Organic Reactions of Alcohols under Hydrothermal Conditions

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Summary – English version

This thesis aimed to study organic reactions under hydrothermal conditions. Furthermore, the knowledge about the advantages of hydrothermal conditions for aspects of green chemistry should be enlarged.

Hydrothermal conditions use water as solvent and, therefore, they offer the advantage of lower toxicity. For organic molecules also the separation of the products from water after the reaction is a clear benefit as the solubility of organic material in water is much higher at elevated temperatures. The nature has yet proven the utility of these reaction conditions by creating life essential compounds.

According to a literature review, hydrothermal conditions were applied on organic syntheses. Theoretic considerations let hope for the synthesis of aromatic compounds out of diols by combining a trimerization with cyclization, dehydrations and transfer hydrogenations. By contrast, 1-phenyl-1,2-ethanediol dimerized and an intramolecular Friedel-Crafts type reaction followed. Thus, there was a cyclization followed by an aromatization yet before a trimerization. Consequently, 2-phenylnaphthalene was formed. A trimerization was not observed.

Further experiments showed several products for ethylene glycol, but the desired trimerization to benzene was hardly obtained. For 1,2-propanediol the trimerization and the aromatization were one of the major reaction pathways, but two other products were formed in higher amounts. Hence, the trimerization and a following aromatization were possible for diols, but only under certain conditions. Other reactions were preferred.

An application based on 1,2-propanediol which was synthesized from glycerol. Following syntheses obtained molecules which can be used as solvents or potentially as fuel, respectively. Further treatments such as hydrogenation or distillation were promising to optimize the generated value of the reaction mixture. The use as biomass-based energy storage was manifest.

The observed intramolecular Friedel-Crafts type reaction was transferred to intermolecular reactions. The studies of the alkylation of naphthalene or phenol, respectively, by benzyl alcohol displayed several dependences. The temperature had outstanding influence on the reaction, namely on the conversion, but also on the yield. In general, hydrochloric acid increased the yield a lot compared to pure water. Otherwise the

lack of hydrochloric acid had to be compensated by a higher temperature. Especially at temperatures below 200°C a solution of NaCl suppressed the Friedel-Crafts type reaction. Anyhow, the toxicity is much lowered, because the usual chloroalkane is replaced by an alcohol, 0.05mol/L HCl replaces stoichiometric amounts of $AlCl_3$ and an excess of the aromatic compound is no more necessary. Organic acids can replace HCl, but much higher concentrations are required.

The transfer of the intermolecular Friedel-Crafts type reaction to other reaction partners showed limits for feasible combinations of alcohol and aromatic compound. However, benzyl alcohol showed polymerization.

This was successfully combined with a selective reduction of metal ions from a solution. Thus, the separation of some metals out of a mixture of metal ions was possible under hydrothermal conditions. This gives access to a better recovery of platinum group metals. A similar separation method using biomass at ambient temperature led to a selective separation of molybdenum.

Both applications, the synthesis of potential biofuel and the separation of metal ions, proved the convenience of the transfer of hydrothermal model reactions to further domains.

In summary, hydrothermal conditions replaced hazardous catalysts by using diluted hydrochloric acid. A much less hazardous potential in general and especially the use of water as solvent contributed to green chemistry while novel reaction pathways were discovered. Therefore, hydrothermal reactions increase significantly the environmental friendliness of industrially relevant reactions.

Résumé (Summary – French version)

Remerciements

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Résumé – Table des matières

1. Introduction

Depuis plus d’un siècle les besoins de l’humanité en énergie ont littéralement explosé. Historiquement, le pétrole et le charbon se sont substitués au bois au moment même où cette source d’énergie ne parvenait plus à couvrir les besoins des sociétés occidentales. Le premier choc pétrolier a conduit, surtout en France, à l’exploitation d’énergie atomique pour la production d’électricité, en remplacement du pétrole, déjà perçu à l’époque comme une ressource peu sûre. Cependant les secteurs industriels, domestiques, des transports et de l’électricité sont toujours dépendants des ressources fossiles. L’inconvénient majeur de cette ressource (indépendamment de l’épuisement progressif des ressources) est l’émission de CO_2 qui est un des gaz contribuant massivement au réchauffement climatique comme en atteste le quatrième rapport d’évaluation des changements climatiques (GIEC) publié en 2007.

Une solution est l’utilisation de la biomasse comme stock d’énergie ou comme stock de CO_2. Sa consommation produit juste autant CO_2 que sa production, d’où un bilan neutre (en théorie). Par ailleurs, la biomasse est aussi une source de matière première potentielle pour la production de produits chimiques.

Une autre possibilité pour accroître la production d’énergie mondiale sans émission de CO_2 supplémentaire, consisterait à augmenter l’efficacité des systèmes de production utilisés. Le rendement des centrales nucléaires est voisin de 36%, du fait de l’utilisation, pour des raisons de sécurité, d’une température relativement basse de la source chaude. Ce rendement augmente à 46% dans les centrales thermiques classique [1], les développements actuels conduisent à un rendement de 60% pour les turbines à gaz [2, 3].

L’objectif de la thèse était, d’une part, de trouver des solutions nouvelles pour la valorisation de la biomasse comme source de carbone lié, tout en permettant, d’autre part, éventuellement, de valoriser la chaleur produite en excès par des centrales électriques actuelles. Pour ce faire nous nous sommes intéressés à l’étude et au développement d’une chimie organique dans l’eau surchauffée.

2. Eléments de base

2.1 Chimie verte

La chimie verte a pour objectif de réduire voire d'éliminer la génération de substances chimiques néfastes pour l'environnement par l'utilisation de procédé ou de voie de synthèse propre. Ce concept s'applique bien évidemment à la diminution des rejets en CO_2 [4], mais plus largement Anastas et Warner ont défini douze principes de la chimie verte en 1998 [5]. Ces concepts, repris par Clark en 1999 [6], sont précisés dans le chapitre 2.1 du manuscrit de thèse version anglais.

Ces principes ont entraîné des changements dans plusieurs domaines, notamment la chimie analytique [7, 8], la chimie organique [9] et l'ingénierie [10].

2.2 Conditions hydrothermales

Les conditions hydrothermales sont obtenues en chauffant de l'eau dans des conditions supérieure de son point d'ébullition. La définition des conditions hydrothermales n'est pas très claire, certains auteurs parlent de milieu hydrothermal dès 75°C [11] et jusqu'à 450°C [12]. Dans ces conditions l'eau reste liquide quand la pression reste inférieur à la pression de vapeur saturante et l'eau possède des propriétés singulières qui font d'elle un solvant qui favorise la conversion thermochimique des macromolécules ligno-cellulosiques. Ces conditions sont utilisées depuis longtemps dans la branche de la chimie inorganique, ce n'est que récemment qu'elles sont employées pour de la synthèse organique.

Le chauffage de l'eau a pour effets de modifier certaines de ses propriétés (voir Figure 2.1). Sa masse volumique diminue, et chute brutalement autour de la température critique. Sa permittivité diélectrique chute jusqu'au point critique à 374°C et 221bar [13] et se stabilise pour des températures plus élevées. Sa constante d'autodissociation est égale à 10^{-14}mol²/L² à la température ambiante, elle augmente jusqu'à 10^{-11}mol²/L² vers 250°C, puis elle chute brutalement à une valeur de 10^{-24}mol²/L² près des conditions critiques et jusqu'à une température proche de 700°C.

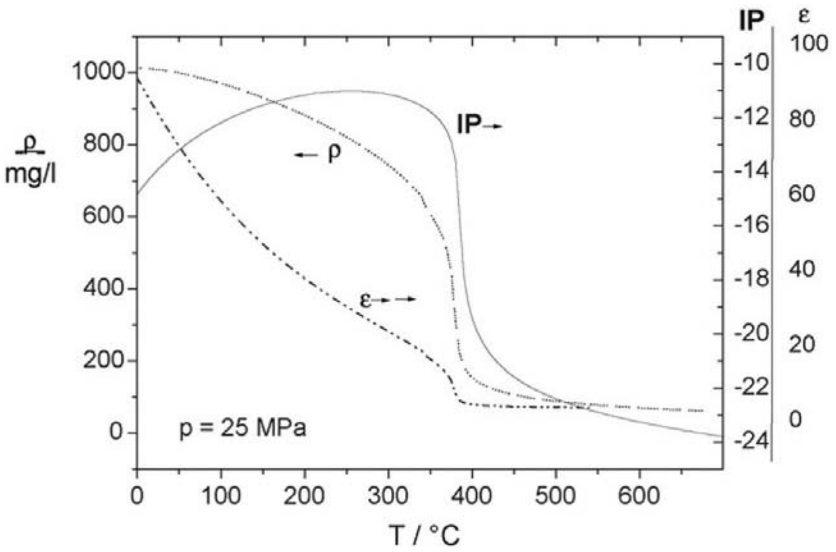


Figure 2.1: Evolution de la masse volumique, de la permittivité diélectrique et du produit ionique de l'eau en fonction de la température, d'après Kruse et al. [14].

La combinaison d'un produit ionique élevé et d'une permittivité diminuée fait que l'eau surchauffée est un bon milieu réactionnel. De plus, dans ces conditions l'eau devient un solvant pour les composés organiques [15-18]. Par ailleurs le produit ionique élevé entraîne une augmentation du potentiel hydrogène (pH) et du pOH qui sont favorable pour la catalyse des réactions acido-basiques [19-22].

2.3 Réactions hydrothermales

Dans le domaine de la chimie inorganique les conditions hydrothermales sont surtout utilisées pour obtenir des catalyseurs [23-27] et des matériaux dopés [28-32]. A cause de l'instabilité des composés organiques à haute température, la chimie organique utilise peu ce type de conditions. Ces conditions existent naturellement au fond de la mer sous forme de sources hydrothermales appelées également fumeurs noirs ou des fumeurs blancs, qui sont des sources d'eau chaude observées à proximité de dorsales océaniques, du fait du réchauffement de l'eau de mer au contact du magna. Dans ces conditions particulières de température, pression et composition, l'eau solubilise de nombreux composés minéraux, par ailleurs ce milieu constitue un écosystème très riche et particulier. Ces sources hydrothermales sont présumées être à l'origine de certains des composés essentiels à la vie [33, 34].

Pour ces raisons l'utilisation des conditions hydrothermales pour réaliser des réactions organiques est très prometteuse.

2.4 Réactions hydrothermales à partir du phényl-1,2-éthanediol

Le phényl-1,2-éthanediol est un composé modèle intéressant pour la chimie en conditions hydrothermales, puisqu'il combine des groupements diol et aromatique au sein de la même molécule ce qui laisse de nombreuses possibilités de réaction (réaction de type Friedel-Crafts, déshydratation et aldolisation). Avola et al. ont montré que le phényl-1,2-éthanediol se convertit en 1,3-diphényl-2-butènal par réaction d'aldolisation en conditions hydrothermales (180°C dans 1.0mol/L NaCl) [35]. Suite à ce résultat intéressant, l'influence des conditions hydrothermales imposées (température et ajout de catalyseurs) sur cette réaction a été étudiée. En effet, le phényl-1,2-éthanediol se transforme en 1-phényl-naphtalène dans l'eau pure à 220°C, cette même réaction a été obtenu dès 160°C lorsque l'on modifie le solvant (ajout de 1.0mol/L HCl). Ces résultats ont permis d'envisager le mécanisme réactionnel présenté sur la Figure 2.2 pour la transformation du phényl-1,2-éthanediol en 2-phénylnaphtalène.

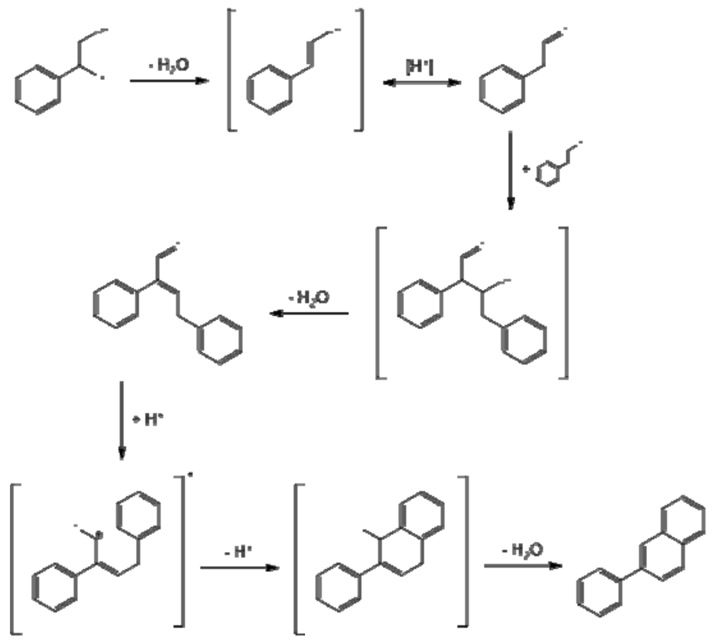


Figure 2.2: Mécanisme de transformation du 1-phényl-1,2-éthanediol en 2-phénylnaphtalène.

Ce mécanisme combine des réactions d'aldolisation et une réaction de type de Friedel et Crafts intramoléculaire. L'étude et la compréhension de ces deux types particuliers de réactivités qui constitue le cœur de ce travail de thèse (chapitres 3 et 4). Enfin dans le paragraphe 5 des applications de cette transformation pour des procédés de séparation des platinoïdes sont présentés.

3. Transformation des diols en conditions hydrothermales

Beaucoup de composés naturels sont des alcools. Par exemple la grande majorité des hydrates de carbone sont des alcools et souvent ils sont des polyalcools. La Figure 3.1 montre une transformation théorique de diols en composé aromatique. Si cette réaction était possible, la chimie des composés aromatiques serait accessible à partir des ressources renouvelables.

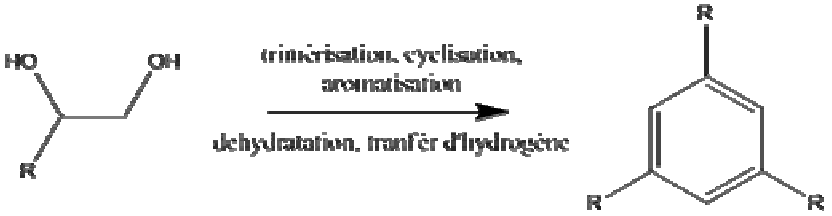


Figure 3.1: Transformation théorique de diols au composé aromatique.

L'utilisation de conditions hydrothermales pour cette réaction peut être envisagée avantageusement puisque l'eau en plus d'être un solvant pour les diols et un composé actif dans cette réaction. De plus, le composé aromatique produit de la réaction hydrothermale a l'avantage d'être facilement séparable de l'eau à la température ambiante. Dans ce qui suit, l'éthylène glycol et le propylène glycol seront étudiés.

3.1 Bibliographie

3.1.1 Transformation hydrothermale de la biomasse

Des travaux montrent que la transformation de composés naturels provenant de la biomasse (sorbitol, xylitol, glycérine) en éthylène glycol [36, 37], ou en propanediol [37, 38] est facilement réalisable. Les composés obtenus sont utilisés à des fins industrielles, le 1,3-propanediol est utilisé comme monomère pour produire des polymères, le 1,2-propanediol est employé comme produit de refroidissement. Le phényléthanediol est également un composé intéressant, mais il n'est pas encore accessible en grande quantité à partir de la biomasse.

Par référence à la réaction théorique on peut attendre que l'éthylène glycol se transforme en benzène, le mésitylène étant synthétisé à partir du 1,2-propanediol.

Une analyse bibliographique indique que ces deux composés chimiques ont souvent été utilisés en tant que solvant dans le domaine de la chimie hydrothermale. Quelques publications rapportent des réactions dans lesquelles ces diols ont été utilisés, mais aucune publication ne fait état des réactions de ces composés sur eux même, bien qu'a priori ces diols devraient présenter une grande réactivité sous conditions hydrothermale du fait de la présence de deux groupes hydroxyles avoisinants.

3.1.2 Biocarburants et bioraffinage

Comme nous l'avons dit, l'augmentation de la concentration en CO_2 dans l'atmosphère, qui est surtout causée par l'usage des ressources fossiles, est une menace pour le futur. C'est pourquoi, si l'on veut conserver le mode de développement des sociétés actuelles, il serait intéressant d'utiliser des matières premières et de disposer de procédés qui n'ont pas de conséquences sur ce paramètre. Dans cette optique, les biocarburants présentent un intérêt certain.

Précisons tout d'abord quelques éléments de langage. Les biocarburants primaires sont les matières premières utilisées depuis toujours telles que le bois, et autres matériaux naturels. Ils sont généralement utilisés dans les habitations pour le chauffage et la cuisine. Les biocarburants secondaires sont obtenus après des modifications. Au Brésil, le biocarburant secondaire le plus connu est le bioéthanol, en Europe, c'est le biodiesel. Plusieurs catégories de biocarburants secondaires ont été développées en fonction de la nature de la bio ressource et du procédé technique utilisé pour les fabriquer [39] (voir Figure 3.2).

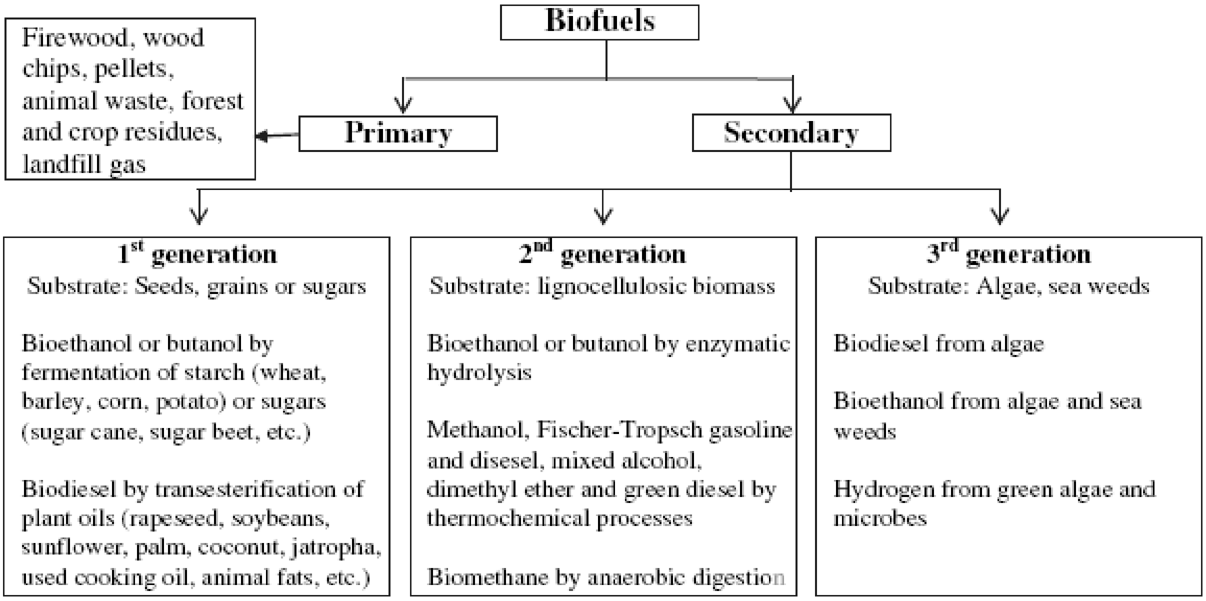


Figure 3.2: Schéma présentant la terminologie utilisée pour définir les différents biocarburants en fonction de la nature de la bio-ressources et du procédé utilisé, d'après Nigam et al. [39].

