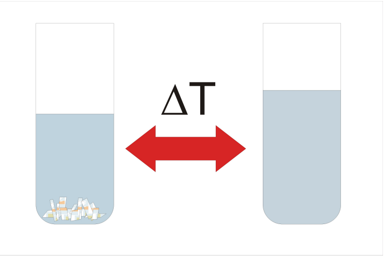
Subcritical conditions offer a broader approach to fine-tuned solvent mixtures. Interesting effects can arise when temperature differences can be brought into effect. Two different situations can occur:

- Two solvents mix at room temperature, but show a liquid-liquid phase separation at HTW conditions. This could favour e.g. reactions with more lipophile products, which migrate into the organic phase and are protected from a back-reaction.



- The solvents do not mix at room temperature (the second substance can be liquid or even solid), but they build a single liquid phase at HTW conditions. At reaction temperature this could facilitate solubilization of the starting materials. Also, especially in the case of solids that facilitates post-reaction separations hugely (in case that the phase crystallizes separately).





The negative side of this idea is that these co-solvents have to fulfill a number of requirements further to solubility properties:

- stable under HTW conditions (acids, bases, temperatures)
- not reacting with synthesis components[2]
- low vapour pressure (to minimize technical challenges of high pressure conditions)
- non-toxic, “green”

---

[2] This may not apply to all cases. As alternative the solvent may be selected to react with the product to stabilize it and/or prevent the backward reaction. Compare also the thoughts in section IV.3.

Various substances have been tested with a specially designed **p**hase **o**bservation **h**eating **d**evice POHD, for details see supporting information, section 5. We already know that simple alcohols are quite stable. Literature also shows that alkyl ether bonds do not decompose at temperatures up to 250°C.[26]

Few substances have been found that match the required criteria, two of them have been examined in detail.

Polyethylene glycol PEG polymers are water-soluble at room temperature, and they are manufactured industrially in all chain lengths desirable. They are cheap, biodegradable, have low flammability and hardly any vapour pressure. With water they can build aqueous biphasic systems (ABS), and they are often used to decrease polarity of the solvent[110] or in two-phase partitioning processes.[111] A PEG with a molecular mass of 6000 g/mol was selected, with a melting point of about 60°C. Its phase diagram with water is shown in figure VI.3.

Under the present parameters the liquid-liquid phase separation only appears at temperatures above 130 °C and low to intermediate PEG concentrations. The cloud point can be lowered greatly, though, upon addition of inorganic salts.[111] This phenomenon is explained by Kjellander et al.[112] with a dissolution of the rigid structures around PEG molecules and subsequent increase of hydrophobic interactions.
For the example of NaCl, results are shown in figure VI.4.

As expected, the curve shifts to lower temperatures due to the increased ionic nature of the aqueous solution. This salting out effect was also studied by Bailey and Callard[113] for different salts, albeit at higher chain lengths. According to their results, SO_4^{2-} for example is even more effective in decreasing

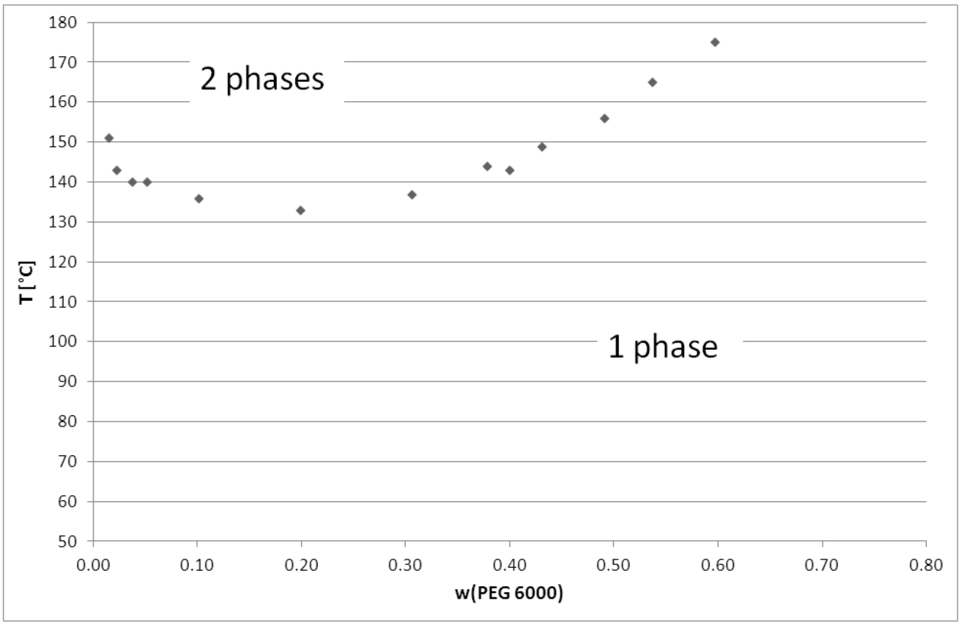


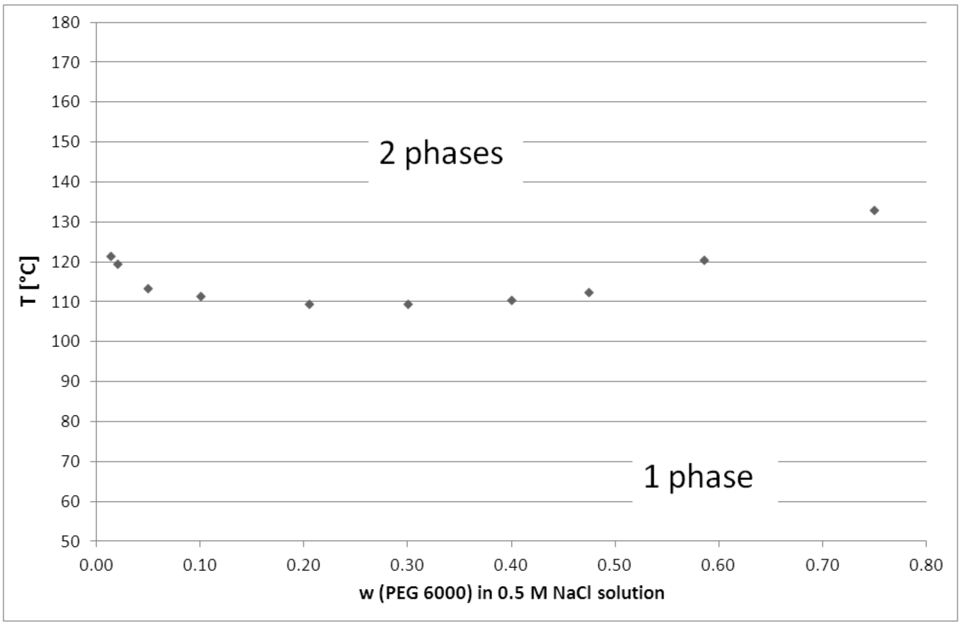
Figure VI.3: Phase diagram of PEG 6000 / water.

the cloud temperature of aqueous PEG mixtures.

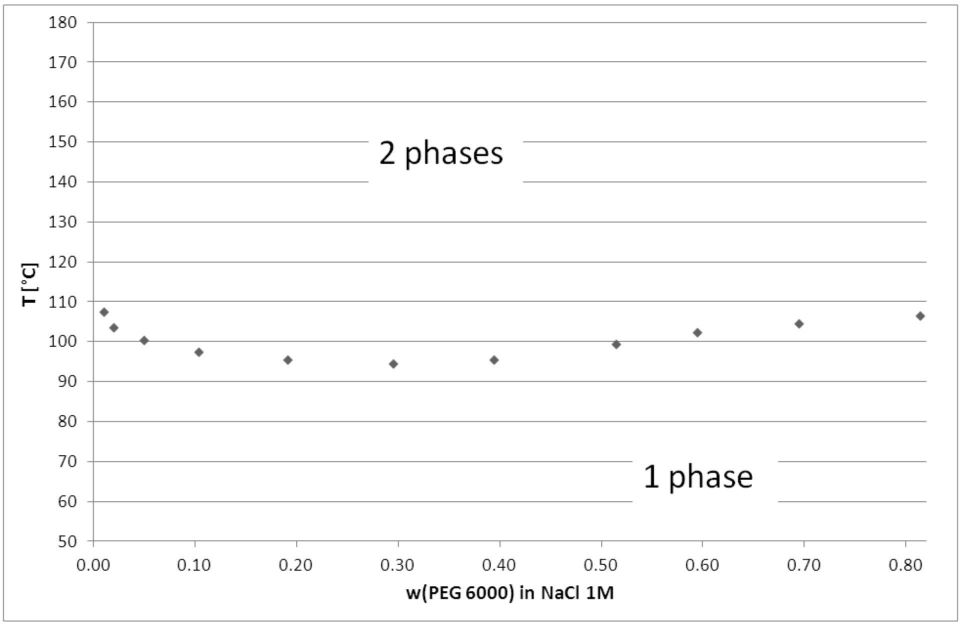
The Hansen Solubility Parameters of PEG 6000 cannot be determined with current group contribution methods, but table VI.2 provides some experimental values from Adamska et al.

For easier comparison, the total solubility parameters from table VI.2 are shown in table VI.3. As one can see, with increasing temperature the solubility parameter of PEG 2000 decreases as expected. The solubility parameters of PEGs with higher chain lengths, however, increase with increasing temperature. This behaviour can induce a phase separation like the one observed in the corresponding phase diagrams.

As second substance, 1,8-octanediol was chosen. It also has a melting point around 60°C, and low vapor pressure. The corresponding phase diagram is shown in figure VI.5. A wide area can be seen with a liquid-liquid biphasic



(a) NaCl 0.5 M.



(b) NaCl 1 M

Figure VI.4: Phase diagram of PEG 6000 / NaCl 1 M solution.

Solubility parameter [$MPa^{1/2}$] at 85°C			
	δ_D	δ_P	δ_H
PEG 2000	19.4±0.4	1.6±0.3	1.2±0.4
PEG 10000	20.5±0.3	2.1±0.3	2.4±0.3
PEG 35000	22.6±0.3	4.8±0.3	3.9±0.3

Solubility parameter [$MPa^{1/2}$] at 95°C			
	δ_D	δ_P	δ_H
PEG 2000	19.0±0.1	1.8±0.1	0.8±0.1
PEG 10000	20.8±0.4	2.9±0.4	2.7±0.4
PEG 35000	23.2±0.3	5.9±0.3	4.8±0.3

Solubility parameter [$MPa^{1/2}$] at 105°C			
	δ_D	δ_P	δ_H
PEG 2000	17.7±0.3	2.9±0.3	0.4±0.2
PEG 10000	22.0±1.4	4.4±1.4	4.0±1.4
PEG 35000	23.5±0.5	6.0±0.5	5.7±0.5

Table VI.2: HSP values of PEGs with different chain lengths, measured by inverse gas chromatography.[114]

	PEG 2000	PEG 10000	PEG 35000
85°C	19.5	20.7	23.4
95°C	19.1	21.2	24.4
105°C	17.9	22.8	24.9

Table VI.3: δ-values calculated from table VI.2.

system, and moderate temperature for transition to the single liquid phase.

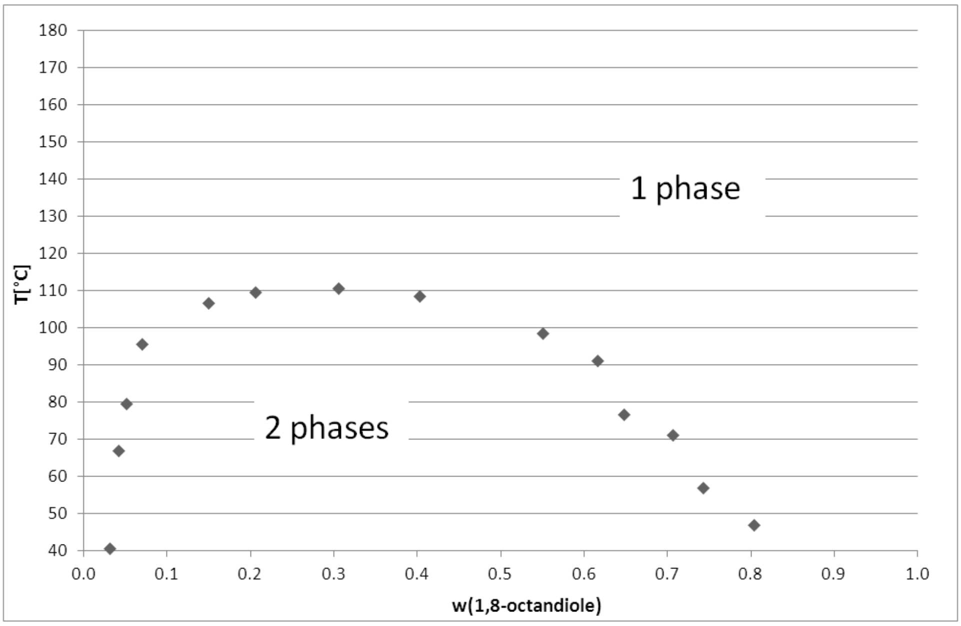


Figure VI.5: Phase diagram of 1,8-octanediol (OD) with water.

Here, addition of NaCl shifts the curve to lower temperatures, which is also explained by the increased ionic concentration in the aqueous phase.

δ_D	δ_P	δ_H	δ
16.7	7.2	19.3	26.5

Table VI.4: HSP values of 1,8-octanediol at 25°C in $MPa^{1/2}$, calculated with the group contribution method of Stefanis and Panayiotou.[109] In literature a value of 22.795 for the total solubility parameter can be found.[115]

The HSP values of 1,8-octanediol shown in table VI.4 are another example of the size dependency of the solubility. While the parameters at room temperature are close to ethanol or glycerol, it is poorly soluble in water. With increasing temperature, however, the Hansen spheres increase due to the bigger influence of the entropy term and octanediol is solubilized by water.

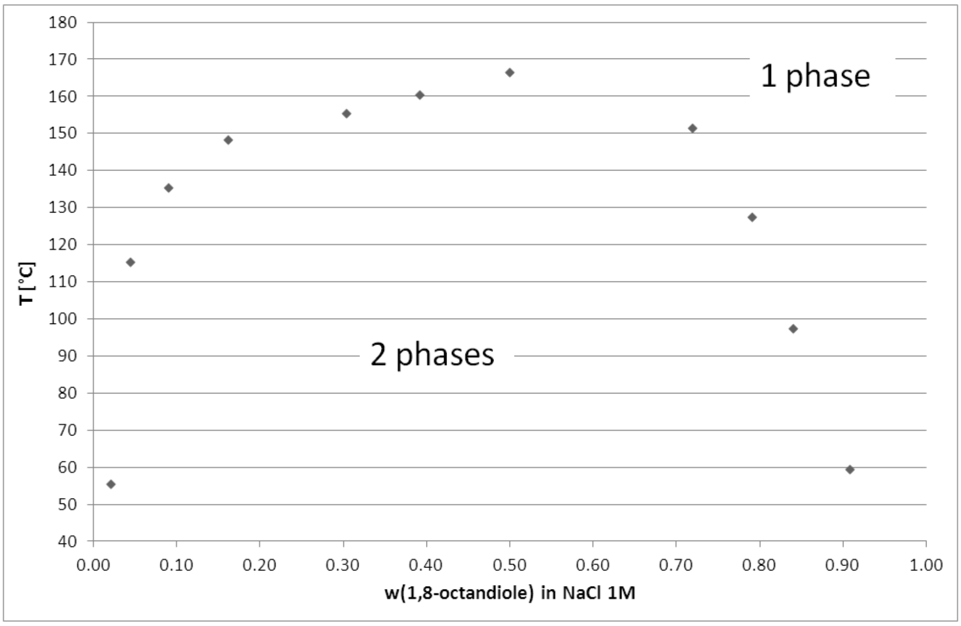


Figure VI.6: Phase diagram of 1,8-octanediol (OD) with 1M NaCl.