Plus généralement, les biocarburants secondaires sont produits par bioraffinage. Conjointement aux biocarburants, d'autres composés chimiques valorisables sont produits par bioraffinage. Sur la Figure 3.3 sont présentés des exemples de composés obtenus après le bioraffinage de la glycérine.

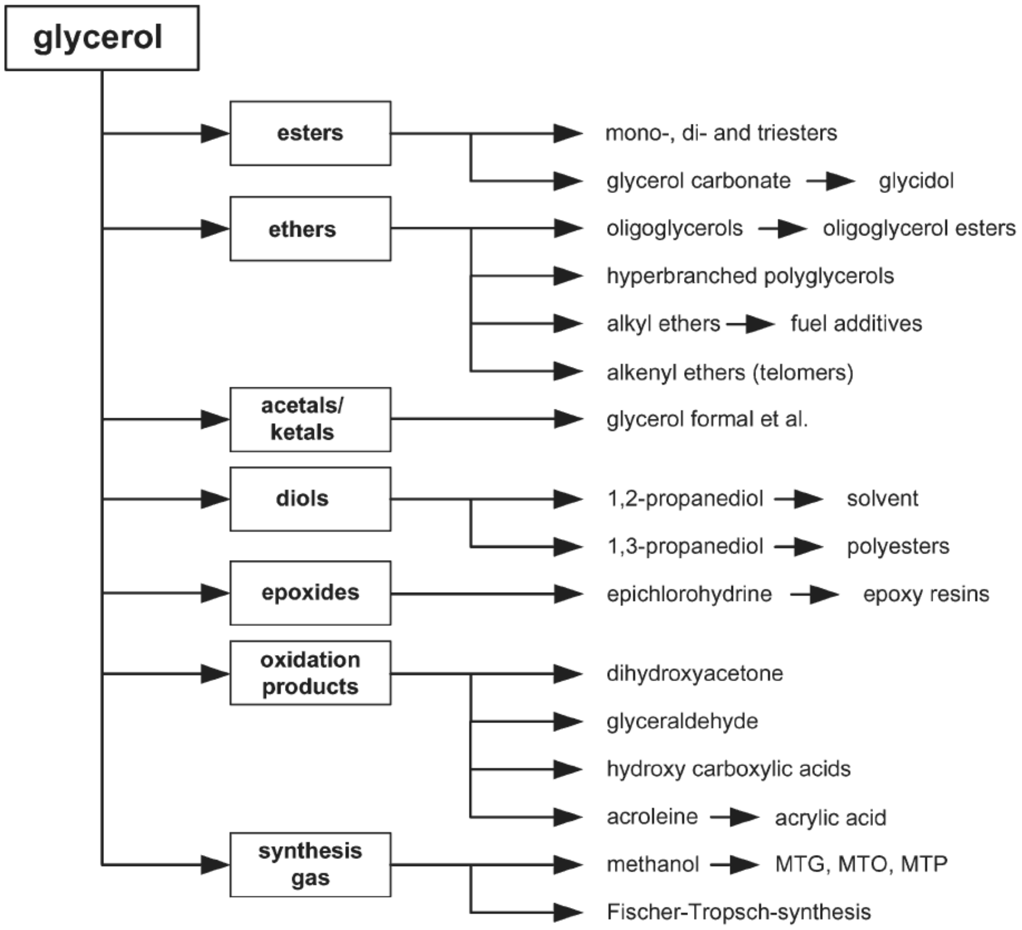


Figure 3.3: Composés obtenus après le bioraffinage de la glycérine, d'après Behr et al. [40] – Reproduced with permission of The Royal Society of Chemistry.

D'une part, la glycérine peut être transformée en produits valorisables tels que des éthers, des esters et produits hydrogéno-carbonés. D'autre part, la glycérine peut aussi être transformée en charbon, CO et CO_2 à partir de lesquelles des biocarburants peuvent être obtenus par une synthèse de Fischer et Tropsch [40]. Certains des composés valorisables peuvent également être utilisés comme matières premières pour des synthèses, c'est le cas notamment du 1,2-propanediol. Ce point sera développé dans le paragraphe suivant.

3.2 Réactions d'éthylène glycol

Les réactions hydrothermales impliquant l'éthylène glycol sont fortement influencées par la température de réaction. Dans l'eau pure aucune réaction n'a été observée jusqu'à 200°C. Au-dessus de cette température quelques composés ont été obtenus en petites quantités. Lorsque NaCl est ajouté dans le milieu réactif, plusieurs composés chimiques, présentant de quatre à six atomes de carbone ont été synthétisés en petite quantité, le 2-

éthyle-butènal est le composé majoritairement obtenu. Des résultats similaires ont été obtenus en utilisant 0.5-1.0mol/L HCl, ou une solution ayant 0.5mol/L HCl et 0.5mol/L NaCl.

Plus intéressante est l'obtention de benzène dans une solution concentrée à 1.0mol/L HCl à 200°C comme le montre le chromatogramme de GC-MS présenté sur la Figure 3.4 sur lequel est représenté le signal de l'échantillon et les signaux des deux fragments les plus intensifs (du benzène et d'une impureté).

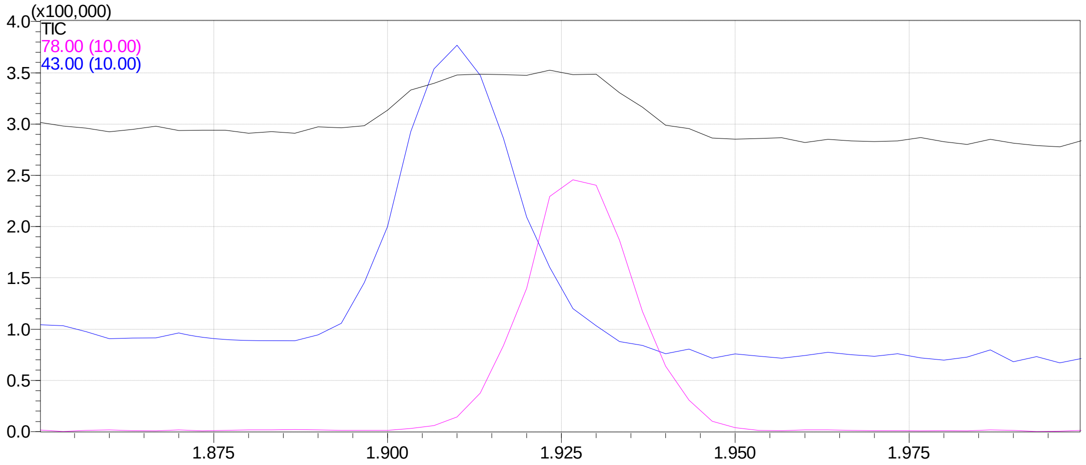


Figure 3.4: Analyse obtenue par GC-MS montrant la présence de benzène dans une solution d'éthylène glycol et d'eau (1.0mol/L HCl) traitée à 200°C.
L'échantillon (noir), le fragment le plus intensif du benzène (rose, multiplié par 10) et le fragment le plus intensif d'une impureté du solvant (bleu, multiplié par 10).

Le mécanisme réactionnel proposé pour expliquer la transformation de l'éthylène glycol en benzène est présenté sur la Figure 3.5. Ce mécanisme débuté par une déshydratation du diol, qui est suivi par un équilibre céto-énolique et une réaction d'aldolisation. Enfin, une déshydratation et une cyclisation permettent d'aboutir à la formation du benzène.

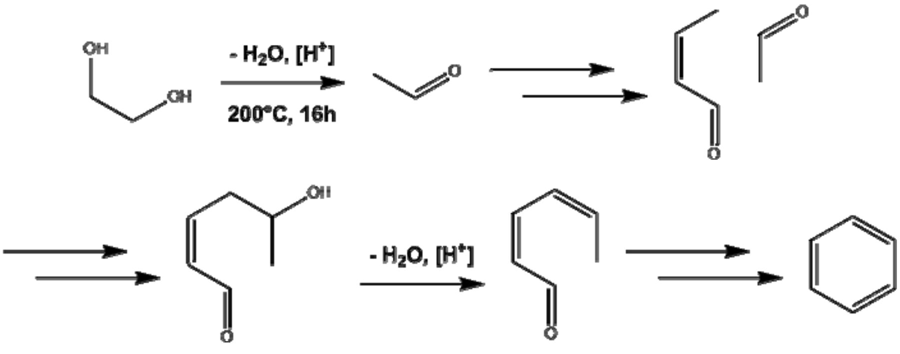


Figure 3.5: Schéma réactionnel proposé pour la formation de benzène à partir de l'éthylène glycol en conditions hydrothermale.

3.3 Transformation du 1,2-propanediol

3.3.1 Synthèse du 1,2-propanediol à partir de la glycérine

L'hydrogénation de la glycérine en 1,2-propanediol est rapportée par quelques groupes qui ont travaillé avec des procédés continus et discontinus [41-44]. Nos propres études ont confirmé la possibilité d'obtenir le composé 1,2-propanediol à partir de la glycérine. Ce produit est obtenu avec une pureté élevée.

La glycérine a été hydrogénée à 80°C sous 10bar d'hydrogène par un catalyseur de palladium sur charbon activé. Pendant 32h 74% de la glycérine ont été transférés en 1,2-propanediol.

3.3.2 Transformation hydrothermale du 1,2-propanediol

D'une façon générale, dès 125°C, le 2-méthyle-2-pentènal est le produit principal de la transformation hydrothermale du 1,2-propanediol dans une solution du NaCl. D'autres composés, un dérivé du cyclopent-2-ènone et le mésitylène ont été obtenus en modifiant le solvant. Les rendements de ces réactions augmentent lorsque la température augmente jusqu'à 220°C. Ces réactions sont présentées sur la Figure 3.5. Les trois produits principaux sont marqués (A), (B) et (C).

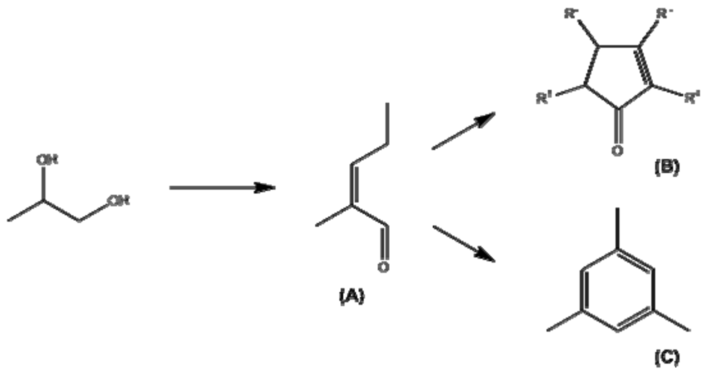


Figure 3.6: Réaction du 1,2-propanediol en conditions hydrothermales. (A) 2-méthyle-2 pentènal, (B) cyclopent-2-énone, (C) mésitylène.

La transformation hydrothermale du 1,2-propanediol a été étudiée de façon plus précise dans différents milieux. Pour cela, 0.5g 1,2-propanediol ont été dissous dans 10mL de différents solvants aqueux : eau pure, 1.0mol/L NaCl, 0.5mol/L HCl, 1.0mol/L HCl. Ces mélanges ont été portés à des températures comprises entre 125°C et 220°C. La masse de réactif 1,2-propanediol et la durée de la réaction sont également des paramètres qui ont été étudiées. L'optimisation du rendement de la réaction a conduit à utiliser les conditions suivantes : 12 grammes de 1,2-propanediol avec 0.5mL, 1.0mol/L HCl à 220°C pendant 20h.

Après distillation et séparation, les produits de la réaction ont pu être identifiés par chromatographie couplé à la spectrométrie de masse (GC-MS). Le produit principal isolé est un dérivé du cyclopent-2-ènone. Néanmoins, la structure exacte a été déterminée à partir d'analyses par RMN en une dimension et deux dimensions et par spectrométrie de masse ont été effectuées.

Le spectre de mass a confirmé la masse molaire de 138g/mol. Il a aussi montré des pertes de 15Th et de 29Th qui correspondent aux groupes de méthyle et d'éthyle.

Après avoir analysé les spectres RMN, le produit principal était identifié. C'est le 2-éthyle-3,5-diméthyle-cyclopent-2-ènone comme indiqué sur la Figure 3.13.

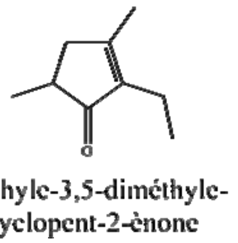


Figure 3.7: Structure du 2-éthyle-3,5-diméthyle-cyclopent-2-ènone.

3.3.3 Mécanisme réactionnel

Le mécanisme de la réaction du 1,2-propanediol en conditions hydrothermale est représenté sur la Figure 3.8.

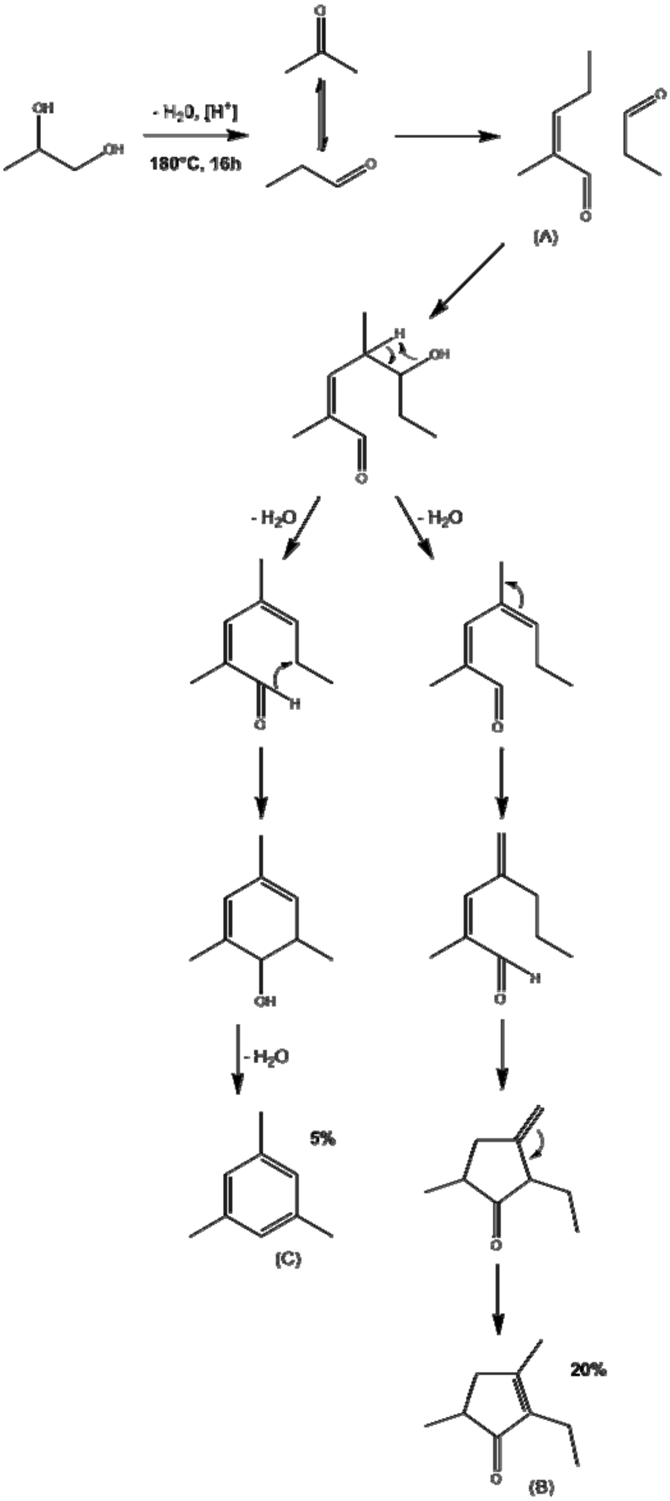


Figure 3.8: Mécanisme réactionnel de transformation du 1,2-propanediol en conditions hydrothermales.

3.3.4 Voies d'exploitation

Ce n'est pas tout de parvenir à synthétiser un mélange de di- et trimère à partir de propanediol, encore faut-il que ces produits aient une utilité.

Comme nous l'avons montré plus haut, la séparation de ces produits est complexe au niveau du laboratoire et pourrait s'avérer coûteuse. Cependant, le mésitylène pourrait être utilisé comme solvant. Les deux autres produits principaux pourraient s'avérer être des synthons d'intérêt pour l'addition de Michael ou la réaction de Diels-Alder.

Cependant une exploitation groupée nous semble plus réaliste. Peut-être comme carburants ou adjuvants de carburants. L'exploitation de ces biocarburants potentiels sans traitement est limitée. La haute viscosité du mélange obtenu impose de trouver une application adaptée et la présence de composants très peu volatiles pourrait conduire à un écrasement de la chambre de combustion si le mélange était directement utilisé comme carburant pour la combustion. Malgré tout, le pouvoir calorifique spécifique du mélange brut a été mesuré à 39MJ/kg, ce qui est comparable aux 40MJ/kg du biodiesel et 45MJ/kg du gazole. En revanche une simple distillation à un plateau théorique permet de réduire grandement les problèmes liés à la viscosité et à la présence de crasses dans le mélange.

3.3.5 Récapitulatif et perspectives de valorisation comme carburant

La transformation du 1,2-propanediol en conditions hydrothermales a permis d'obtenir un mélange des composés riches en carbone et en hydrogène. Trois produits principaux ont pu être obtenus à partir de cette réaction : le 2-méthyle-2-pentènal, le mésitylène et le 2-éthyle-3,5-diméthyle-cyclopent-2-ènone. Le mécanisme réactionnel de cette transformation a pu être établi.

Cette réaction conduit à la formation d'une phase organique valorisable soit comme source de diverses molécules d'intérêt, soit comme mélange combustible.