An additional system is worth mentioning, namely that of tetrapentyl ammonium bromide and water. The phase diagram shown in figure VI.7 has been determined by Japas et al.[116] Unfortunately, classical ionic liquids decompose rapidly in hydrothermal water.[117] For lower temperatures, however, it could pose an interesting alternative to 1,8-octanediol.

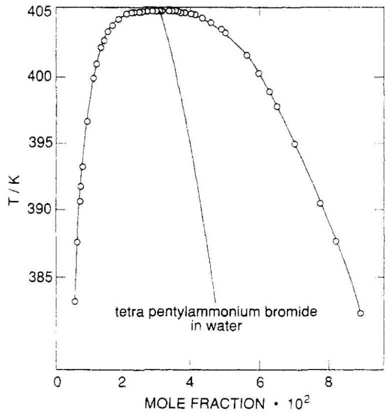


Figure VI.7: Phase diagram of tetrapentyl ammonium bromide.[116] Reprinted with permission from the Journal of Physical Chemistry. Copyright 1990 American Chemical Society.

3 Reactions in Temperature-Switchable Phase Systems

The impact on reaction yields has been examined with three different starting materials: Phenylpropanol, pinacol, and methylcyclohexanol. The solvent consisted of 10w% mixtures of water and either 1,8-octandiole (OD) or PEG 6000. Different equipment was employed for the reactions, with unexpected consequences.

3.1 1-phenyl-1-propanol

	δ_D	δ_P	δ_H	δ
phenylpropanol	18.4	5.4	11.5	22.4
phenylpropene	18.0	3.7	5.3	19.2

Table VI.5: HSP values at 25°C, calculated with the group contribution method of Stefanis and Panayiotou.[109]

HSP values of table VI.5 show that phenylpropanol at room temperature is

	water	10% OD	10% PEG
oven	73.9 (6.8)	67.5 (6.6)	57.4 (5.1)
POHD	43.1 (4.5)	14.7 (2.1)	56.9 (5.1)
MW	28.2 (2.6)	22.3 (2.2)	40.8 (3.9)

Table VI.6: *trans*-phenylpropene yield of HTW reactions at 180°C. Figures in brackets stand for *cis*-phenylpropene yield.

	water	10% OD	10% PEG
oven	10.9	10.2	11.3
POHD	9.6	7.0	11.2
MW	10.8	10.1	10.5

Table VI.7: Ratio of *trans*-phenylpropene to *cis*-phenylpropene yield in HTW from table VI.6.

comparable to octanol or toluene and therefore insoluble in water (which is indeed the case). In consequence, the combination of phenylpropanol and octanediol showed no crystallization after cooling down back to room temperature but a combined phase of octanediol and phenylpropanol/phenylpropene.

The octanediol addition always decreased phenylpropene yield, in contrast to the desired effect of an increased solubility of a single mix phase. PEG had a positive effect when combined with glass vials, but decreased the yield of the Teflon-walled reactions even more than the octanediol. The ratio stayed fairly constant.

3.2 1-methyl-1-cyclohexanol

For HSP calculation of methylcyclohexanol and its reaction products some parameters for group contribution calculation were presently not available.[109]

Microwave reaction results stayed rather constant. Since they were already at the equilibrium concentration, further increase could not be expected when

	water	10% OD	10% PEG
oven	55.1 (1.9)	45.8 (1.9)	51.7 (9.1)
POHD	38.7 (37.1)	55.9 (23.3)	77.3 (6.4)
MW	94.0 (2.8)	93.0 (1.9)	89.7 (7.0)

Table VI.8: 1-Methyl-1-cyclohexene yield of HTW reactions at 180°C. Figures in brackets stand for methylenecyclohexane yield.

	water	10% OD	10% PEG
oven	29.0	24.1	5.7
POHD	1.0	2.4	12.1
MW	33.6	48.9	12.8

Table VI.9: Ratio of 1-methylcyclohexene to methylenecyclohexane yield in HTW reactions of table VI.8.

adding a new phase.

Oven results showed no huge differences of methylcyclohexene yield, but an increase in methylenecyclohexane amount when adding the PEG. This could be a hint at a protection of the thermodynamically more unstable Hoffmann product by the liquid biphasic system.

The highest yield of Hoffmann isomer, however, showed reactions in the POHD without PEG. One difference to these two systems could be catalysis of iron traces from the caps. Another possibility consists in a combination of wall effects and heating method.

3.3 Pinacol

Unfortunately, HSP values of pinacol and its reaction products could not be calculated with the available group contribution parameters either.[109]

The rearrangement reaction of pinacol worked best in the autoclave with water or octanediol. Addition of PEG to the aqueous phase did not have a

	water	10% OD	10% PEG
oven	98.2 (0.6 / 0.3 / 0.1)	91.0 (0.8 / 1.7 / 3.0)	64.5 (0.8 / 2.1 / 0.2)
POHD	57.2 (1.2 / 2.9 / 28.3)	55.2 (1.3 / 4.1 / 13.8)	82.3 (1.2 / 1.8 / 0.1)
MW	7.0 (1.5 / 0.1 / 2.6)	89.0 (0.5 / 1.7 / 1.1)	89.4 (0.2 / 4.9 / 0.4)

Table VI.10: Pinacol conversion in HTW at 180°C. The first figure corresponds to the molar ratio of pinacolon, while the figures in brackets correspond to 2,3-dimethylbuten-3-ol, dimethylbutadien, and the Diels-Alder product, respectively.

	water	10% OD	10% PEG
oven	98.2	16.5	20.8
POHD	1.8	2.9	26.5
MW	1.7	27.0	16.2

Table VI.11: Ratio of pinacol rearrangement product to dehydration products in HTW reactions of table VI.10. The Diels-Alder product was multiplied by two before adding to the total number of dehydration products.

protection effect, nor was it necessary to improve solubility of the starting material since pinacol is already completely soluble in hot water. On the other hand, the total amount of water available for autoprotolysis was decreased by the PEG addition.

In the microwave oven, addition of any phase also increased the rearrangement yield greatly. In pure water, only the Diels Alder product showed a substantial yield.

The highest amount of Diels Alder product, however, was found in the POHD. Occurring reactions there are primarily dehydratation reactions. Particularly the Diels-Alder cyclization was promoted by the combination of POHD and water (and, to a lesser extent, water and octanediol).

3.4 Overall Trend

In all experiments, the glass walls seemed to have a substantial influence on the reaction kinetics. Therefore, a test was done with 0.5 g of silica gel 60 added to the standard reaction conditions of phenylpropanol in the autoclave (180°C, 16 hours, 10mL water). And indeed, the yield of *trans*-phenylpropene was almost cut by half to 40% molar ratio, compared to 74% without the silica.
This leads us to the conclusion that the glass walls of the reaction vials indeed play a part in HTW reactions. Dissolution of the silica makes the solution more basic. This effect is then increased by HTW conditions, comparable to that of basic salts such as Na_2SO_4. Reactions that favour basic conditions have an increased yield, while reactions that prefer acidic conditions are inhibited.

Furthermore, the added PEG is known to have a high affinity to glass. Indeed, it is often used as coating of SiO_2 surfaces.[118,119] Within the frame of this experiment, it assumedly coats the glass walls and decreases both positive and negative effects of the silica. 1,8-octanediol does not have quite that affinity, but acts protectively between the HTW and the glass wall as well.

Reactions that were catalyzed by alkaline salts worked best in the POHD with water. That implies that the conventional heating method dissolves glass even better than microwaves. Counting in that microwaves heat inside the solution instead of through wall heating, this seems only logical.

Also the results from table V.2 are viewed in a new light: While at 180°C the amount of phenylpropene from the oven is higher than that from the microwave experiment, at 160°C the microwave gives a better yield than the oven. Apparently in this case the critical threshold of silica dissolution is located in between these two temperatures. In consequence, at 160°C the positive effect of a microwave heating profile is finally visible.

4 Summary

Examples for solvent mixtures with novel temperature-switchable phase behavior have been presented.
1,8-octanediol and tetrapentyl ammonium bromide build two phases at room temperature and become completely soluble in water at temperature above 100°C. Polyethylene glycol polymers of average molecular mass, on the other hand, separate into two aqueous phases at higher temperatures.
A method to find solvent mixtures with similar possibilities could consist of determination the Hansen Solubility Parameters, which still need more research concerning temperature dependence and improvement of current group contribution methods.

Reaction yields with 10% mixtures of both water/PEG and water/octanediol showed some interesting results. Both increased the production of thermodynamically unfavoured products.

This was overshadowed by another, more substantial effect. While the possible catalysis of HTW reactions by iron ions from steel vessels is already widely known,[35] the influence of the glass walls is not part of the discussion in literature yet. Microsolvation of the silica generates a clearly basic medium which is increased by HTW conditions. Addition of alcohols and PEG polymers were able to decrease this effect by coating the glass walls during the reaction.

VII

CONCLUSION AND OUTLOOK

Hydrothermal reactions play an important role in future chemistry, not only for the abundance of the ever present water. Also the need to replace volatile and environmentally hazardous organic solvents, and to reduce dependence on fossil resources is imperative.

The aim of this work was to investigate the reactions involved in hydrothermal carbonization and related reactions. The research interests include the factors influencing these reactions in reaction kinetics as well as selectivity, and to apply these findings to the synthesis of fine chemicals from biomass derivatives. The results aid in expanding knowledge of current processes as well as developing new strategies in fine-tuning HTW reactions.
Temperatures have been selected in the middle between the critical point and ambient temperatures, to combine the advantages of increased solubility and autoprotolysis with moderate demands to the experimental setup.

Activated alcohols dehydrate easily under these conditions, also Friedel-Crafts reactions, aldol condensations, Michael additions, and rearrangement reactions occurred. Salt addition does not only influence the total ionic strength of the solution (and therefore reaction rates), they influence also the pH *in situ* according to their nature. Hofmeister series, on the other hand, do not play any detectable role in this.

The area profiting most from a well developed HTW technique is, without doubt, biomass conversion. It is abundant, available, renewable, and has some water already incorporated. HTW processes save manufacturers from spending a high energy input for drying biomass. Sea water is a natural source of salt solution ready to be applied in HTW reactions. The whole scheme is non-toxic and environmentally benign.

Microwave radiation can be an interesting alternative to conventional heating due to its easy handling and superior heating capabilities. However, the influence of the standard glass vials must not be neglected in this context.

Reactor materials are a huge issue in HTW reactions. Teflon seems to be the only material currently available that does not react with HTW, but it has other disadvantages like incorporation of reactor contents and increasing softness at higher temperatures. The classical stainless steel contaminates the solution with iron that may catalyze reactions. SiO_2, on the other hand, dissolves from glass walls and creates an alkaline milieu in the vial. At moderate temperatures these processes do not damage reaction vessels substantially, but their effect has to be taken into account when evaluating hydrothermal reactions.

Certainly, a lot of things have yet to be researched and confirmed. On the top place is development of new, resistant materials for HTW reactions. A possible alternative proposed only recently is **glass-like carbon**, also called **glassy carbon**. This material is highly resistant against corrosion, high temperature and pressure, and exhibits a lot more interesting properties.[120,121]

Another consequence of the influence of reactor material consists in a reevaluation of existing processes and published results. For example, reactions that work well in a glass tube do not necessarily have a high yield in other vessels as well. But with the simple addition of a basic salt, the initial yield could be restored.

The next step consists in further research concerning the fine-tuning of HTW conditions. Not only the amount and nature of salts have to be optimized, but also concepts like temperature-switchable phase systems and scavenger reactions have to be brought to a new level.

The third and perhaps most important part is the application of these ideas to biomass exploitation. One fundamental example that is still in need of improvement is the handling of lignin, both as waste material from paper industry and integrated is lignocellulosic biomass such as waste straw. Recovery of aromatic monomers is still not a profitable process, but in future times it could be the main source of aromatics for mankind. As seen in this work, to prevent the freshly cleaved monomers from repolymerization is the key to higher yields. A biphasic system where the monomers accumulate and build inert complexes (or even react with a scavenger molecule), could be a new way to explore. Microwave could aid this path with generating heat directly in the aqueous phase, while the organic phase with lower dipole moment is being cooled externally by pressurized air.

Also glycerol, which is currently produced as waste from biodiesel generation, is a viable field of interest for HTW evaluation. Biodiesel technique leaves the glycerol in low concentration in an aqueous solution. If it can be brought to react hydrothermally into less water soluble products, the expensive cleaning step can be saved. Employing biphasic systems or the scavenger tactics may put a solution to this problem as well. For an example, boric acid could work this way similar to protecting the diol groups in guaiacol, as shown in chapter IV.

We all need to be prepared to part with this opulent use of fossil resources, for environmental reasons as well as for the finite nature of these materials. Hydrothermal reactions have to be explored, improved and applied to fulfill the needs for energy, environmentalism, and consumption of fine chemicals and materials.

Appendix A

Experimental Details

1 Chemicals

chemical	company	purity
1-heptanol	Alfa Aesar	99%
(-)-carveol	Alfa Aesar	97%, mixture of isomers
(-)-isopulegol	Fluka	p.a.
1,2,3,4-tetrahydro-1-naphthol	Acros	97%
1,8-octandiole	Sigma Aldrich	>98%
1-heptene	Alfa Aesar	98+%
1-methylcyclohexanol	Sigma Aldrich	96%
1-phenyl-1,2-ethanediol	Merck	p.a.
1-phenyl-1-propanol	Acros	99%
1-phenylpropene	Sigma Aldrich	>99%
2-heptanol	Acros	99+%
3-phenyl-1-propanol	Sigma Aldrich	98%

acetophenone	Fluka	>98%
$Al(OH)_3$	Merck	p.a.
a-terpineol	Acros	99%
$BaCl_2 \cdot 2\,H_2O$	Merck	p.a.
benzaldehyde	Merck	>99%
benzylidenacetophenone	Merck	>98%
$CaCl_2 \cdot 6\,H_2O$	Merck	p.a.
CsCl	Alfa Aesar	99%
diethyl ether	AnalR Normapur	p.a.
DL-menthol	Alfa Aesar	98+%
exo-norborneol	Sigma Aldrich	98%
H_3BO_3	Merck	p.a.
KCl	Merck	p.a.
LiCl	Merck	p.a.
lignin, alkali, low sulfonate content	Sigma Aldrich	—
$MgCl_2 \cdot 6\,H_2O$	Merck	p.a.
Na_2CO_3	Merck	p.a.
$Na_2HPO_4 \cdot 2\,H_2O$	Merck	p.a.
Na_2SO_4	Acros	99%
NaBr	Merck	p.a.
NaCl	AnalR Normapur	p.a.
$NaClO_4$	Merck	p.a.
NaF	Merck	p.a.
NaI	Merck	p.a.
$NaNO_3$	Merck	p.a.
pinacol	Alfa Aesar	99%
polyethylene glycol 6,000	Alfa Aesar	—

sodium acetate	Merck	p.a.
sodium tetrafluoroborate	Alfa Aesar	97%
sodium thiocyanate	Sigma Aldrich	98-102%
sodium trifluoroacetate	Alfa Aesar	98%
$SrCl_2 \cdot 6\,H_2O$	Merck	p.a.
tetramethyl ammonium chloride	Sigma Aldrich	97%
toluene	Riedel-de Häen	p.a.

2 Autoclave Experiments

Figure A.1: Steel Autoclaves with Teflon Inlet.

The starting material and 10 mL aqueous solution were placed into stainless steel autoclaves with PTFE inlets and an inner volume of 21 mL (see picture A.1) and closed tightly. The pressure during the reaction consisted only of the autogeneous pressure of the solution at reaction temperature. After sixteen hours standard reaction time the autoclaves cooled down to room temperature, and submitted to further treatment.

It has to be mentioned that the Teflon material adsorbed a fraction of the contained substances - therefore the autoclaves were treated with hot water for cleaning after each usage. Also, in general the result is an average value from two or more experiments with the same quantities.