4. Réaction hydrothermale de type de Friedel et Crafts

Comme nous avons dit dans le paragraphe 2.4 les conditions hydrothermales permettent la réalisation d'une réaction de type Friedel et Crafts intramoléculaire. C'est pourquoi, nous avons cherché à étudier les conditions de réalisation de cette réaction par voie intermoléculaire. Ce paragraphe reporte les résultats relatifs à cette étude.

4.1 Bibliographie

Originellement, l'alkylation de Friedel et Crafts consiste à faire réagir un halogénure d'alkyl avec un composé aromatique en présence d'une quantité surstœchiométrique de chlorure d'aluminium [45].

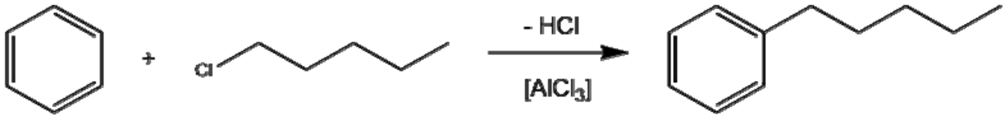


Figure 4.1: Réaction de Friedel et Crafts.

Dans cette réaction le composé aromatique considéré est pris en grand excès, il fait également office de solvant. Du fait de l'emploi d'un halogénure comme agent d'alkylation et d'$AlCl_3$ comme promoteur, une quantité importante de déchet résulte de cette réaction [6]. Ainsi, une amélioration possible consisterait à diminuer l'impact sur l'environnement et de rendre cette réaction plus verte. Plusieurs études [46-49] ont montré, par exemple, que la réalisation de cette réaction était possible dans l'eau supercritique sans catalyseur. Toutefois dans ces conditions, qui sont par ailleurs difficiles à mettre en œuvre, le rendement de la réaction est faible [50]. Un autre inconvénient de cette réaction est l'utilisation d'un hydrocarbure halogéné. L'emploi des alcools (alcool benzylique ou alcool allylique) permet d'éviter ce problème comme cela a été montré dans plusieurs travaux [51-54]. Excepté dans le cas où la réaction est réalisée en conditions aprotiques [48], la concentration ou l'activité des ions H^+ est le paramètre prépondérant sur cette réaction en conditions hydrothermales. C'est pourquoi des acides dilués ont été utilisés comme solvant dans le cadre de cette étude.

4.2 Réactivité de naphtalène

L'alkylation du naphtalène par l'alcool benzylique est la première réaction de type de Friedel et Crafts en conditions hydrothermales qui a été étudiée.

Dès 125°C, l'alcool benzylique a alkylé le naphtalène dans l'acide chlorhydrique. L'augmentation de la température a amélioré le rendement de cette réaction. Les produits obtenus sont le 1-benzyl-naphtalène et le 2-benzyl-naphtalène. D'autres produits tels que l'éther dibenzylique et l'alcool benzylbenzylique ont également été produits en moindre quantité. La formation d'alcool benzylbenzylique est caractéristique d'un début de polymérisation.

La benzylation du naphtalène a eu lieu dans des solvants d'une faible concentration de l'acide chlorhydrique est également dans des acides acétique ou formique d'une concentration élevée.

L'alkylation du naphtalène par d'autres alcools a donné le résultat que les alcools primaires ne sont pas capables de faire une alkylation du naphtalène, sauf s'ils sont activés. Le 2-propanol et le 2,3-butanediol font l'alkylation du naphtalène mais les autres alcools secondaires n'en font pas s'ils ont un effet stérique. Le pinacol comme un alcool tertiaire ne fait pas cette alkylation hydrothermale.

4.3 Réactivité du phénol

Ensuite nous avons étudié l'alkylation du phénol, qui est souvent plus complexe en conditions de Friedel-Crafts classiques.

La benzylation du phénol a été obtenue dès 125°C dans HCl mais à partir de 150°C la quantité des sous-produits diminue et à partir de 180°C les produits de l'alkylation sont synthétisés. Ce résultat est une conséquence du fait que les éthers formés ne sont pas stables à haute température.

La benzylation du phénol dans l'acide chlorhydrique a été quantifiée en fonction de la température. Des résultats quantitatifs sur les produits formés par cette réaction sont présentés dans le Tableau 4.1.

Solvant	Température (°C)	Conversion (%) [a]	Rendement du produit de Friedel et Crafts mono-alkylé (%)[b]	Rapport o/p
L'eau	125	0	0	-
	150	0	0	-
	180	1	1	-
	200	7	7	61 : 39
	220	14	14	59 : 41
0.5M HCl	125	100	89	50 : 50
	150	99	72	52 : 48
	180	100	66	53 : 47
	200	100	67	53 : 47
	220	100	63	53 : 47
1.0M HCl	125	84	71	48 : 52
	150	100	75	50 : 50
	180	100	69	51 : 49
	200	94	65	51 : 49
	220	100	62	52 : 48

Tableau 4.1: La benzylation du phénol dans les solvants aqueux.

Conditions opératoires de la réaction: 0.5mmol alcool benzylique, 15mmol phénol, 10mL solvant chauffé pour 16h. a) 100% diminué par le rapport entre la quantité d'alcool benzylique finale sur la quantité initiale, b) Rapport entre la quantité de produit mono-alkyl produite sur la quantité initiale de l'alcool benzylique.

Apparemment, les produits substitués en position ortho sont obtenus préférentiellement dans l'eau. Par contre, dans l'acide chlorhydrique la sélectivité diminue. La réaction du phénol avec l'alcool benzylique peut aussi être réalisée dans l'acide chlorhydrique plus dilué. Par référence à la Figure 4.2 l'effet de 0.04mol/L HCl est similaire à une concentration de 0.5mol/L HCl.

Des acides organiques, notamment l'acide acétique et l'acide formique, peuvent remplacer l'acide chlorhydrique mais l'acide acétique de 2.0mol/L n'est pas suffisant pour obtenir le même résultat comme dans 0.005mol/L HCl. L'acide formique est plus efficace que l'acide acétique mais on a besoin de 0.5mol/L acide formique pour obtenir un résultat similaire à celui obtenu avec 0.005mol/L HCl.

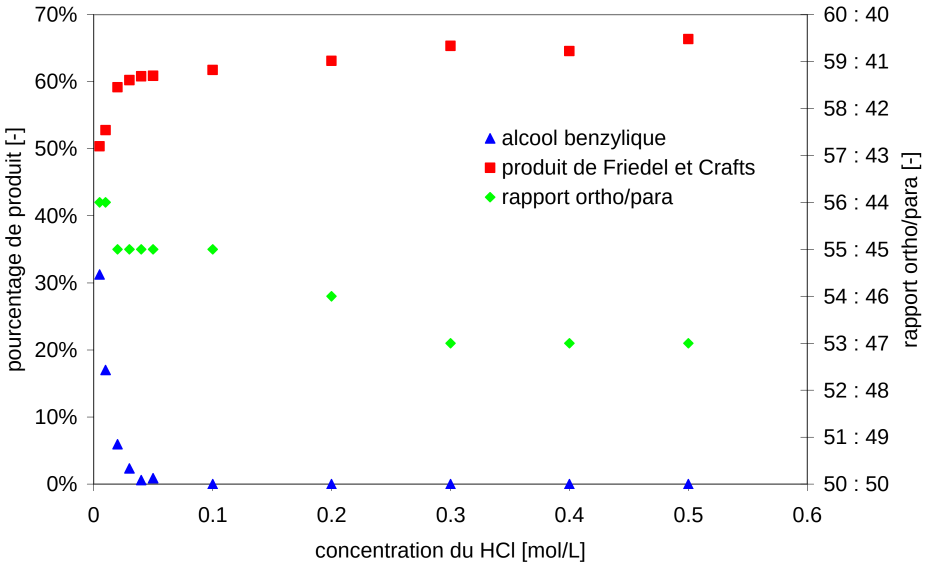


Figure 4.2: Rendement de conversion de la réaction du phénol avec l'alcool benzylique en fonction de la concentration du HCl à 180°C.

Les pourcentages de l'alcool benzylique non-convertis et du produit d'une mono-alkylation sont reportés sur l'axe de gauche, le rapport ortho/para est reporté sur l'axe de droite.

Les alcools primaires n'ont pas attaqué le phénol mais l'alcool cinnamylique est assez actif pour le faire, un résultat similaire a été obtenu avec l'alcool furfurylique. Les dérivés de l'alcool benzylique permettent d'obtenir l'alkylation du phénol.

Les alcools secondaires tels que le 1-phényl-1-éthanol, le 2-propanol, le 2,3-butanediol ou le cyclohéxanol permettent d'obtenir l'alkylation du phénol. Les diols qui sont constitués d'un alcool primaire et d'un alcool secondaire ont besoin d'avoir un groupe phénylique pour réagir avec le phénol. Le pinacol, un alcool tertiaire ne réagit pas avec le phénol, et le styrène entraîne une double alkylation qui permet d'obtenir le produit bisalkylé. Les différents alcools ont des sélectivités différentes qui sont présentées dans le Tableau 4.2. Le rendement ortho/para est également indiqué dans ce tableau.

N°	Alcool	Rendement du produit de Friedel et Crafts mono-substitué (%)[a]	Rapport ortho/para[b]
1	alcool benzylique	78	56 : 44
2	1-phényl-1-éthanol	93	34 : 66
3	alcool 4-hydroxybenzylique	68	18 : 82
4	alcool cinnamylique	47	-
5	cyclohexanol	3	59 : 41
6	n-hexanol	0	-
7	2-propanol	3	64 : 36

Tableau 4.2: Rendement de l’alkylation de type de Friedel et Crafts à partir de l’alcool considéré et sélectivité associée.

Conditions opératoires de la réaction: 0.5mmol alcool benzylique, 15mmol phénol, 10mL solvant chauffé pour 16h. a) 100% diminué par le rapport entre la quantité d’alcool finale sur la quantité initiale, b) Rapport entre la quantité de produit mono-alkyl produite sur la quantité initiale de l’alcool.

De plus, le recyclage du solvant a été étudié. La réaction de l’alcool cinnamylique avec le phénol a été répétée en gardant l’acide chlorhydrique dilué en tant que solvant. Le recyclage du solvant est favorable car le rendement augment d’un cycle à l’autre. L’augmentation des quantités de produits est montrée dans la Figure 4.9.

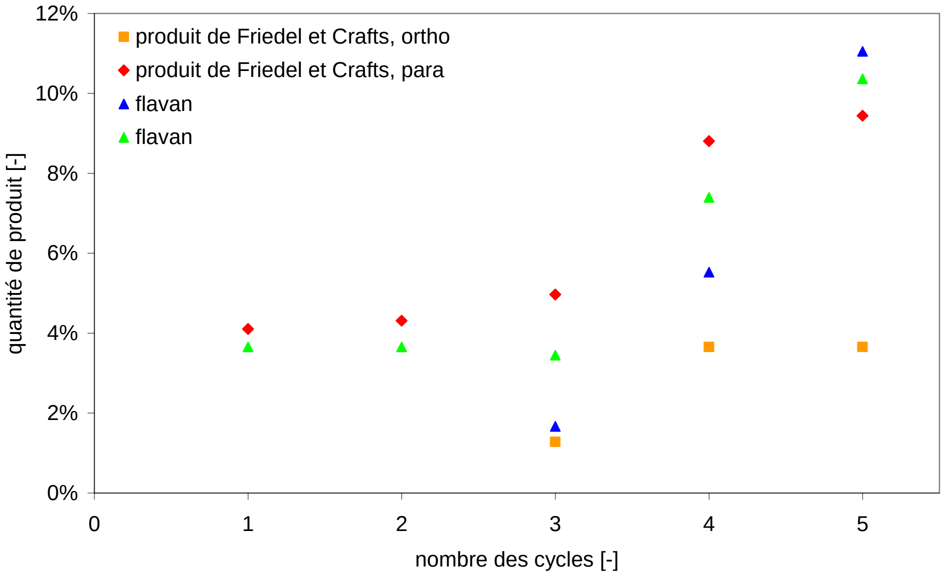


Figure 4.3: Quantité des produits en recyclant le solvant.

4.4 Réactions de type Friedel et Crafts – Vue générale

Des alcools différents et des composés aromatiques sont combinés. Les quantités approximatives de produits mono-alkylés de leurs réactions sont indiquées dans un aperçu tabulaire (voir Tableau 4.3).

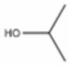
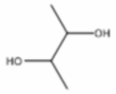
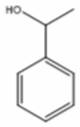
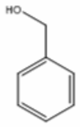
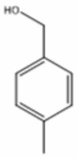
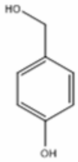
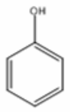
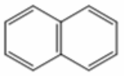
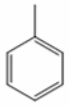
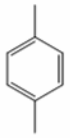
						
	+	-	+++	++	++	-
	-	-	+	+++	++	-
	-	-	+	++	++	-
	+	-	-	+++	++	-

Tableau 4.3: Quantités approximatives des produits de la réaction de type Friedel et Crafts en combinant des alcools et des composés aromatiques différents.

4.5 Alcool polybenzylique

Comme on a déjà vu dans une réaction parallèle, l’alcool benzylique est capable d’alkyler une autre molécule d’alcool benzylique. Selon ce même processus, il serait possible d’obtenir un polymère en conditions hydrothermales. C’est pourquoi cette réaction a été étudiée en détail.

4.5.1 Polymérisation de l’alcool benzylique

La polymérisation de l’alcool benzylique dans 0.5mol/L HCl est fortement dépendante de la température de la réaction. A 160°C on obtient au maximum des pentamères. Des octamères sont accessible à 220°C. Par ailleurs, une augmentation de la quantité de produit de départ ou une diminution de la durée de réaction favorise l’obtention de dimères, trimères et tétramères. A 220°C, la température détermine la réaction et il n’y a presque plus d’influence des autres paramètres sur le rendement et la nature des produits de la réaction.

4.5.2 Caractérisation de l’alcool polybenzylique

Dans un premier temps, l’analyse IR a été mise en œuvre pour le dosage de ces polymères. Le principal changement observé est la disparition de la bande attribuable aux groupements OH sur les produits de la réaction. Les spectres UV/Vis indiquent la présence d’une bande d’absorption vers 300-400nm qui est attribuable à la présence de polymères dans le produit obtenu. Des spectres de fluorescence ont également été effectués sur les produits de la réaction. Une bande de fluorescence a été observée dans la région correspondant aux longueurs d’ondes comprises entre 400-450nm lorsque les échantillons sont irradiés par un faisceau monochromatique de longueur d’onde 350nm. Cette fluorescence n’a pas été observée lorsque l’on analyse l’alcool benzylique, ce qui atteste la formation d’un polymère.

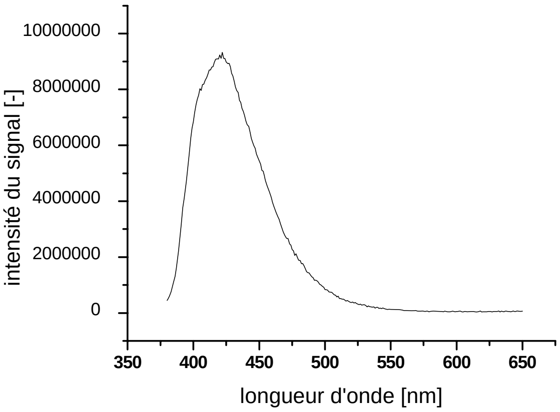


Figure 4.4: Spectre de fluorescence de l’alcool polybenzylique après une irradiation de 350nm.

Cette fluorescence peut résulter d’une délocalisation des électrons des cycles aromatiques vers les groupements méthylènes

4.6 Récapitulatif et perspectives

La réaction de type de Friedel et Crafts est très facile à mettre en œuvre en conditions hydrothermales, ce qui est un avantage incontestable en terme d’impact sur l’environnement. .Le chlorure d’alkyl est remplacé par un alcool, le grand excès du composé aromatique n’est pas nécessaire et la réaction se déroule dans l’eau surchauffée. En plus, le catalyseur $AlCl_3$, est remplacé par l’acide chlorhydrique en concentration de 0.05mol/L. Le recyclage de ce solvant est également réalisable, avec une amélioration du rendement de la réaction.

La polymérisation de l’alcool benzylique est un autre avantage lié à l’utilisation de conditions hydrothermales. L’emploi de température élevée (220°C) favorise la formation d’oligomères plus longues.

La perspective d’utiliser ce type de réaction à grande échelle est parfaitement réaliste.

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5. Procédés de séparation

Dans cette partie de la thèse on a cherché à appliquer les résultats décrits précédemment ci-avant à la chimie séparative.

Dans une première étape, une séparation sélective en conditions hydrothermales d'un platinoïde a été étudié, dans une seconde étape l'étude a porté sur la séparation sélective d'un d'espèces de type molybdate grâce à l'emploi de biomasse. Ces résultats sont décrits ci-après.

5.1 Séparation sélective des platinoïdes en conditions hydrothermales

5.1.1 Contexte et bibliographie

Certains pays ont fait le choix d'adopter un cycle du combustible nucléaire fermé permettant le recyclage d'une partie de l'uranium et du plutonium toujours contenu dans le combustible usagé. Pour ce faire, on dissout les pastilles de combustible dans l'acide nitrique et on sépare l'uranium et le plutonium des produits de fissions et d'activation toujours contenus dans la solution. Le procès utilise à l'heure actuelle s'appelle procédé PUREX (process of Plutonium and Uranium Recovery by EXtraction). Parmi les produits de fission on retrouve des platinoïdes. La présence de ces platinoïdes est un handicap à la vitrification de cette solution de déchets, qui constitue l'étape finale du procédé de traitement du combustible usé. C'est pourquoi de nombreux travaux ont été entrepris pour séparer ce groupe des métaux de la solution de produits de fission.

La littérature propose des extractions cationiques et anioniques mais également des échanges d'ions. D'autres solutions ont consisté à adsorber ces éléments sur charbon actif, à les précipiter, ou à les séparer par voie électrochimiques. Les avantages des procédés pyrométallurgiques au lieu des procédés hydrométallurgiques sont la diminution des volumes d'effluents et la stabilité du procédé vis-à-vis de l'irradiation. Cependant, la purification des éléments des platinoïdes est généralement faite par voie hydrométallurgique. [55, 56]

5.1.2 Idée et approche

L'idée consiste à utiliser l'alcool benzylique (0,48mol/L) pour séparer les platinoïdes (0,02mol/L). L'alcool benzylique est un composé réducteur [57-59] qui peut réduire les ions métalliques [60, 61]. Les particules métalliques sont incorporées dans une matrice d'alcool polybenzylique (1vol-% de particules métalliques) qui se forme autour des particules métalliques car ces particules provoquent la polymérisation de l'alcool benzylique [62].