3 Microwave Experiments

(a) CEM Discover S-class synthesis microwave

(b) Microwave glass vials with InteliVent Cap

For the microwave experiments the model Discover S-class from the company CEM GmbH was used. The substance was put into a 10 mL glass vial together with 5 mL aqueous solution, and heated according to the information in the text. With the phenylpropanol batches the GC sample directly taken from the hydrophobic phase on top. 25 μL of that liquid was mixed with 1mL diethyl ether and 107μL (=1mmol) toluene. Calibration was done in a similar way, mixing 3mmol phenylpropanol and 2mmol phenylpropen with 5mL aqueous solution, then taking 25 μL off the top phase (compare with section 4).

The standard frame conditions during the microwave radiation were upper limits of 20 bar pressure and 150 Watt power, temperature and time depended on the individual experiments. The time for reaching the initial reaction temperature was usually around 100 seconds, while the cooling down process was aided by pressurized air and lasted only minutes.

4 GC Analysis of the Samples

Figure A.2: Gas chromatograph Hewlett Packard 6890 GC Series

The reaction mixture was extracted three times with 5 mL diethyl ether each time. The extracts were analyzed with gas chromatography GC, usually connected with a Flame Ionization Detector FID or a mass spectrometer MS. The mass spectra were used to identify the products using the NIST database. After assigning the corresponding retention times, FID analysis was needed to quantify the substances. Toluene was used as an internal standard (to minimize errors during the injection process, e.g. bubbles).

The column was packed with a polar phase (Supelco 36615-06B Supelcowax 10, Capillary 30m x 320μm x 0.25μ), and the heating program was adapted to suit the individual component mixtures for each reaction.

Quantification via FID can be made in two different ways:

For 1-phenyl-1-propanol and the lignin products the FID response factor was determined by reference standards, subjected to the same extraction procedure and then evaluated with GC-FID. As the area is directly proportional to the amount of substance, it is calculated via

$$n_x = \frac{A_x}{A_T} \times n_T \times F \tag{A.1}$$

with A_T being the area of toluene, n_T the amount of toluene, and F the response factor of the substance (calculated from the chromatograph of known quantities).

As most of the possible products were not available, FID peak areas during the alcohol screening were evaluated using the response factor prediction model from Jorgensen,[122] refined by Kállai.[123]

The mechanism of ion formation in the flame was discussed in a review by Holm.[124] With simple hydrocarbons, chemi-ionization of CHO radicals are the main source for ion formation.

$$\begin{aligned} \mathrm{C_nH_m} &\longrightarrow n\,\mathrm{CH}\bullet + (m-n)\,\mathrm{H}\bullet \\ n\,\mathrm{CH}\bullet + n\,\mathrm{O}\bullet &\longrightarrow n\,\mathrm{CHO}\bullet \\ n\,\mathrm{CHO}\bullet &\longrightarrow n\,\mathrm{CHO}^+ + n\,\mathrm{e}^- \end{aligned} \tag{A.2}$$

The signal of the detector is directly proportional to the number of ions. Assuming the above-mentioned mechanism and complete conversion, the signal of a simple hydrocarbon is directly proportional to its carbon number. In literature this is expressed by definition of the effective carbon-atom number ECN. The presence of heteroatoms, however, alter this response in characteristic ways. Kállai et al.[123] provided a wide database to average these incremental shifts of the ECN caused by different functional groups.

In comparison with the internal standard (mostly toluene) this results in a

	Δ ECN
alkanes	-0.02
aromatic	-0.54
alcoholes	-0.72
ketones	-0.99
phenols	-0.83

Table A.2: Heteroatomic Shifts of the Effective Carbon-Atom Number used in this work.

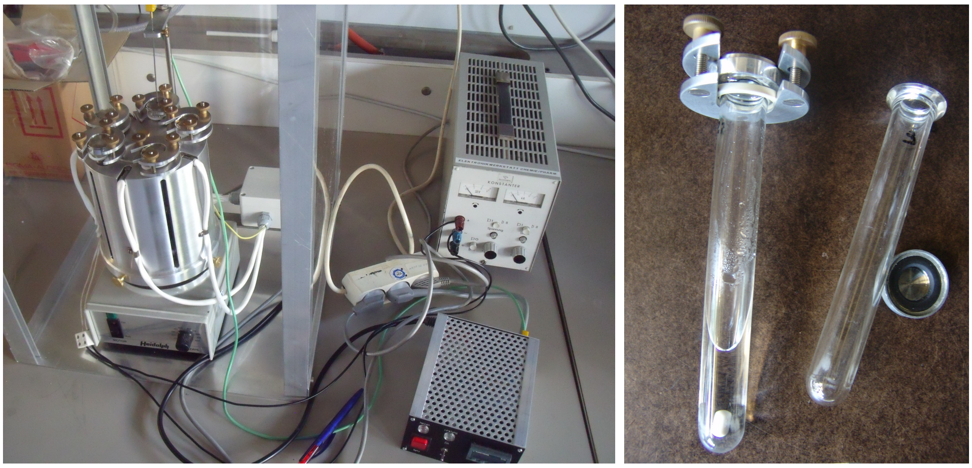
response factor of

$$F = \frac{ECN_T}{ECN_x}. \tag{A.3}$$

5 Phase Diagrams

Phase diagrams were created using a custom-made heating device. It consists of a electrical heating core mounted on a simple magnetic stirrer. Small windows permit view of the phase separations (see picture A.3a).
The samples are mounted inside in pressure-stable glass vials, closed with steel caps equipped with VITON O-rings.

Accuracy of the temperature readings was about 1°C around the actual value. Also, the steel caps were slightly cooler than the vials, creating a little reflux circulation inside. Within the parameters of the experiments of this work this was considered to be acceptable, but should be considered for other applications.



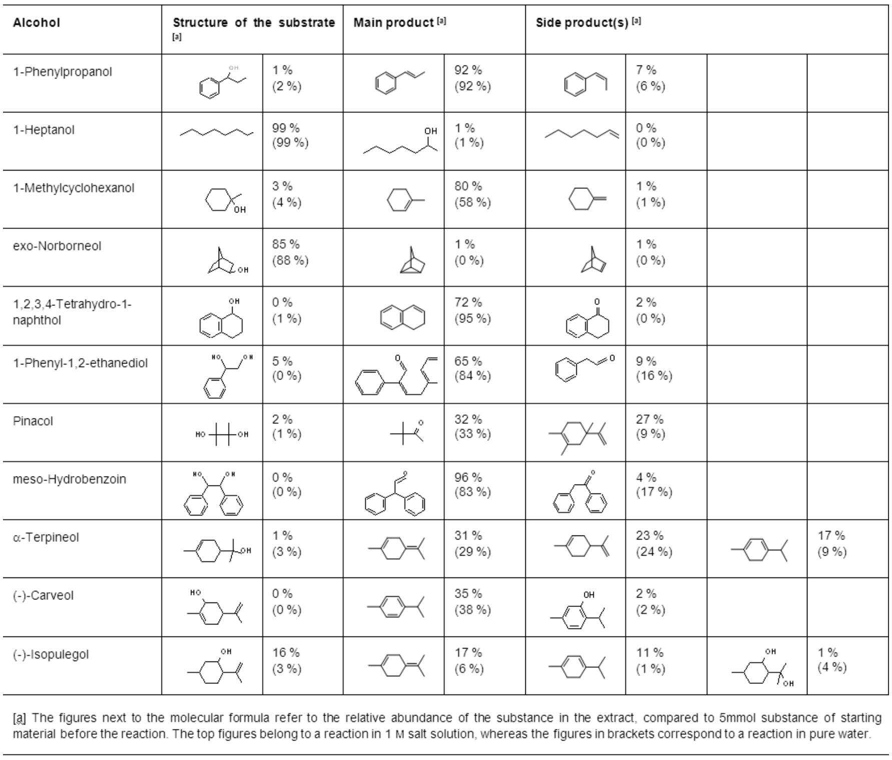
(a) Complete experimental setup **(b)** glass vial

Figure A.3: Equipment for the creation of phase diagrams under autogenous pressure, short: **p**hase **o**bservation **h**eating **d**evice or POHD.

Appendix B

Supplementary Information

1 Alcohol Variation



Alcohol	Structure of the substrate [a]		Main product [a]		Side product(s) [a]			
1-Phenylpropanol		1 % (2 %)		92 % (92 %)		7 % (6 %)		
1-Heptanol		99 % (99 %)		1 % (1 %)		0 % (0 %)		
1-Methylcyclohexanol		3 % (4 %)		80 % (58 %)		1 % (1 %)		
exo-Norborneol		85 % (88 %)		1 % (0 %)		1 % (0 %)		
1,2,3,4-Tetrahydro-1-naphthol		0 % (1 %)		72 % (95 %)		2 % (0 %)		
1-Phenyl-1,2-ethanediol		5 % (0 %)		65 % (84 %)		9 % (16 %)		
Pinacol		2 % (1 %)		32 % (33 %)		27 % (9 %)		
meso-Hydrobenzoin		0 % (0 %)		96 % (83 %)		4 % (17 %)		
α-Terpineol		1 % (3 %)		31 % (29 %)		23 % (24 %)		17 % (9 %)
(-)-Carveol		0 % (0 %)		35 % (38 %)		2 % (2 %)		
(-)-Isopulegol		16 % (3 %)		17 % (6 %)		11 % (1 %)		1 % (4 %)

[a] The figures next to the molecular formula refer to the relative abundance of the substance in the extract, compared to 5mmol substance of starting material before the reaction. The top figures belong to a reaction in 1 M salt solution, whereas the figures in brackets correspond to a reaction in pure water.

Figure B.1: Complete table of alcohol variation experiments from chapter III. Reactions were conducted at 200°C in 1M NaCl solution, compared to pure HTW.

2 Aldol Condensation

Mass spectra from the products of the HTW reaction of benzaldehyde with acetophenone.

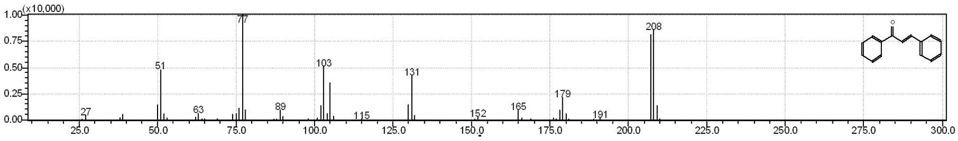


Figure B.2: Mass spectrum BAP

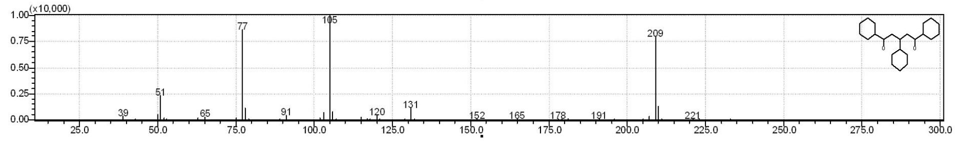


Figure B.3: Mass spectrum Michael product

3 Microwave

Heating profiles of HTW microwave reactions. Figure B.4 is an exemplary curve from the standard heating method, while the other were test with decreasing power rates. The corresponding phenylpropene yields are shown in table B.1.

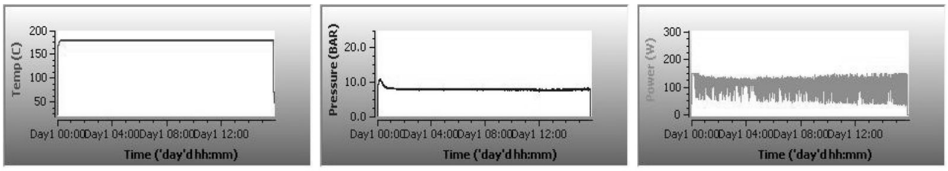


Figure B.4: Parameter changes of microwave adjustments 150 W (standard method): Maximum temperature 181°C, maximum pressure 11 bar.

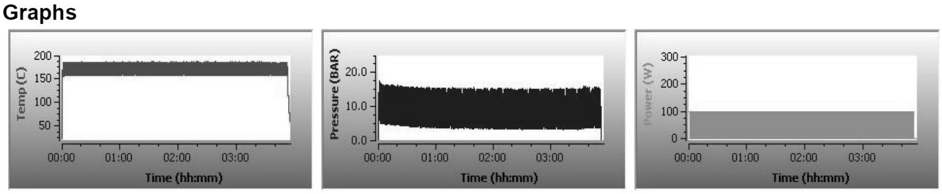


Figure B.5: Parameter changes of microwave adjustments 100 W: Maximum temperature 188°C, maximum pressure 18 bar.

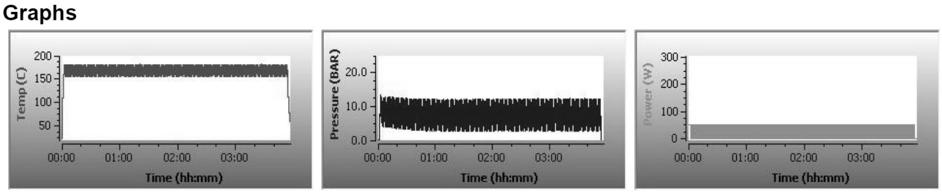


Figure B.6: Parameter changes of microwave adjustments 50 W: Maximum temperature 182°C, maximum pressure 14 bar.

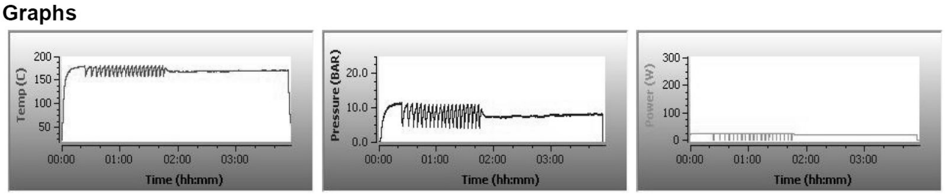


Figure B.7: Parameter changes of microwave adjustments 25 W: Maximum temperature 180°C, maximum pressure 12 bar.

	x(cis-phenylpropene)	*x(trans-phenylpropene)*	*x(phenylpropanol)*
power 0	5.7	62.7	31.6
power 1	4.1	45.2	50.7
power 2	2.8	30.7	66.5
power 3	4.0	47.8	48.2

Table B.1: Molar ratios of a HTW reaction of phenylpropanol in the microwave at a reaction time of four hours and different power input.

4 Group Contribution Tables

Tables specified in reference[109] for calculation of the Hansen Solubility Parameters.

First-order groups	δ_D	δ_P	δ_H	Examples (occurrences)
$-CH_3$	-123.01	-1.6444	-0.7458	Propane (2)
$-CH_2-$	1.82	-0.3141	-0.3877	Butane (2)
$-CH<$	82.94	0.6051	-0.2064	Isobutane (1)
$>C<$	182.13	2.0249	-0.0113	Neopentane (1)
$CH_2=CH-$	-126.15	-2.017	-1.1783	Propylene (1)
$-CH=CH-$	28.65	-0.5037	-0.1253	cis-2-Butene (1)
$CH_2=C<$	-31.62	-0.9052	-0.7191	Isobutene (1)
$-CH=C<$	62.48	-1.1018	-1.7171	2-Methyl-2-butene (1)
$>C=C<$	50.1	0.9957	-1.9773	2,3-Dimethyl-2-butene (1)
$CH_2=C=CH-$	-161.71	***	-0.7545	1,2-Butadiene (1)
$CH=C-$	45.86	-1.5147	1.2582	Propyne (1)
$C=C$	9.56	-0.9552	-1.0176	2-Butyne (1)
ACH	29.87	-0.5771	-0.3554	Benzene (6)
AC	98.84	0.7661	-0.1553	Naphthalene (2)
$ACCH_3$	27.67	-0.6212	-1.1409	Toluene (1)
$ACCH_2-$	89.07	0.8019	-0.2298	m-Ethyltoluene (1)
CH_3CO	-29.41	2.1567	-1.1683	Methyl ethyl ketone (1)
CH_2CO	114.74	3.6103	-0.3929	Cyclopentanone (1)
CHO (aldehydes)	-31.35	3.3159	0.2062	1-Butanal (1)
COOH	-38.16	0.7153	3.8422	Vinyl acid (1)
CH_3COO	-53.86	-0.6075	1.7051	Ethyl acetate (1)
CH_2COO	89.11	3.4942	1.3893	Methyl propionate (1)
HCOO	***	1.7056	2.3049	n-Propyl formate (1)
COO	27.57	3.3401	1.1999	Ethyl acrylate (1)
OH	-29.97	1.0587	7.3609	Isopropanol (1)
ACOH	58.52	1.052	6.9757	Phenol (1)