La Figure 5.1 montre schématiquement les étapes clefs de ce procédé.

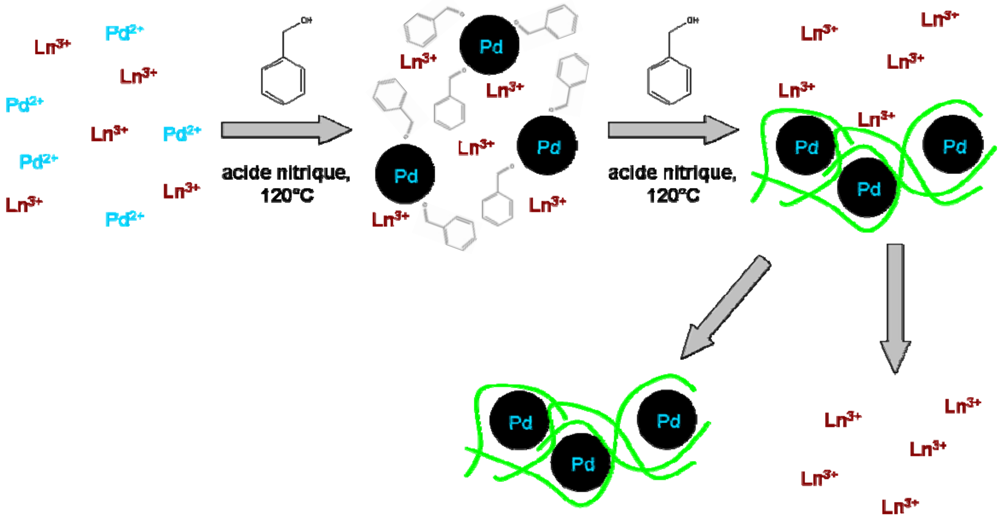

Figure 5.1: Schéma des étapes du procédé de séparation de 0,02mol/L palladium de 0,02mol/L lanthane par 0,48mol/L alcool benzylique en conditions hydrothermales.

5.1.3 Essais en solution modèle simplifiée

Dans une étape préliminaire une solution modèle simplifiée a été utilisée. Cette solution contenait du palladium et du cérium comme des ions métalliques. La quantité d'alcool benzylique et la température sont les paramètres qui ont été modifiés. La durée de la réaction a été fixée à 16h.

Finalement, au moins 319mg alcool benzylique par 10mL de la solution et au moins 150°C ont enlevé le palladium quantitativement sans diminuer la concentration du cérium plus que 36%. Cette séparation est presque complète après 8h et possède un facteur de séparation de 4,5.

D’autres alcools sont également capables de précipiter sélectivement le palladium, surtout le 1-phényléthanol. Par contre, l’hydroquinone précipite entièrement le cérium, mais pas le palladium.

En résumant, l’alcool peut ou doit être choisi en dépendance de la sélectivité souhaitée.

La Figure 5.8 montre des particules obtenues à l’issue de ce traitement. On observe une agglomération des particules métalliques qui sont enrobées dans la matrice organique.

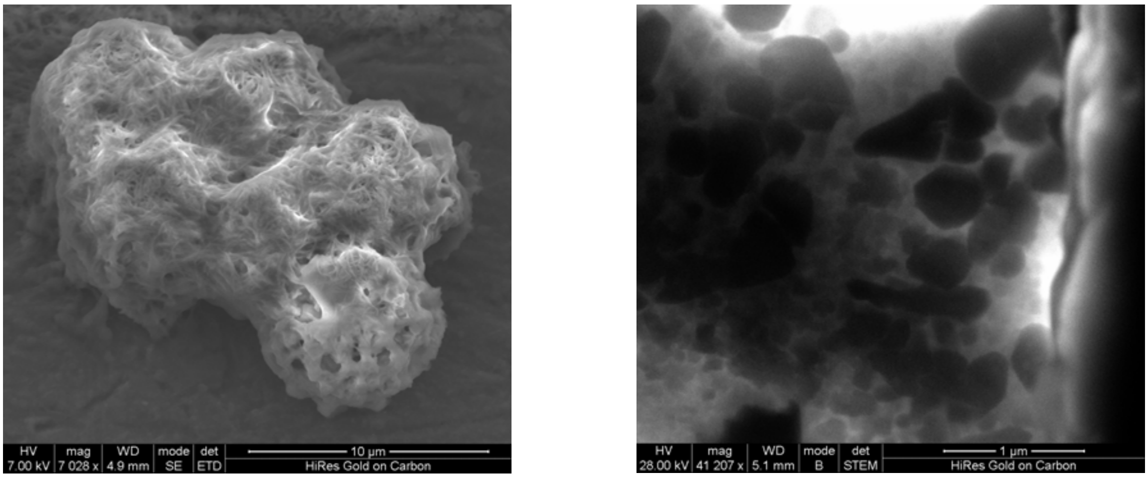

Figure 5.2: Clichés des particules précipitées, analysées par le MEB (microscopie électronique à balayage ; à gauche) et par le STEM (microscopie électronique à balayage par transmission ; à droite).

5.1.4 Essais en solution modèle

Une solution modèle de solution de produits de fissions a été traitée dans les mêmes conditions que la solution modèle simplifiée. Le résultat obtenu montre que le procédé de séparation décrit ci-dessus est bien applicable dans ces conditions.

5.1.5 Récapitulatif et perspectives

L’emploi d’alcool benzylique en conditions hydrothermales douces permet bien de séparer sélectivement les platinoïdes des autres produits de fissions. Cette découverte a fait l’objet d’un brevet.

5.2 Procédé de séparation non-hydrothermale

5.2.1 Contexte et bibliographie

Parmi les produits de fissions et d'activation pouvant poser problème lors de l'étape de vitrification on peut également citer le molybdène. En effet ce dernier est présent sous forme anionique dans les solutions d'attaque (molybdate) et présente donc une solubilité réduite dans les matrices vitreuses (tout comme l'ion sulfate).

On trouve dans la littérature l'emploi de dérivés d'acide tannique pour la séparation sélective du molybdène en conditions très acides (> 1mol/L) en acide chlorhydrique. Au dessous de cette concentration, des cations commencent également à être co-extraits [63].

D'autres auteurs ont également reporté l'emploi de tannin pour l'extraction du l'uranium à des acidités très faibles [64].

En revanche rien ne garantissait a priori la possibilité d'extrapoler ces résultats à l'extraction de molybdates dans l'acide nitrique concentré.

5.2.2 Idée et optimisation

Après avoir testé plusieurs composés organiques, y compris l'acide tannique, il a été établi que ce dernier pouvait séparer le molybdène d'une solution acide nitrique. De plus, la séparation était sélective car d'autres ions métalliques n'ont pas été enlevés.

Une augmentation de la masse de l'acide tannique utilisée cause une augmentation du pourcentage du molybdène séparé. Figure 5.13 montre la dépendance.

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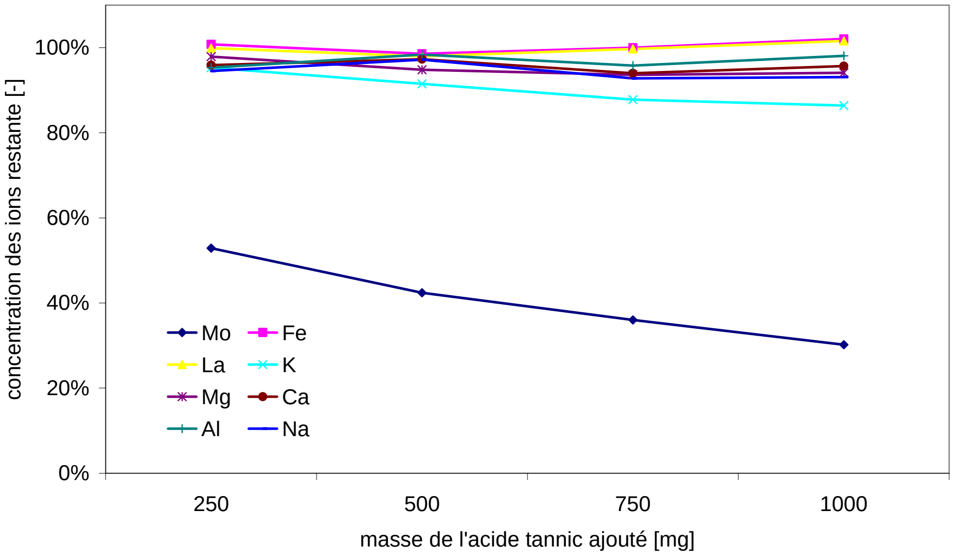

Figure 5.3: Quantité non-enlevée des ions des métaux comme fonction de la quantité de l'acide tannique utilisée.

En outre, la cinétique d'extraction a fait l'objet d'une étude séparée. Un exemple type est présenté comme Figure 5.14.

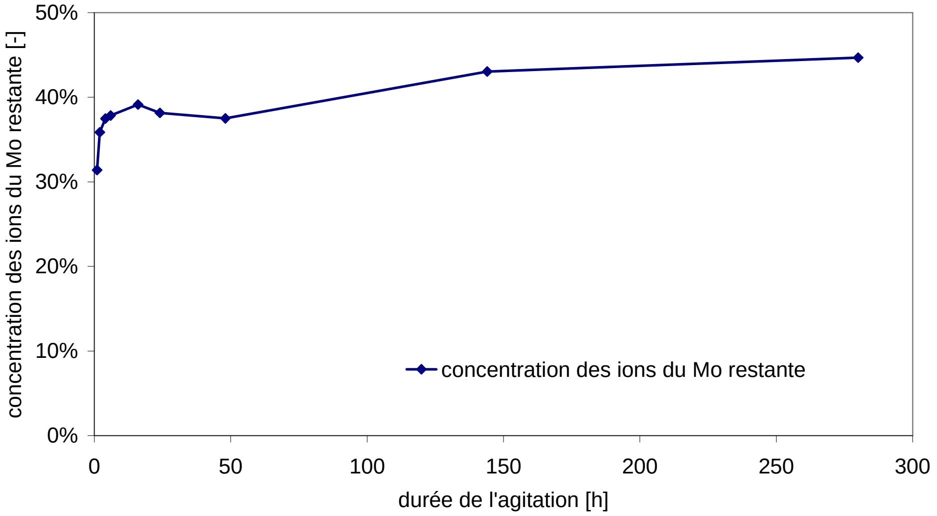

Figure 5.4: Dépendance en temps de la concentration des ions molybdène restante après l'ajoute de l'acide tannique.

5.2.3 Récapitulatif et perspectives

La séparation du molybdène par l'acide tannique s'avère à la fois sélective et très rapide. Cette propriété semble être limitée à l'acide tannique les autres composés organiques testés n'ayant pas donné les mêmes résultats.

6. Conclusion générale

L'objet de cette thèse était l'étude de quelques aspects de la chimie organique en eau surchauffée.

En conditions hydrothermales les diols présentent une réactivité complexe conduisant le plus souvent à la formation de nombreux produits (les composés aromatiques visés à l'origine n'étant qu'une part minime des produits réellement obtenus). La valorisation des mélanges obtenus passera soit par une étape de séparation supplémentaire soit par une recherche de débouchés pour le mélange brut ou purifié potentiellement comme combustible.

Dans un second temps, l'étude de réaction de Friedel et Crafts a été bien plus satisfaisante. En effet l'utilisation des conditions hydrothermales a permis :

- d'employer des alcools comme agents alkylant,
- d'employer HCl dilué comme promoteur de ces réactions (ce même HCl dilué étant recyclable) et
- de limiter les quantités de réactifs mises en jeu.

L'application des conditions hydrothermales à la séparation des ions du groupe des platinoïdes a permis d'effectuer une séparation de ces éléments sur des solutions réalistes avec une bonne sélectivité. Les tests sur divers alcools ont montré que cette propriété n'était pas limitée à l'alcool benzylique. De manière générale les alcools de la famille de l'alcool benzylique présentaient de bonnes performances. La séparation du molybdène par l'acide tannique ne demande pas des conditions hydrothermales. Cette adsorption est très sélective et rapide.

L'emploi de la chimie organique hydrothermale semble donc promis à un bel avenir en chimie verte et industrielle.

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1. Introduction

For several centuries the anthropogenic demand for energy increased faster than the population and in the last few centuries people became aware of the problems related to this consumption. In the 17th to 19th century the lack of wood was seen as the first energy crisis. Nevertheless, these crises were rather temporary and local threads than general facts [1]. However, they resulted in strong public support for the development of coal and oil production. Public programs for civil use of nuclear energy were boosted as a consequence of the oil crises in the 1970s. Despite that, fossil fuels increased their predominant status for both, energy and bonded carbon for chemistry in western countries. That is why the carbon dioxide (CO_2) emissions caused by human energy demand increased and increased.

Since some decades the aim of ecologists and some engineers is to come back to renewable energies. But only for a couple of years, beginning with the publication especially of the fourth part of the Fourth Assessment Report of the United Nations Intergovernmental Panel on Climate Change in February 2007, the problems of anthropogenic CO_2-emissions are almost worldwide recognized.

One way to reduce the CO_2-emmissions is the use of renewable resources, including biomass. Biomass is extremely decentralized and almost everywhere available. With respect to the use of energy, the use of biomass itself is not CO_2-free, but the amount of produced CO_2 is exactly the same amount, which is needed to build up the biomass. There is production of CO_2 in the moment of the energy use, but there is no net CO_2-production. Thus, it counts as CO_2-neutral, even if its preparation consumes energy which is usually provided by fossil sources. Additionally, biomass can be seen as a CO_2-storage or as energy storage. This leads to the great advantage of biomass: It can be stored and it is available independently of the current weather.

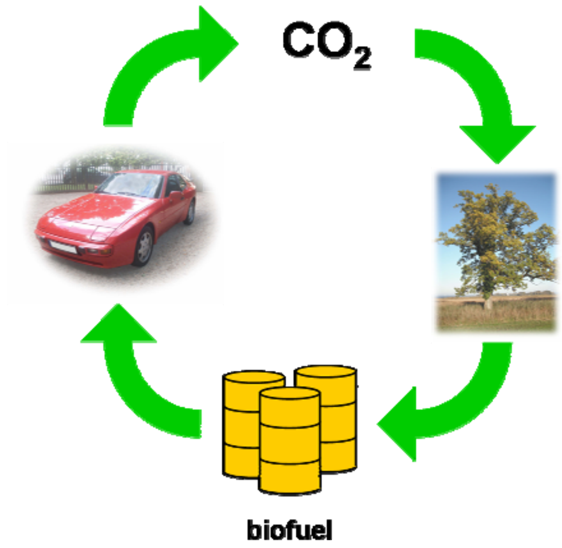


Figure 1.5: Carbon cycle for biofuels.

Besides, biomass cannot only be used for energy production, but also as raw material in chemistry. For this purpose it has to compete against materials from fossil sources. This competition can be won by the price or by the marketing for biomass based products.

A higher efficiency of energy transformation and energy usage is another solution for lower CO_2-emissions as less energy would be needed. This approach faces the challenge to increase also the efficiency of existing processes whose excess heat cannot yet be used. One possible client can be power stations as most big power plants are not in direct neighborhood to the potential consumers who would be able to use the excess heat. Due to a worldwide average of the electrical efficiency of coal-fired power plants in the range of 20% and 30% in Europe, respectively, new developments with up to 46% for coal fired power plants help to reduce the waste heat [2]. Using the heat for industrial or domestic purposes contribute also to less fuel consumption. However, using the heat often decreases the electrical efficiency. Nevertheless, even in the ideal case of Carnot, it is nowadays still almost half the spent energy which leaves the power station without being used for electricity production [3]. The percentages hardly depend on the source of heat (see Figure 1.6). It depends especially on the way of using the generated heat in order to obtain electricity and the losses during the energy transformations and energy transmissions. So, this is generally valid for nuclear power plants as well as for coal-, gas- or oil-fired ones, but, of course, also for biomass-fired and solar thermal power plants. The only fired power plants with higher efficiencies are recent developments for gas-fired power plants with Combined Cycle Gas Turbines (CCGT). They achieve about 60% electrical efficiency [4, 5].

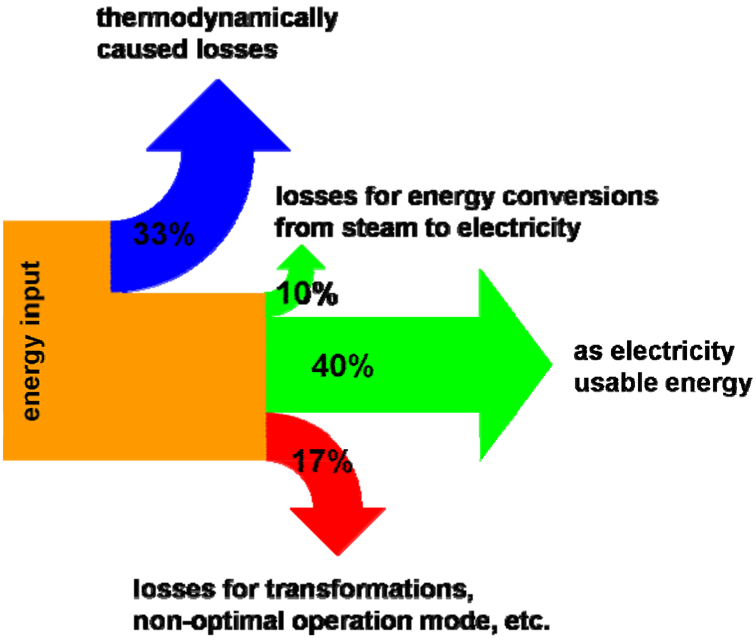


Figure 1.6: Efficiency of modern fired power plants.

Chemistry can contribute to achieving higher efficiencies, too. To achieve this, the amount of byproducts and waste has to be lowered while producing the same amount of products. Often this is achieved by higher selectivity or improved processes.

With regard to a further target, namely producing added value to biomass, the number of approaches is almost unlimited. New boundaries are reached by taking yet known reactions and looking besides the beaten tracks or to go further. In any case, it is favorable to start with cheap materials with intent to add value. In the optimum case waste can be used and fine chemicals are produced. Additionally, the starting material has to be known and has to be available in amounts, which permit to scale up. Nevertheless, there is the need of an existing market for this product as it is less easy to create a product and a market at the same time. Thus, it is preferable to replace an existing product by a new one or to change the chemical process of its production. For all these reasons, the use of cheap biomass as chemical platform is desirable.