First-order groups	δ_D	δ_P	δ_H	Examples (occurrences)
CH_3O	-68.07	0.0089	0.2676	Methyl ethyl ether (1)
CH_2O	13.4	0.8132	-0.1196	Ethyl vinyl ether (1)
CHO (ethers)	111.46	1.6001	0.4873	Diisopropyl ether (1)
$C_2H_5O_2$	15.51	3.388	8.5893	2-Methoxy-ethanol (1)
CH_2O (cyclic)	49.32	0.1227	0.1763	1,4-Dioxane (2)
CH_2NH_2	-49.96	-0.3449	2.728	1-Amino-2-propanol (1)
$CHNH_2$	18.53	-1.4337	0.5647	Isopropylamine (1)
CH_3NH	***	0.506	5.7321	n-Methylaniline (1)
CH_2NH	96.18	0.2616	1.4053	di-n-Propylamine (1)
CH_3N	170.59	1.0575	1.85	Trimethylamine (1)
CH_2N	152.54	2.6766	1.5557	Triethylamine (1)
$ACNH_2$	253.66	1.6493	4.4945	Aniline (1)
$CONH_2$	-1.22	5.9361	5.3646	2-Methacrylamide (1)
$CON(CH_3)_2$	95.97	5.5309	3.2455	N,N-dimethylacetamide (1)
CH_2SH	214.84	-0.994	4.5321	N-butyl mercaptan (1)
CH_3S	***	0.2451	-1.2669	Methyl ethyl sulfide (1)
CH_2S	168.57	0.573	-0.0838	Diethyl sulfide (1)
I	197.67	0.106	0.3321	Isopropyl iodide (1)
Br	109.79	0.5207	-0.9087	2-Bromopropane (1)
CH_2Cl	47.17	0.5013	-0.4498	n-Butyl chloride (1)
CHCl	73.01	2.6796	-1.3563	Isopropyl chloride (1)
CCl	385.39	1.8196	0.1473	t-Butyl chloride (1)
$CHCl_2$	197.67	1.6255	-3.0669	1,1-Dichloropropane (1)
CCl_2	72.6	0.1035	-1.322	Pentachlorocyclopropane (2)
CCl_3	***	1.106	-2.5679	Benzotrichloride (1)
ACCl	141.54	-0.0941	-0.7512	m-Dichlorobenzene (2)
ACF	27.74	0.1293	-0.6613	Fluorobenzene (1)
Cl-(C=C)	45.32	2.2673	-0.5258	2,3-Dichloropropene (1)
CF_3	-13.79	-2.1381	-1.2997	Perfluorohexane (2)

First-order groups	δ_D	δ_P	δ_H	Examples (occurrences)
CH_2NO_2	***	6.6451	-1.0669	1-Nitropropane (1)
$CHNO_2$	***	7.7753	-2.1087	2-Nitropropane (1)
$ACNO_2$	219.22	4.464	-0.7302	Nitrobenzene (1)
CH_2CN	-29.09	6.3586	-0.7297	n-Butyronitrile (1)
CF_2	-103.83	***	***	Perfluoromethylcyclohexane (5)
CF	20.32	***	***	Perfluoromethylcyclohexane (1)
F (except as above)	-80.11	***	***	2-Fluoropropane (1)
$CH_2{=}C{=}C<$	6.64	***	-1.7087	3-Methyl-1,2-butadiene (1)
O (except as above)	18.09	3.5248	0.0883	Divinyl ether (1)
Cl (except as above)	76.35	1.7491	-0.2917	Hexachlorocyclopentadiene (2)
>C=N-	-10.55	-0.1692	-5.382	2,4,6-Trimethylpyridine (1)
-CH=N-	186.4	2.7015	0.5507	Isoquinoline (1)
NH (except as above)	***	-0.0746	2.0646	Dibenzopyrrole (1)
CN (except as above)	49.36	6.3705	-0.5239	cis-Crotonitrile (1)
O=C=N-	15.22	1.4695	4.1129	n-Butyl isocyanate (1)
SH (except as above)	190.87	1.8229	4.9279	2-Mercaptobenzothiazole (1)
S (except as above)	201.91	8.5982	-0.4013	Thiophene (1)
SO_2	182.83	11.0254	-0.3602	Sulfolene (1)
>C=S	-0.46	0.5216	3.0519	n-Methylthiopyrrolidone (1)
>C=0 (except as above)	-127.16	0.7691	1.7033	Anthraquinone (2)
N (except as above)	267.06	2.2212	1.3655	Triphenylamine (1)

Table B.2: First-order group contributions to the dispersion partial solubility parameter, δ_D, the polar partial solubility parameter, δ_P, and the hydrogen-bonding partial solubility parameter, δ_H.

Second-order groups	δ_D	δ_P	δ_H	Examples (occurrences)
$(CH_3)_2$-CH-	7.63	0.0365	0.3019	Isobutane (1)
$(CH_3)_3$-C-	-0.03	1.1593	-0.1924	Neopentane (1)
Ring of 5 carbons	-81.93	-2.3673	0.2586	Cyclopentane (1)
Ring of 6 carbons	-26.15	-3.6661	***	Cyclohexane (1)
-C=C-C=C-	-5.69	-3.31	-1.2207	1,3-Butadiene (1)
CH_3-C=	-4.45	0.3461	0.4418	Isobutene (2)
-CH_2-C=	-29.67	-2.3189	-0.5613	1-Butene (1)
>CH or C-C=	-5.38	***	-1.0241	3-Methyl-1-butene (1)
String in cyclic	-54.05	***	***	Ethylcyclohexane (1)
$CH_3(CO)CH_2$-	3.57	-0.4108	-0.3628	Methyl ethyl ketone (1)
C_{cyclic}=O	-46.57	0.1972	-0.4496	Cyclopentanone (1)
ACCOOH	-37.57	-0.6284	-0.8552	Benzoic acid (1)
>CH or C-COOH	***	-0.245	1.2554	Isobutyric acid (1)
CH_3(CO)OCH or C<	-40.56	-0.0652	0.3864	Isopropyl acetate (1)
(CO)CH_2COO	***	-2.3624	0.8545	Ethyl acetoacetate (1)
(CO)O(CO)	-92.46	-0.9818	1.5759	Acetic anhydride (1)
ACHO	46.84	-1.812	-0.9192	Benzaldehyde (1)
>CHOH	16.54	0.2366	-0.2453	2-Propanol (1)
$>C < OH$	-5.97	-0.0069	1.3813	Tert-Butanol (1)
-C(OH)C(OH)-	***	0.6669	0.2493	1,2-Propanediol (1)
-C(OH)C(N)	-7.03	0.875	-0.7322	1-Amino-2-propanol (1)
C_{cyclic}-OH	-6.4	-3.6065	0.5836	Cyclohexanol (1)
C-O-C=C	25.23	0.548	1.1279	Ethyl vinyl ether (1)
AC-O-C	35.82	0.7781	0.6689	Methyl phenyl ether (1)
>NH or C(in cyclic)	53.29	-1.6876	-0.0132	Cyclopentimine (1)
-S-(in cyclic)	91.57	0.2513	0.2663	Tetrahydrothiophene (1)
ACBr	33.35	-0.4478	0.3149	Bromobenzene (1)
(C=C)-Br	-85.85	0.0686	-1.1154	2-Bromopropene (1)
Ring of 3 carbons	15.35	1.7962	-0.7224	Cyclopropane (1)

Second-order groups	δ_D	δ_P	δ_H	Examples (occurrences)
ACCOO	-38.39	0.367	-0.234	Methyl benzoate (1)
$AC(ACH_m)_2AC(ACH_n)_2$	-33.14	-1.4784	0.7468	Naphthalene (1)
O_{cyclic}-C_{cyclic}=O	13.89	2.7261	0.2185	Diketene (1)
AC-O-AC	-136.1	-3.4995	1.8763	Diphenyl ether (1)
$C_{\mathrm{cyclic}}H_{\mathrm{m}}=N_{\mathrm{cyclic}}-C_{\mathrm{cyclic}}H_{\mathrm{n}}=C_{\mathrm{cyclic}}H_{\mathrm{p}}$	53.11	-0.5075	-2.1004	2,6-Dimethylpyridine (1)
N_{cyclic}Hm-C_{cyclic}=O	93.54	2.0813	1.2226	2-Pyrrolidone (1)
-O-CH_m-O-CH_n-	31.52	0.3293	0.2527	Methylal (1)
C(=O)-C-C(=O)	-61.38	-0.4126	1.224	2,4-Pentanedione (1)

Table B.3: Second-order group contributions to the dispersion partial solubility parameter, δ_D, the polar partial solubility parameter, δ_P, and the hydrogen-bonding partial solubility parameter, δ_H.

First-order groups	$\delta_P < 3$ MPa$^{(1/2)}$	$\delta_H < 3$ MPa$^{(1/2)}$
CH_3-	-0.7107	0.299
-CH_2-	-0.1361	-0.1161
-CH<	0.6477	0.1386
CH_2=CH-	-0.2511	1.3552
-CH=CH-	-0.1503	0.4819
CH_2=C<	0.6956	0.1115
-CH=C<	1.2761	-0.0307
>C=C<	***	-0.1212
CH_2=C=CH-	-0.2453	***
CH=C-	-0.7049	0.4385
C=C	***	-0.3511
ACH	-0.193	0.1353
AC	0.1745	-0.174
$ACCH_3$	-0.4493	-0.2873
$ACCH_2$-	-0.2857	-0.8808
ACCH<	0.9303	-1.4467

First-order groups	$\delta_P < 3$ MPa$^{(1/2)}$	$\delta_H < 3$ MPa$^{(1/2)}$
-COOH	2.9098	
CH_3COO	1.7711	***
CH_2COO	2.2096	***
COO	1.4783	0.372
OH	***	***
CH_3O	-0.36	***
CH_2O	***	***
CHO	***	-0.4067
CH_2O (cyclic)	-0.2919	***
CH_2NH_2	***	***
CH_2NH	0.8875	***
CHNH	1.2391	***
CH_3N	***	-0.17
CH_2N	0.7055	-1.0369
CH_2S	***	0.1461
CH_2Cl	***	0.4895
CHCl	***	0.13
$CHCl_2$	***	0.5254
ACCl	-0.0927	0.4424
CCl_2F	***	***
ACF	***	-0.3718
Cl-(C=C)	***	0.6606
CF_3	***	-0.0887
CH_2=C=C<	1.2654	***
O (except as above)	-0.5555	***
Cl (except as above)	***	1.1251
S (except as above)	0.0445	***
>C=0 (except as above)	***	-0.0553

First-order groups	$\delta_P < 3$ MPa$^{(1/2)}$	$\delta_H < 3$ MPa$^{(1/2)}$

Table B.4: First-order group contributions to the polar partial solubility parameter δ_P and the hydrogen-bonding partial solubility parameter δ_H when $\delta_P < 3$ MPa$^{(1/2)}$ or $\delta_H < 3$ MPa$^{(1/2)}$.

Second-order groups	$\delta_P < 3$ MPa$^{(1/2)}$	$\delta_H < 3$ MPa$^{(1/2)}$
$(CH_3)_2$-CH-	0.2246	0
Ring of 5 carbons	-0.9657	0.1944
Ring of 6 carbons	-0.9615	0
-C=C-C=C-	0.6463	***
CH_3-C=	-0.0063	-0.0614
-CH_2-C=	0.0192	0.066
>CH or C-C=	-0.446	0.3422
AC(ACH$_m$)$_2$AC(ACH$_n$)2	0.0669	***
-O-CH$_m$-O-CH$_n$-	0	***
String in cyclic	***	-0.2809
ACCOO	***	0
AC(ACH$_m$)$_2$AC(ACH$_n$)$_2$	***	0.0864

Table B.5: Second-order group contributions to the polar partial solubility parameter δ_P and the hydrogen-bonding partial solubility parameter δ_H when $\delta_P < 3$ MPa$^{(1/2)}$ or $\delta_H < 3$ MPa$^{(1/2)}$.

5 Phase Tryouts

heptanol	two phases
toluene	two phases
1,8-octandiole	two phases, one phase above 120°C
PEG 6000	one phase, two phases above
PEG 400	one phase
Akypo RSPE66 (alkylether carbonic acid)	one phase
Akypo SOFT 45NV (sodium laureth-6 carboxylate)	one phase
limonene	decomposition
Oleyl-glycerin	decomposition
Silica Gel	corrosion of glass vial
2-MeTHF	corrosion of seals

Table B.6: Complete list of phase tests in HTW.

6 Unwanted HTR in Biogas Generation

Some crude test were conducted to find an additive for a positive influence of HTW carbonization reaction. As model substances for animal biomass gelatine was selected, for plant biomass commercially available cornmeal. Gelatine is a mixture of peptides and proteins extracted from skin, bones, etc. of domestic cattle. 0.5 g of either substance was placed in an autoclave with 10 mL water and additive. After 180°C and 8 hours the residues were filtered and the filter dried at 70°C over night. Table B.7 shows the results.

additive (50mg)	gelatine (G) or cornmeal (C)	visual confirmation of carbonization (Yes/No)	weight of solid residues [g]	pH before	pH of filtrate
none	G	N	0.03	5.05	8.05
	C	Y	0.08	6.33	3.1
NaCl	G	N	0.03	5.23	7.09
	C	Y	0.1	6.02	3
Na_2HPO_4	G	N	0.04	7.5	8.25
	C	Y	0.1	8.2	3.51
methanol	G	N	0.05	4.9	8.02
	C	Y	0.09	6.19	3.1
proline	G	N	0.06	4.9	7.08
	C	Y	0.11	6.19	3.55
$FeCl_3 \cdot 6\,H_2O$	G	N	0.04	3.47	4.24
	C	Y	0.14	2.22	2.2
acetic acid 100%	G	N	0.05	4.01	4.37
	C	Y	0.1	3.23	2.97
urea	G	N	0.05	5.08	9.01
	C	Y	0.1	6.23	7.79
glycerol	G	N	0.06	5.03	7.85
	C	Y	0.12	6.22	3.05
$CaCO_3$	G	N	0.06	6.7	8.66
	C	Y	0.11	7.57	4.41
NaOH	G	N	0.05	12.67	9.56
	C	N	**	12.63	9.78
sodium acetate	G	N	0.05	5.92	8.2
	C	Y	0.09	6.68	3.88
milk powder	G	N*	0.06	5.83	6.47
	C	Y	0.13	6.75	3.21
cornmeal	G	Y	0.14	5.82	3.23

Table B.7: HTW biomass experiments; * dark brown coloring of the liquid; ** dark brown, highly viscous liquid not filtratable

The results show that the cornmeal usually carbonizes under these conditions, except with NaOH addition. The pH of the solution decreases substantially, which is in favour of a conversion of the carbohydrates to carbonic acids (compare e.g.[54] and other reviews). Gelatine, on the other hand, shows no carbonization processes under the experimental conditions. This is ascribed to the partially basic nature of proteins. Further experiments are needed to quantify this observation, but from this first overview it can be concluded the following: Biogas generation could profit from mixing different kinds of biomass rather than employing pure plant material.

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Declaration

I hereby declare that I have composed this work on my own and used only the quoted references and resources. Literally or correspondingly adapted material has been marked accordingly.

Eidesstattliche Erklärung

Ich erkläre hiermit an Eides statt, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus anderen Quellen direkt oder indirekt übernommenen Daten und Konzepte sind unter Angabe des Literaturzitats gekennzeichnet.

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Regensburg, den 22. November 2012