The valorization of biomass requires chemical processing. To keep this process environmental responsible, the principles of green chemistry (see chapter 2.1) have to be considered. Therefore, water is an ideal solvent as it is not toxic and a good solvent especially for ionic compounds, but also for organic compounds when heated. In combination with excess heat, hydrothermal conditions are chosen for the valorization of biomass [6]. Incidentally, hydrothermal conditions are not only a natural phenomenon on the sea floor, but maybe also the source of our life where prebiotic syntheses were possible (see also chapter 2.4).

Therefore, this thesis aims at finding pathways to use and valorize biomass in hot water and, thus, to contribute to a lower dependency on fossil resources. In an ideal case the employed reaction parameters enable to employ excess heat to provide the needed energy for such processes.

2. **Fundamentals**

2.1 Green Chemistry

An increased awareness of the anthropogenic impact on the environment initiated a change in thinking. Principles such as cradle-to-cradle, also called C2C, follow the thought that the resources may be used, but in an efficient way, and the waste has to be the source for a new application. Below the line, the product comes from the nature and goes back to the nature. Thus, the ecologic footprint of our lives should be minimized [7].

In this context, there are developments to implement according principles to more specialized fields. For example, green chemistry is defined by a bedrock article of Clark in 1999 [8], and yet before, in 1998, by Anastas and Warner in "Green Chemistry: Theory and Practice". They manifested twelve principles for green chemistry:

"1. It is better to prevent waste than to treat or clean up waste after it has been formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. 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. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires." [9]

These twelve principles have a very high importance for green chemistry. They are constantly evoluting [10, 11] due to the importance of this relatively new topic. Some developments focus stronger on sustainability [12]. Nevertheless, there is also an extension of additional twelve principles which aim to gain more knowledge and awareness on side reactions, to find ways to diminish them and to document extensively [13]. Not only green chemistry is developed, but also green engineering. So, there are 24 principles of green chemistry and green engineering [14] and 13 principles of green chemistry and green engineering for a greener Africa [15]. These aim to decrease the footprint as much as possible by using local sources, for example the sun, to contribute to a common welfare and to avoid the mistakes which were yet made elsewhere [15].

The principles are also specialized for organic chemistry [16] or for analytical chemistry [17, 18]. The applicability and the direction of further developments are reflected in several publications [12, 19-23].

Recent investigations show the vast variety of green chemistry. Modern methods such as photo catalytic processes [24-27] are studied as well as the large-scale domain of fuels and chemicals based on biomass. One highlight is a cost-effective process to convert ligno-cellulosic biomass to liquid hydrocarbon fuels [28]. Another publication presents a promising one-step fractionation of catalyzed depolymerization of ligno-cellulosic materials [29]. Both contribute to a more efficient use of wood. Yu et al. published a combination of an ionic liquid as solvent with microwave irradiation as energy source in order to produce fatty acid methyl ester as biodiesel by enzymes [30]. Foley et al. suggested in the domain of the third generation of biofuels that a byproduct from algae has to be identified, because a scale-up of the biofuel production from algae will also increase the amount of byproducts. And this can generate or ruin the profitability [31]. The extraction of algal lipids during the production of biofuel from algae is also reported [32] so that a possible byproduct is yet found.

All in all, the twelve principles which were introduced by Anastas and Warner have an outstanding character and modifications for several fields of interest keep it up to date and adapted to more specialized domains. Besides, research in green chemistry still affords investigations of important topics such as photocatalysis and biofuels. Nevertheless, the publication of an organotin-oxomolybdate coordination polymer as green catalyst [33] shows further potential for green chemistry – regardless the yet achieved improvements.

2.2 Hydrothermal conditions

Among the various options to achieve greener chemical processes, the utilization of water as solvent is one possibility. Water is not toxic, cheap and almost everywhere available. In general it is not only a green, but also a good solvent for polar and ionic substances. Therefore it attracted more attention in recent years. But it is well known that especially organic compounds are hardly or insufficiently soluble in water. This can be improved by increasing the temperature. As a result many properties of water change, so also the solubility of organic compounds in water does. Replacing organic solvents by water or by other solvents having higher boiling points aims to decrease the emissions of Volatile Organic Compounds (VOC). And simplifying the separation after the reaction is a further argument for green chemistry to use hot water. In general, hydrothermal water is used in inorganic chemistry for a longer time, but in organic chemistry this method is just at the beginning of its possibilities.

Literature uses different conditions in dependence on the applications and calls them hydrothermal. This terminology is used for water from 75°C [34] to 450°C [35], but also for a gaseous mixture of hydrogen, nitrogen and water at 500°C [36]. Of course, in almost all cases the pressure is important as usually the water is liquid, as long as it is not above the critical point. When keeping a pressure being at least equal to the vapor pressure at this temperature, at least a part of the water remains liquid.

All in all, a lot of conditions are called to be hydrothermal as long as there is water included in the solvent and the temperature exceeds 100°C, the boiling point of water under normal pressure. Also reactions in the gas phase might count as hydrothermal reactions. However, solvothermal means the analogue, but in a solvent which is not water-based. This work bases on reactions in different, water-based solvents at temperatures from 125°C to 220°C.

2.3 Properties of hydrothermal water

Every hydrothermal reaction profits from the properties of hot water. As usually in nature, the properties change continuously as a function and every point of the function has only one derivative. However, regions of drastic changes exist and the critical point of a compound is one example. Therefore, hydrothermal water can be divided into several domains, but not all of them have well defined borders. The domains start with hot water and superheated water, proceed with subcritical and near-critical water, pass the critical point and end up with supercritical water. However, the nomenclatures of these domains are not always consistent.

As just mentioned the nomenclature is not always congruent. The critical point of water at 374°C and 221bar [37] acts as constant point of orientation in this field. Therefore, the upper limits of subcritical water and near-critical water as well as the lower limit of supercritical water are well defined.

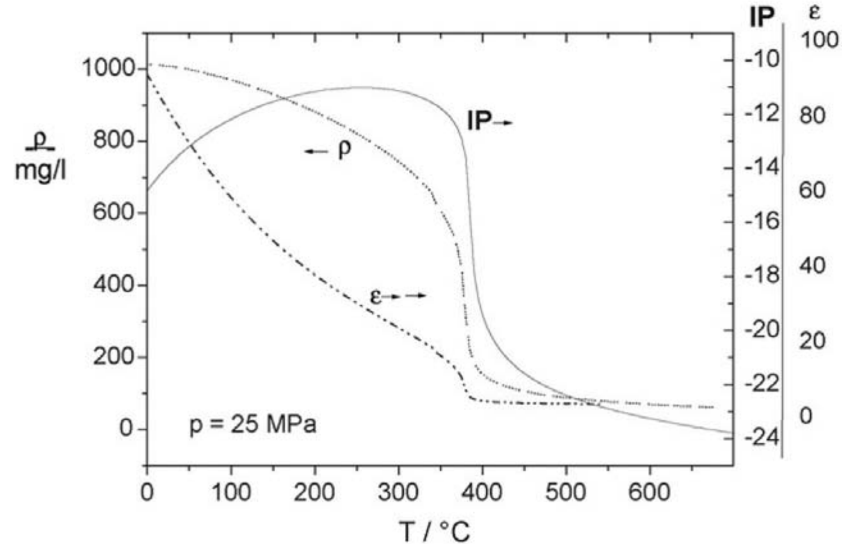


Figure 2.1: Density, dielectric constant and common logarithm of the ion-product of water in dependence of the temperature, from [38].

Figure 2.1 shows the temperature dependences for the density, ρ, the dielectric constant, ε, and the common logarithm of the ion product, IP, better known as $-pK_W$, at a pressure of

250bar. Obviously, all these three properties undergo important changes. The decrease of the density of water is well known from 4°C to 100°C, but above 100°C the decrease does not stop. Quite the contrast, the decrease gets more pronounced and, thus, the density of water lowers faster and faster while keeping the same heating rate. After passing the critical point the density lowers less and a plateau is almost reached. Then, the density changes depend on the pressure, but hardly on temperature. The lowered density is a result of weaker hydrogen bonds and causes higher convection rates in hydrothermal water.

The dielectric constant decreases rapidly with increasing temperature. Just before reaching the critical point the decrease per temperature difference reaches a minimum and then the dielectric constant drops off until approaching a very low, almost constant value at temperatures above the critical point. Also in this case, the pressure dependence increases.

The ion product is known to be 10^{-14}mol²/L² for water at 25°C. It can be seen in Figure 2.1 that this changes notably with the temperature. A maximum of 10^{-11}mol²/L² is reached at about 250°C and then it decreases again to about 10^{-12}mol²/L² at 350°C, but the value falls below 10^{-19}mol²/L² yet before 400°C. The maximal decrease is at the critical point. At 700°C 10^{-24}mol²/L² are within reach, but a minimum or a plateau is not yet obtained [38, 39]. Because of the low polarity of supercritical water, it is seen as a perfect substitute for organic solvents and the other parameters are expected to make it a good reaction medium [40-43].

A lower density of water eases the macroscopic mixture with other compounds due to a lower physical force supporting a separation. The decreased dielectric constant makes the water less polar and, respectively, more lipophilic and supports, thus, the microscopic miscibility of water and organic compounds under hydrothermal conditions. The changes of the ion product influence the pH and the pOH of water. This has important impacts on solubilities and on reactions in water, especially on acid- and base-catalyzed ones [44-47].

2.4 Hydrothermal reactions

Very different reactions have been reported to take place under hydrothermal conditions. In inorganic chemistry the productions of catalysts [48-52] and doped materials are particularly interesting [53-57]. But also several publications at the borderline between inorganic and organic materials are reported [58, 59]. The underrepresentation of organic chemistry comes from the lack of stability of several organic materials which decompose under hydrothermal conditions. By contrast, this opens the way toward the use of hydrothermal carbonization [60, 61].

Nevertheless, also organic reactions are possible under these conditions. Marshall reports the possibility to synthesize amino acids and amines above 150°C under hydrothermal conditions. For the reaction he takes the materials near hydrothermal vents into consideration [62]. Thus, he proposes a prebiotic synthesis of molecules being essential for life using hydrothermal vents which exist on the sea floor. They offer an energy source often in an environment without light. Thus, they are like an oasis in a desert with its own biosphere. The energy for these chemosynthetic-based ecosystems comes from the ground as the hydrothermal vents are at geological active zones [63]. Anyhow, there are also differences between hydrothermal vents themselves and black smokers especially in contents of chlorine, minerals and gas, but also in the temperature [64]. Both types are shown in Figure 2.2.

Figure 2.2: Hydrothermal vent (left) [65] and black smoker (right) [66].

However, not only life-essential reactions are possible, but also several, rather special organic syntheses such as the formations of esters, amides, alkyl amides, alkanes, and alkanoic acids can be carried out hydrothermally [67, 68]. Examples are shown in chapter 3.1. By contrast, behavior and more fundamental reactions of simple organic compounds under hydrothermal conditions are not well studied.

Besides, hydrothermal waste treatment raises interest [69-72]. For example, the recycling of nylon 6 can be done in subcritical water and ε-caprolactam is obtained [73].

Summing up, hydrothermal conditions offer many fields of applications. Their use can lead to a better comprehension of the beginning of life on earth, to an improved waste treatment or to new reaction pathways in synthesis of inorganic and organic chemistry.

2.5 Analyses

Most analyses were carried out per Gas Chromatography – Mass Spectroscopy (GC-MS) and quantified per Gas Chromatography – Flame Ionization Detector (GC-FID). Both instruments were fabricated by Shimadzu. The GC-MS was a GC2010 with a GCMS-QP2010S and an autosampler AOC-20i. The GC-FID was a GC-2014 with an AOC-20i. The GC-MS was used to identify the products and the GC-FID to quantify them. The quantification of the organic compounds was done due to the procedure published by Jørgensen et al. [158] with the increments given for the functional groups. Only for complex mixtures estimations for not identified products were made. For the quantification of the molecules the databases of GCMSsolutions, namely NIST05.LIB and NIST05s.LIB, were used. When necessary, they were verified by the Spectral Database for Organic Compounds (SDBS) of the National Institute of Advanced Industrial Science and Technology (AIST).

The heating rate of the column was 20°C per minute in a range from 40°C to 300°C. The hold time was 1min before and 5min after the heating. The FID detected all the time, whereas the MS started to detect after 1.5min, 1.75min or 2.0min in dependence on the necessity and ended after 19min. The detection was carried out in a m/z-range from 10 to 300. In order to assure a good transferability, both GCs were equipped with SUPELCO-columns of the type SLB 5MS with a length of 30m, a thickness of 0.25µm and a diameter of 0.25mm.

Toluene was used as internal standard to quantify the amounts of products as each change for the FID changed the intensity of the signals. This was not only influenced by the amounts of injected sample, but also by the pressure of hydrogen, the pressure of air and so on. Here, also the pressures in the gas lines behind the manual regulator valves were of interest.

Another used analytic instrument, used for results shown in chapter 5 was the Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) from Spectro Arcos. This was calibrated each time before using it and between the samples were some blank values in order to verify that there was no drift during the measurements. This instrument was used to quantify concentrations of metal ions.

To have comparable results the solutions had been diluted after centrifugation by the factor of 10 and these diluted solutions had been diluted by a factor of 40 to have a dilution of 1:400. These with 2% $HNO_{3(aq)}$ diluted solutions were used to make analyses by an ICP-OES with a Scott Spray Chamber and cross flow nebulizer. The calibrations and the measurements were taken out for palladium at 340.458nm and 324.270nm. For cerium the signals for wavelengths of 418.660nm and 448.691nm were analyzed. Each measurement point was averaged from three individual measurements at each of the two mentioned wavelengths. So every measurement point is calculated from six single results to increase the certitude.

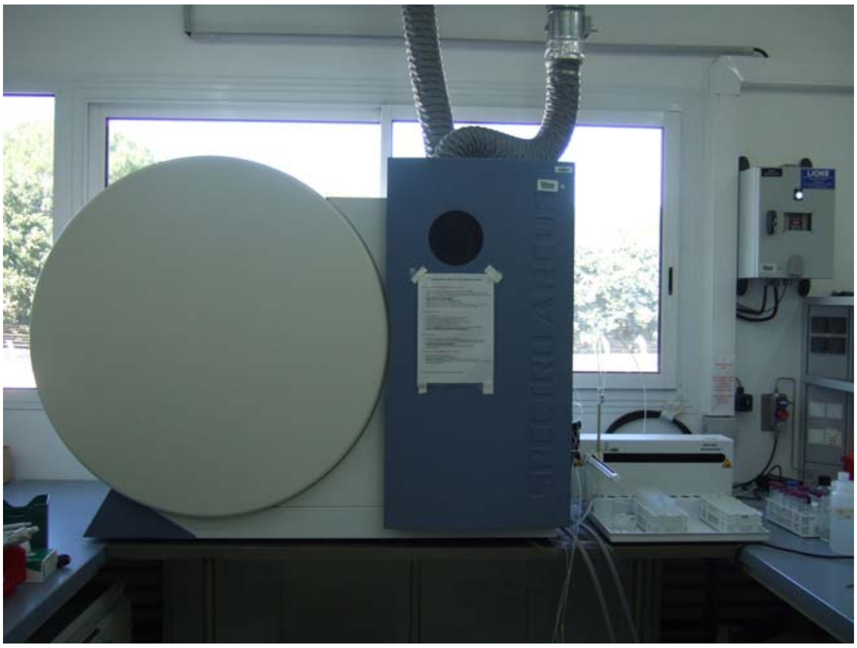


Figure 2.3: Picture of ICP-OES.

2.6 Sample preparation

The starting materials were used as bought. Especially Sigma-Aldrich, but also Fluka and Riedel-de Haën were the main suppliers. The given exactitudes are always a minimum. Thus, for example, if 1.0g is written, the mass was between 0.98g and 1.02g and therefore often in the range of the exactness of the balance. Writing 1.0g should keep the correctness without loosing the readability. Differing from this exactness is mentioned.

The samples were prepared in autoclaves with inlets made of polytetrafluoroethylene (PTFE) as shown in Figure 2.4. The reaction volume was about 21mL, usually about 10mL solution were used. The inlets were cleaned before usage.

Figure 2.4: Autoclaves made of metal and inlets made of PTFE.

The samples were heated in compartment dryers from Binder. The models ED 23 and ED 53 were used. The electronically controlled preheating chamber assured a temperature accuracy of 0.3°C standardized at 70°C.

After the reaction the reaction mixture was taken out of the inlet, the inlet was cleaned with 3.0mL EtOAc and after unifying these two volumes it was mixed in order to extract the organic compounds into the organic phase. For the analyses usually 100µL of this extract were mixed with 900µL of a solution of EtOAc which contained 100µL toluene per 100mL solution. This was used as internal standard. If the concentration in the extract was too low, another ratio was applied.

2.7 Reactions of 1-phenyl-1,2-ethanediol

Avola et al. showed in previous work that 1-phenyl-1,2-ethanediol was converted to 2,4-diphenyl-3-butenal at 180°C in 1.0mol/L NaCl by an aldol condensation [74]. This raised the question, if the reaction could advance in other solvents or at higher temperatures.

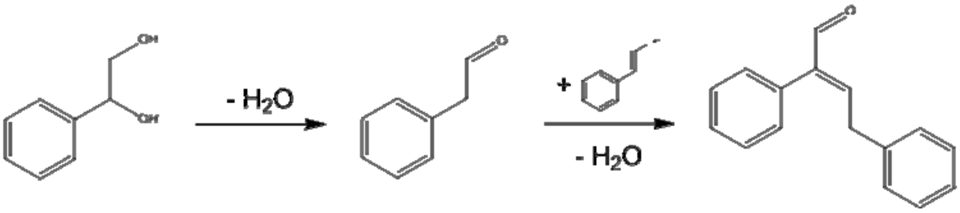


Figure 2.5: Reaction from 1-phenyl-1,2-ethanediol to 2,4-diphenyl-3-butenal.

Therefore, the reactions of 1-phenyl-1,2-ethanediol were studied in this work using different solvents at temperatures from 160°C to 220°C.

1-Phenyl-1,2-ethanediol reacted in pure water to phenylethanal and 2,4-diphenyl-3-butenal. From 200°C on the conversion was complete. 2-Phenylnaphthalene was additionally obtained at 220°C.

Using 1.0mol/L NaCl as solvent gave the same results as pure water. Only the yields in general and the selectivities for phenylethanal at 180°C, for 2,4-diphenyl-3-butenal at 200°C and for 2-phenylnaphthalene at 220°C were higher.

HCl as solvent led to 2-phenylnaphthalene as main product yet at 160°C. At 180°C the yield of 2-phenylnaphthalene was higher. At 200°C and at 220°C it was obtained pure.

Taking everything into consideration, 1-phenyl-1,2-ethanediol reacted stepwise to 2-phenylnaphthalene. Especially in pure water the reaction was well determined by the temperature. HCl decreased the needed temperature significantly. Drawing conclusions from the studies according to the products as a function of the temperature and of the solvent, the mechanism shown in Figure 2.6 was developed. This reaction is a way how to synthesize 2-phenylnaphthalene from 1-phenyl-1,2-ethanediol very efficiently. As 2-phenylnaphthalene is very unpolar, the separation at room temperature can be carried out easily after the reaction.

The first part of the mechanism of this reaction combines dehydration with an aldol reaction. Then an intramolecular Friedel-Crafts type alkylation follows. Finally, a dehydration leads to an aromatization and 2-phenylnaphthalene is obtained.

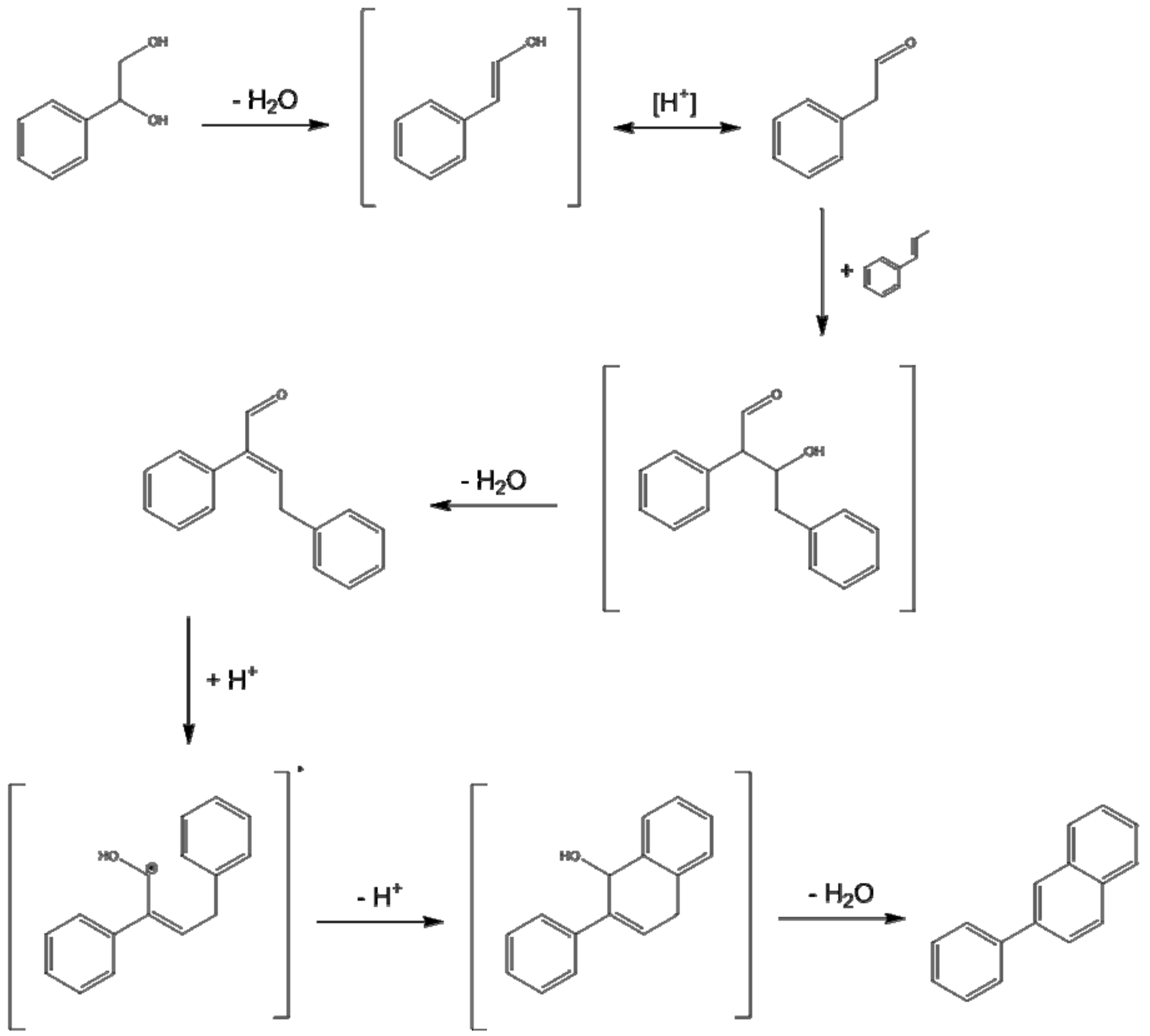


Figure 2.6: Mechanism from 1-phenyl-1,2-ethanediol to 2-phenylnaphthalene.

1-Phenyl-1,2-ethanediol reacted stepwise to 2-phenylnaphthalene. The steps were influenced by the temperature and by the solvent. HCl decreased the needed temperature remarkable.

2.8 Perspective

On the one hand, dehydration and aldol reaction make the chemistry of diols under hydrothermal conditions interesting. The high amount of possible combinations opens doors to various products.

On the other hand, an attempt followed for applying the observed intramolecular Friedel-Crafts type reaction also for intermolecular reactions. The use of an alcohol is one of several advantages for a greener chemistry of the Friedel-Crafts reaction. That is why the Friedel-Crafts type reaction of an alcohol with an aromatic compound under hydrothermal conditions is object of further investigation.

Therefore, studies on diols can be found in chapter 3. There are not only fundamental studies, but also an application as biofuel is reported. Results of studies on Friedel-Crafts type reactions are given in chapter 4. Benzyl alcohol can act both as alcohol and as aromatic compound and, thus, polymerization is accessible under hydrothermal conditions. Industrial applications of the polymerization for separation processes as well as other biomass-based separation processes are topic of chapter 5. In the end, a conclusion and perspectives round up in chapter 6.

3. Reactions of diols under hydrothermal conditions

Nature produces a lot of alcohols. Among others, most of the carbohydrates are alcohols. Biologic and synthetic reactions of alcohols are yet well known, but many carbohydrates are also diols. Their reactions are less studied.

For reasons of formal reaction possibilities the trimerization of diols could form ring systems and after dehydration aromatic compounds would be accessible as shown in Figure 3.1. This formation of aromatic compounds would allow synthesizing derivatives of benzene from renewable resources. As this is still very limited, for example to a complete analysis of a compound and a following Fischer-Tropsch synthesis, this reaction would offer a much directer way from biomass to aromatic compounds.

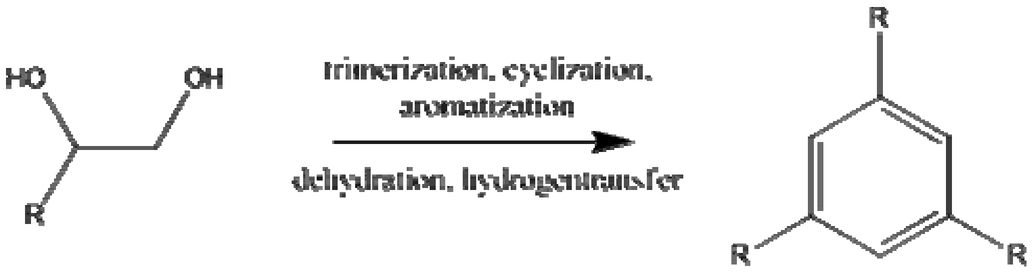


Figure 3.1: Theoretic reaction from mono-substituted diols to aromatic compounds.

The use of hydrothermal conditions for this reaction might be advantageous as water is not only solvent for the diols, but also an agent taking part in the reaction. Additionally, the obtained aromatic compounds will easily separate from the solvent when the reaction mixture cools down after the reaction time. Thus, the separation will be very simple and environmental friendly.

That is why diols will be investigated here under hydrothermal conditions. The simplest diol, ethylene glycol will start and then 1,2-propanediol will follow.

3.1 Literature review

Diols such as ethylene glycol or 1,2-propanediol cannot be exploited directly from natural sources. Of course, they are accessible from fossil sources via ethene, epoxide, glycidol and other intermediary molecules, but chemistry also allocates possibilities how to generate them based on biomass. The approach of chemical platforms in this domain becomes established.

Ethylene glycol can be obtained from sorbitol or xylitol [75, 76]. Glycerol is obtained from the production of biodiesel out of vegetable and animal fat and oil and can provide ethylene glycol as well as 1,2-propanediol and many other compounds [76, 77]. Lactic acid is found in milk, but it can also be prepared from glucose by fermentation [78]. Then it is the gate to acrylic acid, polylactics, 1,2-propanediol or other useful molecules [76].

Due to the availability of two neighbored functional groups, it is expected that diols react under hydrothermal conditions. The number of possible reaction pathways is high and because of dehydration also aldol reactions occur as yet observed for 1-phenyl-1,2-ethanediol. Thus, the formation of new C–C bonds is probable and would end up in new synthesis routes for more complex compounds. This is of interest as until now biomolecules mostly loose complexity and mass during their treatment. Nevertheless, simple molecules are easier to handle, but often of lower value, and therefore the C–C bonding can create added value to simple compounds. Hydrothermal reactions of simple diols are a promising strategy.

One way to use glycerol is to transform it into lactic acid. The corresponding dehydrogenation is described as an alkaline hydrothermal conversion at 280°C which obtains a yield of 89.9% lactic acid after 90min. Additionally, both dehydrations and decarboxylations were reported [79]. In contrast to an older opinion, hydrothermal dehydration is thermodynamically feasible due to Shock [80, 81] and therefore in coherence to observations. Also a water transfer can be justified [82].

But acid- and base-catalyzed reactions are also reported from organic chemistry. Several ways of hydrothermal conversions such as keto-enol tautomerism, β-hydroxycarbonyl elimination, rearrangement, oxidation, hydrothermolysis, and hydrolysis are reported by Jin. In the same work effects of metal ions on the hydrothermal conversion of glycerol into lactic acid are mentioned. Due to a change of the associated hydroxides and a change of the mechanism of the reaction alkali metal hydroxides led to a much higher yield of lactic acid than alkaline earth metal hydroxides [6].

Ramírez-López et al. reported the synthesis of lactic acid from sorbitol. Due to the high functionality not only keto-enol tautomerism, but also a reverse aldol-condensation and an intramolecular Cannizzaro reaction were observed [83]. This ends up in several parallel pathways for the conversion of sorbitol and other organic compounds with a high number of functional groups. In addition, also carbon-carbon cleavage is possible under hydrothermal conditions. This offers the potential to cut 6-carbon compounds such as glucose into 2-carbon, 3-carbon and 4-carbon compounds [84]. CO_2 and formic acid complete the accessibility of 1-carbon and 5-carbon compounds. This is achievable by hydrothermal reactions, too [6, 83].

Of course, there are also hydrothermal reactions with catalysts. It is proposed that alcohols can be used for alkylations, if a chlorine functionalized tin dioxide converts the alcohol to the corresponding chloroalkane before the reaction takes place between the chloroalkane and an aromatic compound [85].

Another reaction mentioned in the literature is the abiotic condensation of ethylene glycol with alkanoic acids to mono- and bisalkanoates. The reaction scheme is given in Figure 3.2. Besides, due to Rushdi et al. this type of reaction is transferable to glycerol, whereas trialkanoates are not reported [39].

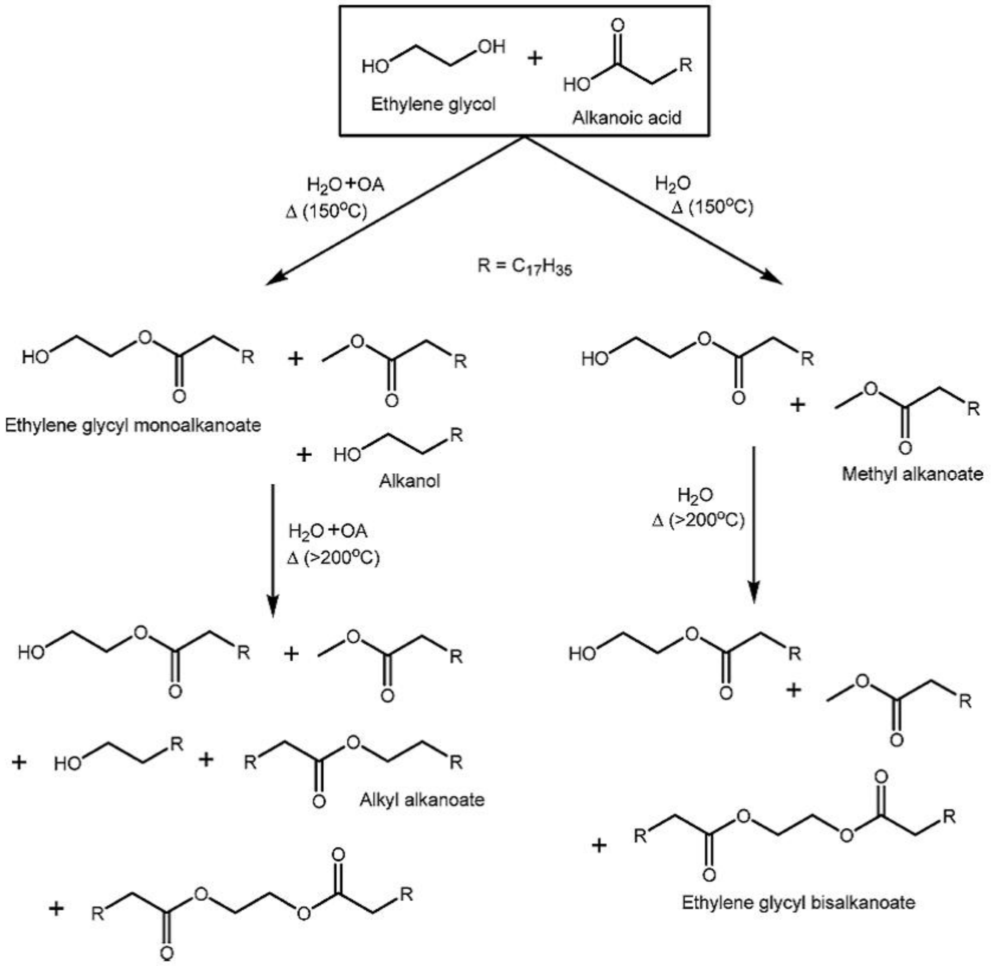


Figure 3.2: Abiotic condensation of ethylene glycol, from [39].

Thus, organic lipid compounds can be synthesized easily without a bio-organism starting from these fatty acids and alcohols. However, the hydrothermal synthesis opposes the decomposition of the products [39].

These first insights show a broad overview over the variation of organic reactions under hydrothermal conditions. In the following the reactions of simple diols are described.

Regarding published hydrothermal reactions, the simplest diol, ethylene glycol, was solvent or auxiliary agent in several studies in hydrothermal media. As part of the solvent it has influences on growth, shape and properties of crystals [86-88]. Only in a minority of publications ethylene glycol takes part in the hydrothermal reaction. For example, it is the product of an hydration of ethylene oxide [89], it if formed out of corn starch [90] or it is used as reducing agent [91]. Other articles described its role for the acetalization of cyclohexanone [92] or reformed it to hydrogen and carbon dioxide [93]. But there was no publication found which reported reactions of the simplest diol, ethylene glycol, on itself. Due to the fact that there is one functional group per carbon atom it is expected that hydrothermal reactions take place.

None of the hits for hydrothermal reactions of propanediol used 1,2-propanediol as starting material. In one case formation of 1,2-propanediol out of propylene oxide was subject [94]. As propanediol in general and especially 1,2-propanediol are simple diols with two functional groups within a 3-carbon compound, it could be supposed that hydrothermal reactions can be carried out. Therefore 1,2-propanediol is tested as the most comparable compound to ethylene glycol. Besides, glycerol is known to pose some problems as it undergoes not only hydrothermal reactions, but also hydrothermal carbonization. The latter causes a coal-like slurry which is hard to be analyzed and also hard to be treated.

Summing up, there are a lot of scientific articles about hydrothermal reactions. Fewer articles contain hydrothermal organic reactions. Basic studies on reactions of simple diols such as ethylene glycol and 1,2-propanediol are still lacking. Nevertheless, due to the high ratio of functional groups per carbon atoms they are feasible candidates for a number of possible reactions.

Hence, reactions of diols and equivalents of diols will be investigated qualitatively under hydrothermal conditions.

3.2 Reaction conditions

In chapter 3 the reaction conditions were standardized. For these investigations 0.5g organic compound were heated up for 16h and the reaction temperature was changed between 125°C and 220°C. The kind of solvent was also changed, but the volume of 10mL was constant. Table 3.1 and followings summarize which compound was tested at which temperature and in which solvent.

	125°C	150°C	180°C	200°C	220°C
Water	+	+	+	+	+
1.0mol/L NaCl	+	+	+	+	+
0.5mol/L NaCl, 0.5mol/L HCl	+	+	+	+	+
0.5mol/L HCl	+	+	+	+	+
1.0mol/L HCl	+	+	+	+	+
1.0mol/L $BaCl_2$	-	-	-	-	-
1.0mol/L $FeCl_3$	-	-	-	-	-

Table 3.1: Investigated reaction conditions for ethylene glycol (0.81mol/L).

	125°C	150°C	180°C	200°C	220°C
Water	+	+	+	+	+
1.0mol/L NaCl	+	+	+	+	+
0.5mol/L NaCl, 0.5mol/L HCl	+	+	+	+	+
0.5mol/L HCl	+	+	+	+	+
1.0mol/L HCl	+	+	+	+	+
1.0mol/L $BaCl_2$	-	-	-	-	+
1.0mol/L $FeCl_3$	-	-	-	-	+

Table 3.2: Investigated reaction conditions for propanediol (0.66mol/L).

	160°C	180°C	200°C	220°C
Water	+	+	+	+
1.0mol/L NaCl	+	+	+	+
0.5mol/L NaCl, 0.5mol/L HCl	+	+	+	+
0.5mol/L HCl	+	+	+	+
1.0mol/L HCl	+	+	+	+
1.0mol/L $BaCl_2$	+	+	+	+
1.0mol/L $FeCl_3$	+	+	+	+

Table 3.3: Investigated reaction conditions for phenyl-ethanediol (0.36mol/L).

	220°C
water	+
1.0mol/L NaCl	+
0.5mol/L NaCl, 0.5mol/L HCl	+
0.5mol/L HCl	+
1.0mol/L HCl	+
1.0mol/L $BaCl_2$	+
1.0mol/L $FeCl_3$	+

Table 3.4: Investigated reaction conditions for acetone (0.86mol/L).

	180°C
water	+
1.0mol/L NaCl	+
0.5mol/L NaCl, 0.5mol/L HCl	+
0.5mol/L HCl	+
1.0mol/L HCl	+

Table 3.5: Investigated reaction conditions for acetophenone (0.42mol/L).

3.3 Reactions of ethylene glycol

The reaction of ethylene glycol on itself was studied from 125°C to 220°C in different aqueous solvents.

Using pure water as solvent did not lead to products until 200°C. At 220°C a cyclopent-2-enone derivative with alkyl side chains was obtained. Besides, 2-methyl-dioxolane was formed. But also a derivative of fumaric acid and 4-carbon and 6-carbon compounds were observed.

A solution of 1.0mol/L NaCl as solvent gave 2-ethyl-butenal, the aldol condensation product, at 125°C. At 150°C a bit of chloroethanol was observed and at 180°C and 200°C low amounts of 2-methyl-1,3-dioxolane were formed. Heating to 220°C with the same solvent led to the same products as with pure water except for the cyclopent-2-enone derivative.

A solution with 0.5mol/L NaCl and 0.5mol/L HCl as well as 0.5mol/L HCl and 1.0mol/L HCl gave almost the same results. At 125°C chloroethanol was formed. More chloroethanol was obtained at 150°C and 2-methyl-1,3-dioxolane was a byproduct. At 180°C 1,4-dioxane was formed as main product which was accompanied by the products obtained at 150°C and additionally 2-butenal and methyl-cyclopent-2-enone. Especially 1.0mol/L HCl led to higher amounts of byproducts. After reaction at temperatures of at least 200°C the amount of byproducts increased further and several 4-carbon, 6-carbon and 8-carbon compounds were obtained. Among these were a cyclopent-2-enone with three carbon atoms in the side chains and benzene.

Thus, the solvent and the temperature influenced the reaction of ethylene glycol. A higher temperature led to a higher amount of products and the kind of products was influenced by the solvent. Usual reactions under hydrothermal conditions such as dehydrations, ether formations and aldol reactions are necessary to form the observed compounds.

Benzene gained special interest. It was formed at 200°C in 1.0mol/L HCl in very low amount. Figure 3.3 displays the GC-MS chromatogram of the products after the reaction and in a second step it is zoomed to the peak for benzene. Even if the peak of an impurity of the solvent is just next to the peak for benzene, the existence of benzene was proven by the MS-data, but also by a reference sample of benzene. The synthesis of benzene out of a diol would open the way from biomass to the benzene based chemistry. That is why the formation of benzene is interesting in this case even though it is formed in traces. Unfortunately, the obtained reaction mixture was too complex to consider this approach as reasonable to produce benzene industrially. Therefore, ethylene glycol was not further investigated as a possible starting material for hydrothermal syntheses.

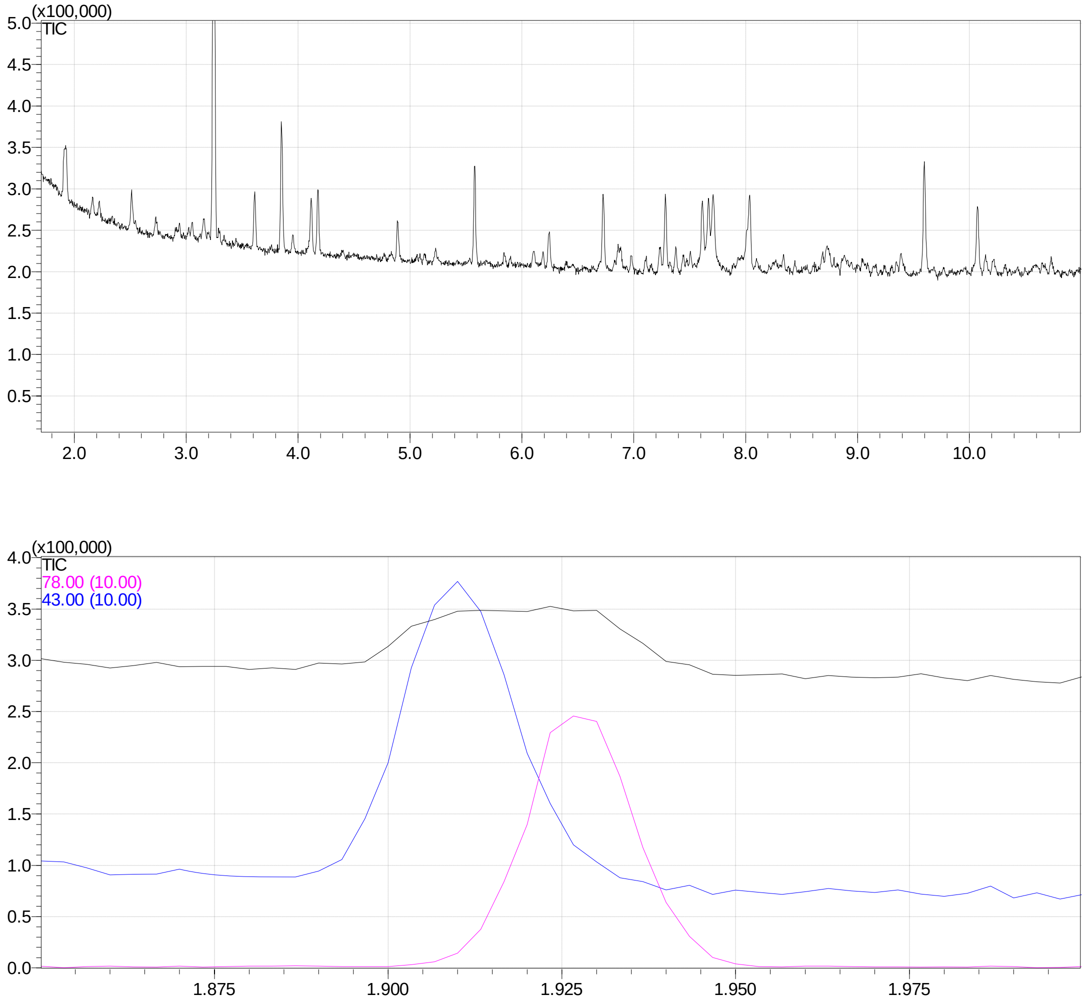


Figure 3.3: GC-MS chromatogram of ethylene glycol after reaction in 1.0mol/L HCl at 200°C and an excerpt with a low trace of benzene.

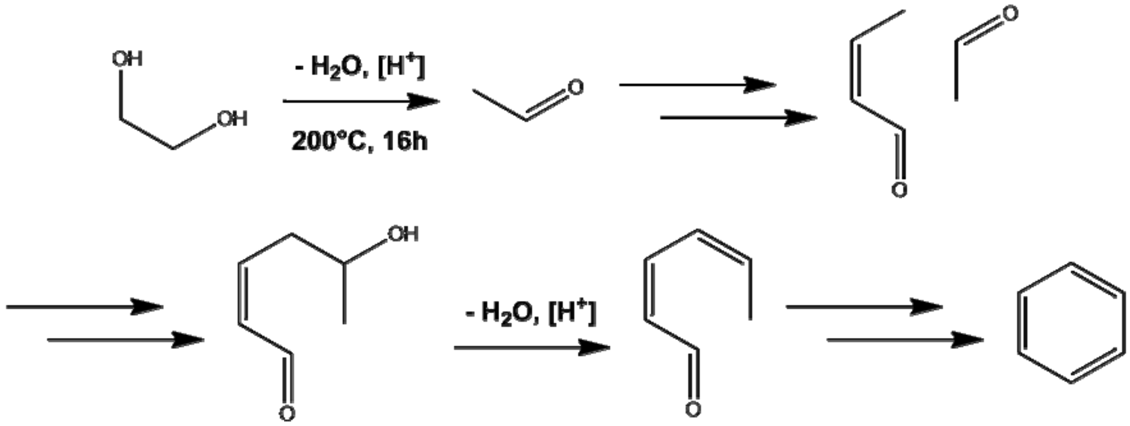


Figure 3.4: Reactions scheme for the formation of benzene from ethylene glycol.

Ethylene glycol formed several products in dependence on the solvent and the reaction temperature. Mainly 4-carbon, 6-carbon and 8-carbon compounds were formed. Benzene was the product of highest importance.

3.4 Reactions of 1,2-propanediol

As for ethylene glycol, temperatures from 125°C until 220°C were studied for the reaction of 1,2-propanediol. Additionally, the solvent was also changed.

Pure water as solvent at 125°C did not lead to products. From 150°C on low amounts of 2-methyl-2-pentenal, a derivative of cyclopent-2-enone and two isomers of 2-ethyl-4-methyl-1,3-dioxolanes were formed in low amounts. At 180°C mesitylene (C) was formed additionally and 2-methyl-2-pentenal (A) was the main product (see also Figure 3.5). 200°C and 220°C led to 2-ethyl-4-methyl-1,3-dioxolanes as main products and 2-methyl-2-pentenal was byproduct. At 220°C low amounts of (C) and a derivative of cyclopent-2-enone (B) were also formed.

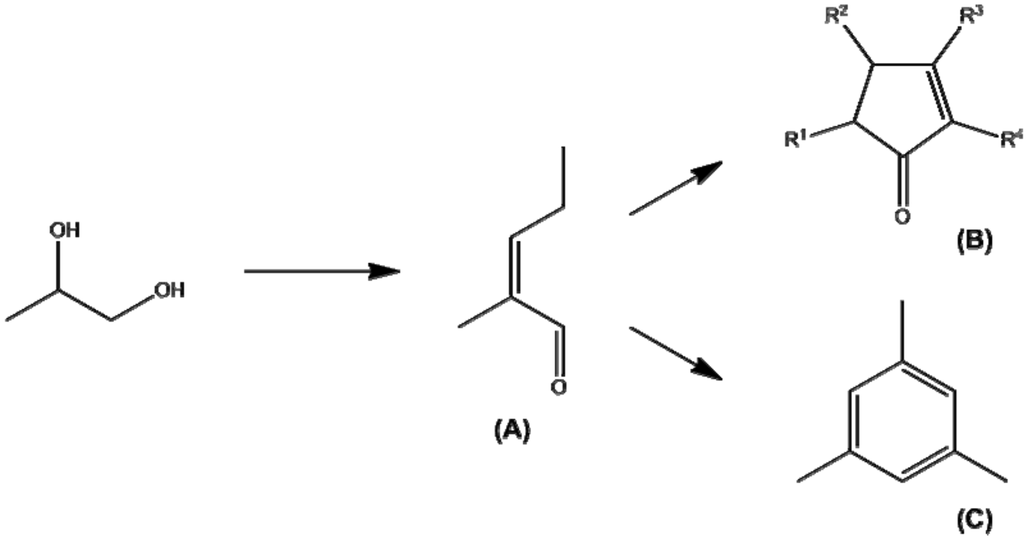


Figure 3.5: Reaction of 1,2-propanediol to its main products.

There were no products in 1.0mol/L NaCl until 150°C. At 180°C two isomers of 2-ethyl-4-methyl-1,3-dioxolanes were formed. Their amount was higher at 200°C, but at 220°C it was only byproduct. (A) was obtained as byproduct at 200°C and as main product at 220°C. (B) was formed as byproduct at 220°C in 1.0mol/L NaCl.

Also three HCl containing solutions were used as solvents. These were 0.5mol/L HCl, 1.0mol/L HCl and a solution of 0.5mol/L HCl and 0.5mol/L NaCl. At 125°C they resulted in traces of 2-chloro-1-propanol and the main product was 2-methyl-2-pentenal. Two isomers of 2-ethyl-4-methyl-1,3-dioxolane and (B) were byproducts. In 1.0mol/L HCl also (C) was obtained in traces. At 150°C and higher temperatures (A), (B) and (C) were the product. (B) was main product and (A) lost importance with increasing temperature and especially in 0.5mol/L HCl and 1.0mol/L HCl. 1.0mol/L HCl led at temperatures of 200°C and 220°C to higher amounts of impurities.

Even if 1-chloro-2-propanol was formed here only in traces, in literature it was yet suggested to be a reactive compound. The formation of mesitylene confirms the postulated reaction of diols (see Figure 3.1). Besides, the yield of mesitylene is much more satisfying than the scarce formation of benzene from ethylene glycol under similar conditions. A derivative of cyclopentenone raises the question for the exact mechanism which is topic of chapter 3.6.2.5. Further investigations with a more application-oriented point of view follow in chapter 3.6 after studies on equivalents of diols.

(B) and (C) are produced by a combination of three molecules of the starting material. (A) consists of only two molecules, but it is an intermediate for the formation of the other two main products.

The reaction of 1,2-propanediol under hydrothermal conditions (see Figure 3.5) was strongly influenced by temperature and solvent. Choosing the solvent optimized the yield of the desired product. Especially, high amounts of trimerization products were achieved.

3.5 Reactions of acetone and acetophenone

Acetone and 1,2-propanediol can interconvert under hydrothermal conditions and, thus, they are equivalents. For this purpose, a dehydration of 1,2-propanediol has to be followed by a keto-enol tautomerism or vice versa. For the same reasons acetophenone is expected to be in equilibrium with 1-phenyl-1,2-ethanediol.

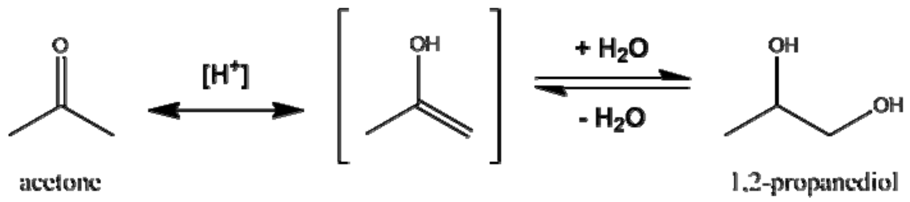


Figure 3.6: Equilibrium between acetone and 1,2-propanediol.

Acetone reacted at 220°C in pure water to the main products mesitylene, a derivative of cyclopent-2-enone and 4-methyl-3-penten-2-one. The derivative of the cyclopent-2-enone was the same as for 1,2-propanediol. In 1.0mol/L NaCl the results were the same.

Using HCl containing solvents, namely 0.5mol/L HCl, 1.0mol/L HCl or a solution of 0.5mol/L NaCl and 0.5mol/L HCl, led especially to mesitylene and to a compound similar to 2-hexanone, probably a methyl-pentanone. Other isomers of 2-hexanone were also observed. Besides, a lot of byproducts were formed which diminished the purity.

Thus, acetone forms some products as 1,2-propanediol does, but other products show differences. Due to that, acetone and 1,2-propanediol do not reach equilibrium under the tested conditions and another mechanism occurs or occurs additionally. The formation of 5-methyl-2-pentenone is shown in Figure 3.7. A consecutive reaction to mesitylene is possible.

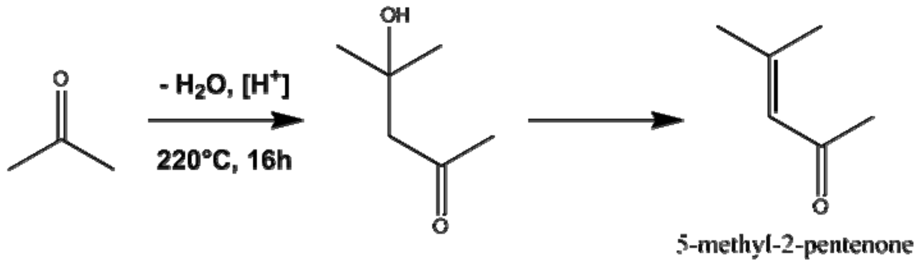


Figure 3.7: Main reaction of acetone.

Acetophenone did not react remarkable on itself at 180°C in pure water, in 1.0mol/L NaCl, in 0.5mol/L HCl, in 1.0mol/L HCl nor in a solution with 0.5mol/L HCl and 0.5mol/L NaCl. Thus, this was independent of the choice of the solvent.

Only low amounts of styrene were observed using NaCl as solvent. Benzaldehyde was found in low quantities, when pure water or 1.0mol/L NaCl was used.

Therefore, at 180°C acetophenone was apparently not in equilibrium with 1-phenyl-1,2-ethanediol. It is also worth noticing that the above described aldol condensation was not observed.

In conclusion, the equilibria of ketones and the corresponding 1,2-diols are possible under hydrothermal conditions, but this does not include that the two starting materials are interchangeable without any side effect. These two examples show certain interchangeability for acetone, but not for acetophenone. The influence of the reaction conditions on the reaction was confirmed in the case of acetone.

Acetone showed a certain degree of interchangeability with 1,2-propanediol, but not all of the obtained products were yet known from 1,2-propanediol.

Acetophenone did not react at 180°C in the tested solvents. It is not interchangeable with 1-phenyl-1,2-ethanediol.

3.6 Valorization of 1,2-propanediol as product from glycerol

Taking these promising results into account, the hydrothermal reactions of 1,2-propanediol were investigated in more details for two reasons. Firstly, 1,2-propanediol can be obtained from glycerol which is byproduct of the biodiesel production and, thus, based on biomass. Secondly, 1,2-propanediol gave a remarkable amount of trimerized products which could be useful. Therefore, a biomass-based product can be converted into trimerized products and even aromatic ones.

3.6.1 Literature review

Fossil fuels are synthesized under hydrothermal conditions from biomass [6]. Anyhow, renewable resources can also obtain an added value by hydrothermal treatment within several hours. Therefore, these conditions are promising not only for the preparation of compounds of high carbon-contents. Many publications about biofuels and biorefinery are published and in the following overviews over these topics are given.

3.6.1.1.Biofuels

Primary biofuels such as wood, wood pellets or biological residues are untreated. Often they are used for heating. This can be in a stove for cooking, but also for firing a power plant. Due to the simple employment of and the easy access to primary biomass, its use is broadly known for a long time [95].

Secondary biofuels are received after treating biomass. In Brazil the most popular secondary biofuel is ethanol from sugar cane, while especially in Europe still biodiesel in the form of Fatty Acid Methyl Ester (FAME) is better known. Secondary biofuels can be divided into several generations of biofuels due to different feedstocks and technical processes [95].

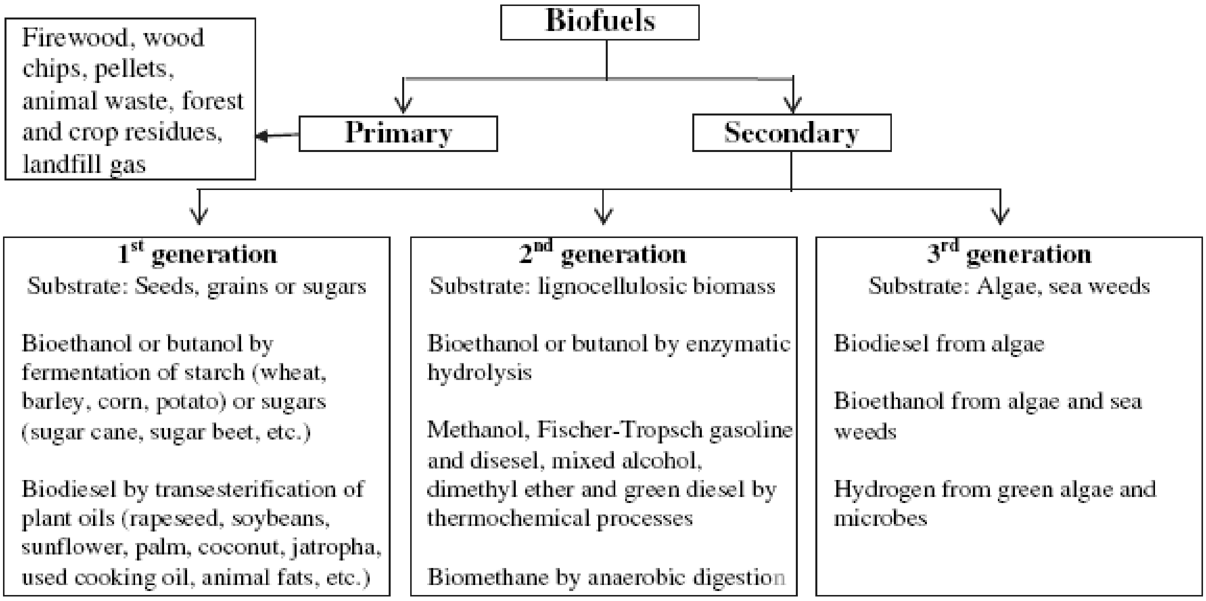


Figure 3.8: Scheme explaining the different biofuels, from [95].

Before the raise of biofuels, vegetable oil has been used in diesel engines without further treatment. The oil has been called Green Diesel. For this purpose also cheap oil from supermarkets has been put into the tanks instead of using it for alimentation.

In dependence of the definition, the first generation of biofuels comprises biodiesel, bioethanol and biogas. These products are obtained by esterification of biologic oils, fermentation of starch or other fermentable agricultural products. In general these products are prepared from stocks which can be used as food. Increasing amounts of these biofuels compete with food production for the feedstock and therefore also for used area. In some regions of the world the plantation of Jatropha might be one solution. This plant also flourishes on poor soils which cannot be used for food agriculture, but the vegetable residues can help to fertilize other soils and the oil can be transformed into biodiesel [96].

Second generation biofuels are in less competition to human alimentation. This is due to the fact that some of these technologies also can use inedible parts of plants. Thus, the whole plant can be used – some parts for food and the rest for fuel. Or the whole plant can be used for fuel production what would in both cases increase the efficiency of the plant and decrease the needed area. One way to produce second generation biofuel is a synthetic way. For this purpose the low-value biomass such as straw or wood is carbonized and than the biofuel is synthesized in a way similar to the Fischer-Tropsch synthesis [96].

The third generation biofuels base on microscopic organisms. Thus, the competition between food and fuel should be eliminated, but the remaining demands on research increase. Some types of algae, but also fungi and yeasts are expected to be suitable [95].

The generations of biofuels are not well defined as some authors pay more attention to the used resources while others to the employed technologies. Therefore, also a fourth generation of biofuel can be introduced as well as, for example, a generation between the first and the second generation. In any case, the here defined generations allow the statement that the first generation has reached the market, the second generation exists yet in rather small pilot plants and the third generation is still in research.

3.6.1.2.Biorefinery

Due to a more general view, secondary biofuels are products from biorefinery as they are transformed from their natural form to a more specialized product. But the transformation of biomass results also in the formation of byproducts. For example, glycerol is the main product of the process of biodiesel production.

As the production of biodiesel increases the recent years also the production of glycerol increases. Nevertheless, the increase of glycerol production lacks in glycerol applications. Glycerol is used in many domains such as agriculture, pharmaceutics, cosmetics, food additives and for heating, but pathways how to use it in huge quantities as building block in chemical industry are not yet implemented. However, some ways are known how to start the biorefinery in order to replace fossil sources by glycerol-based products.

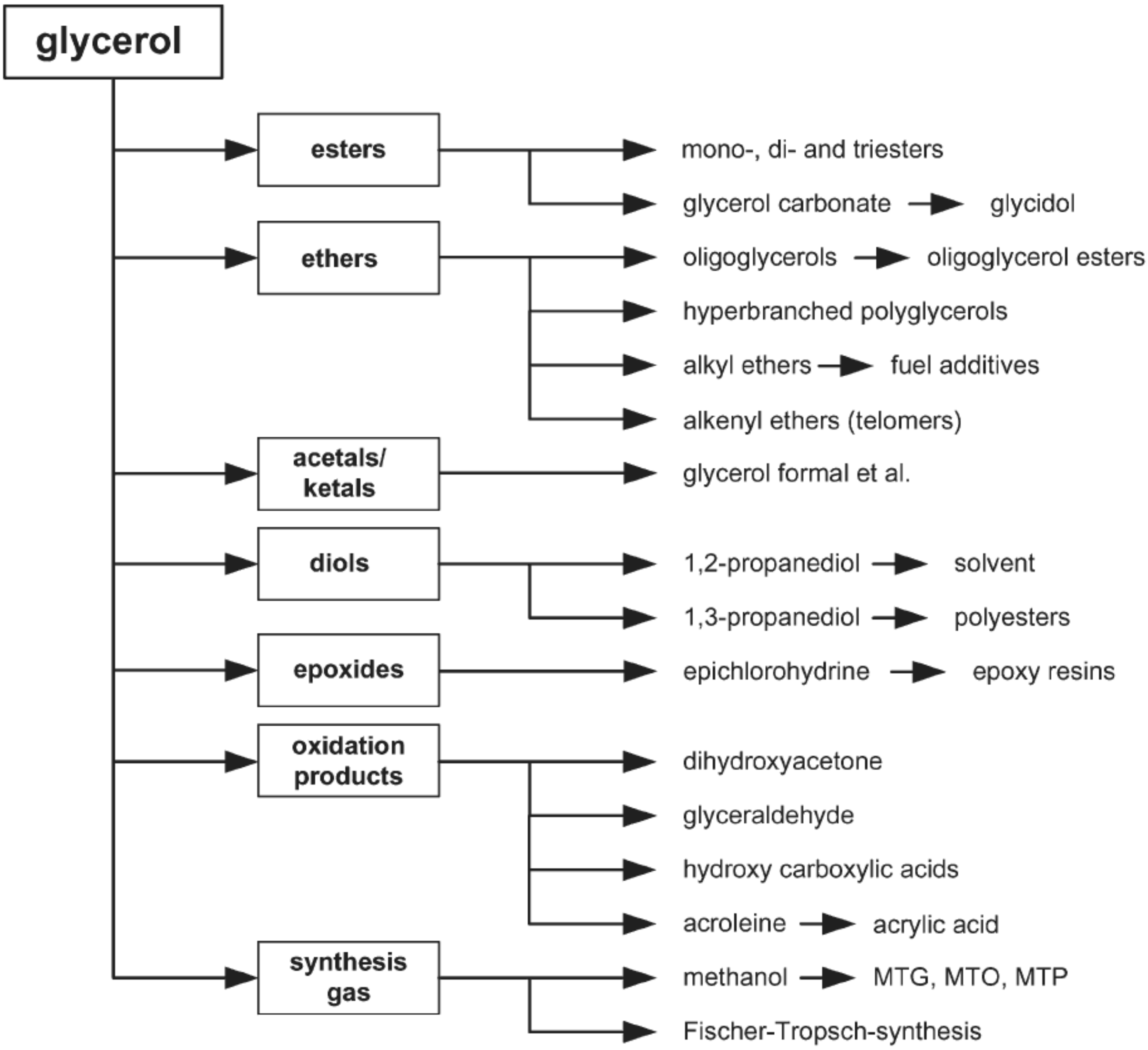


Figure 3.9: Biorefinery of glycerol and its products, from [97] – Reproduced with permission of The Royal Society of Chemistry.

On the one side, glycerol can be transformed to esters, ethers, carbonates, and alkyl esters without destroying the original structure of glycerol. Also some acetals and ketals of glycerol which can be used as additives for fuels are technically feasible and useful at the same time. On the other side, glycerol can be used to generate synthesis gas. Therefore, glycerol is broken down to 1-carbon compounds. After purification, this synthesis gas can be stored or used directly for Fischer-Tropsch syntheses, for example for the formation of synthetic biofuels [97].

Between these two extremes of keeping the structure of glycerol or destroying its structure completely, is the possibility to modify glycerol partly. This can be done by forming acryl derivatives. Another pathway is the creation of 1,2-propanediol or 1,3-propanediol. The latter serves mainly as monomer for polymerization and gained interest for this application. By contrast, 1,2-propanediol finds application as additive in nutrition products and cosmetics as well as wetting agent, solvent, lubricant or anti-freezing agent [97].

This part of this thesis aims to generate products from 1,2-propanediol by adding value so that they can serve as specialty chemicals.

3.6.2 Reactions of 1,2-propanediol

After the studies on 1,2-propanediol mentioned in chapter 3.2 it was decided to explore this reaction in detail. In the beginning were the time dependence and optimizations in order to get higher product amounts per time unit. Nevertheless, the characterization of the products was not neglected.

3.6.2.1.Synthesis of 1,2-propanediol from glycerol

It was of broad interest that the production of 1,2-propanediol could be carried out from glycerol and, thus, the here reported syntheses, including an aromatic compound, could be based on glycerol, a byproduct of biodiesel production. Some working groups published this process [98-100] even as flow process [101]. Own studies were made with 10% of glycerol in methanol at 80°C for 32h. Using palladium on activated carbon as catalyst and working under 10bar hydrogen pressure led to a molar yield of 74% for 1,2-propanediol and confirmed that this process could be carried out as a batch process as well. Besides, the purity was significantly higher than with continuous flow.

Further studies at higher temperatures showed that carbonization and hydrogenation could not be combined to a one-pot reaction just by adding HCl as mainly carbonization occurred. Thus, the synthesis was preferably carried out as a two step reaction. In the first step glycerol was converted into 1,2-propanediol and in the second step, after adding HCl, the aromatic compound was formed. However, a one-pot reaction was possible, but due to the low amounts of the desired products, the one-pot reaction was not favorable.

3.6.2.2.Optimization of the hydrothermal trimerization of 1,2-propanediol

In the beginning, the reactions of 0.5g 1,2-propanediol in 10mL pure water, 0.5mol/L HCl and 1.0mol/L HCl were known. After investigating some dependences, the reaction was optimized here to obtain higher product amounts per time unit so that the main products could be isolated in a laboratory scale. But before, it was the aim to decrease the concentration of the acid as much as reasonably possible. According to the dependence on the concentration of HCl, the concentration of HCl was decreased to 0.05mol/L HCl.

The time dependence was investigated and its studies led to the results summed up in Figure 3.10. There are only few products mentioned for each batch in order to show just the major products and neither all identifiable products nor all existing ones. It has to be kept in mind that the amount of products in general raised with the reaction time.

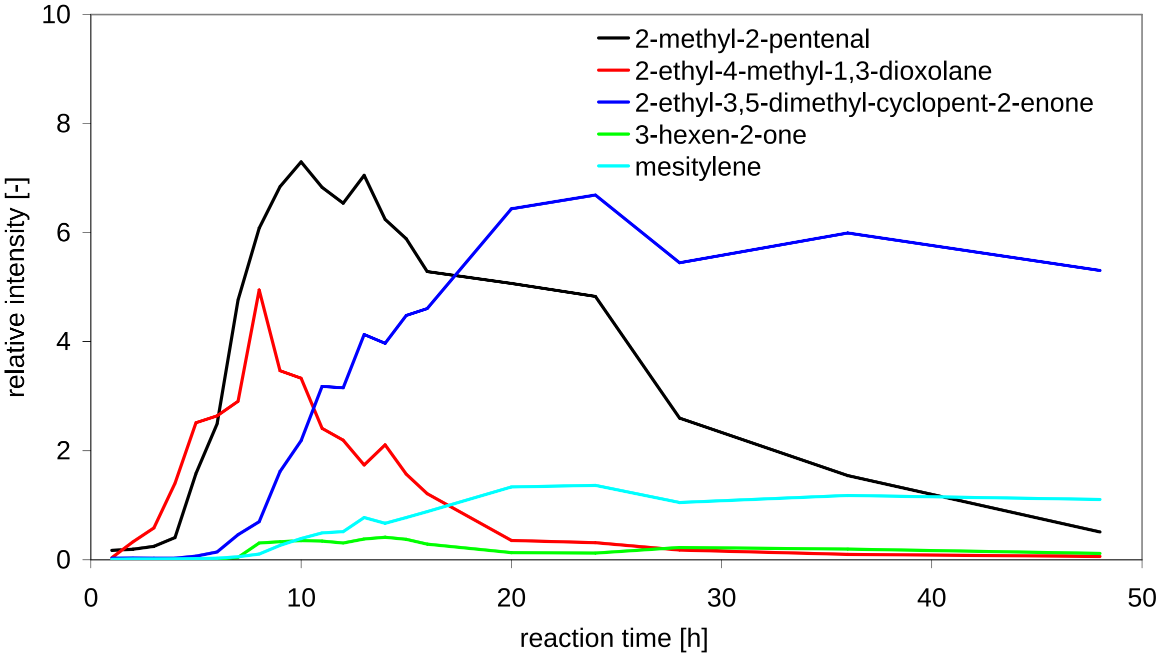


Figure 3.10: Time dependent, relative amounts of products after reaction of 1,2-propanediol in 0.05mol/L HCl at 180°C.

Figure 3.10 illustrates that the dioxolane derivative and 2-methyl-2-petenal (A) are formed especially in the beginning of the reaction. Then more and more of the cyclopent-2-enone (B) is obtained, but after a maximum yield, its amount decreases in favor of other products. Mesitylene (C) is produced after several hours, but after 20h its amount does neither increase a lot nor decrease a lot.

The proposed mechanism (see Figure 3.5) is in coherence with this data as (A) is formed before (B) and (C). Additionally, the amount of (B) increases when the amount of (A) decreases.

With these results the reaction time was kept at 16h in order to assure a high conversion and still reasonable amounts of impurities. The dependency of reaction products on the molar ratio of 1,2-propanediol to HCl was also examined. But the kind of products was almost independent of the amount of HCl per molecule 1,2-propanediol. Rather the reaction time influenced the result of the reaction. In extreme cases, this led to the formation of an organic phase.

However, the organic phase was formed after saturating the aqueous phase. Thus, the organic phase could yet be observed at 180°C after 16h reaction time for 7.0g 1,2-propanediol with 5.1mL 0.2mol/L HCl, but it could not be separated. After two days at 180°C there was a high enough amount of organic phase to separate it. With regard to molar conversions the amount of mesitylene reached 7%, the cyclopentenone derivative 27% and the 2-methyl-pent-2-enal 13%. Due to dehydrations the percentages in mass are lower and correspond to 3%, 14% and 7%, respectively. After four days at 180°C the amount of organic phase did not obviously increase further. This could be confirmed by a reaction time of 19 days.

Due to the reaction dependence on the ratio of 1,2-propanediol to hydrochloric acid, it was found that the reaction mixture of 1,2-propanediol and hydrochloric acid did not need to be diluted with water so that it was possible to go to even higher amounts of 1,2-propanediol per unit HCl. As a result, the reaction of 12.0g 1,2-propanediol with 0.1mL HCl in the concentration of 1.0mol/L for two days led to a biphasic system with a dark brown, organic phase above an aqueous phase which contained the starting material and some traces of colored compounds. When the reaction time was elongated to four days, the conversion was approximately complete for the aspect of molar conversion. Therefore, the ratio of the volume of the organic phase to the volume of the aqueous phase reached about 7 : 5.

The last step made for higher yields of organic phase per time unit for a given volume was to take 200°C for 20 hours in combination with 0.5mL 1.0mol/L HCl and 12.0g 1,2-propanediol. This also led to about 5mL aqueous phase and about 7mL organic phase. That correlated to the expected amounts of generated water in the case of an almost quantitative dehydration of 1,2-propanediol.

So, in the case of 180°C a reaction time of 19 days had no further advantage for the amount of organic phase. This furnished evidence that all the starting material was converted – at least until equilibrium with the products – and further hydrochloric acid could not catalyze the reaction anymore. Though, the composition changed in favor of one single product which was a derivative of cyclopent-2-enone. This accounted certainty that this product was the optimal receivable product under the used conditions.

3.6.2.3.Separation of the products

In order to analyze more quantitatively this reaction, product separation had to be carried out.

By collecting the organic phases of many batches a preparative separation of the main products could be carried out. In order to reach high enough contents of the main products which were just of some percent for each product, it was advantageous to start by a distillation as all the main products had boiling points less than 200°C. Thus, the very dark brownish liquid got separated into a high viscid, almost black residue and a clear, greenish-yellow liquid. The dark residue was not further investigated. The greenish-yellow liquid could be separated. After the evaporation, the product remained in high quality as residue.

It was favorable to separate two times by a rotary evaporator. The first time the product could be evaporated with the solvent of the separation so that the product was further purified. The second time the distillation had to be more precise. The purified products were analyzed by NMR and gave the below mentioned results.

3.6.2.4.Identification of the derivative of cyclopent-2-enone

The attention was focused on the three main reaction products. As previously stated, thanks to the MS-data bases of the National Institute of Standards and Technology (NIST) and National Institute of Advanced Industrial Science and Technology (AIST) the products (A) and (C) were identified with high degrees of confidence. (A) was identified as 2-methyl-2-pentenal and (C) as mesitylene. Both results were confirmed by further analyses. (A) was verified by NMR, whereas (C) was confirmed by NMR and a reference sample in the GC-MS. For (B) a cyclopent-2-enone derivative was proposed, but more characterization was required to ascertain its formula and to discover its exact structure. Additionally, each of the main products has several isomers and changing some side chains will not have extensive effects on the MS-spectra. Therefore, especially the cyclopent-2-enone derivative was object of further studies.

For the identification of the derivative of cyclopent-2-enone MS-data and especially NMR-data were used. Therefore the spectra for ^{1}H, ^{13}C, DEPT135, HSQC, HMBC and COSY were made and analyzed.

The molar mass of (B) is 138g/mol. MS-Data showed losses of 15Th and 29Th which correspond to methyl and ethyl groups. At whole, side chains with four carbon atoms were necessary to be in complete coherence to the molecule mass. The formation of a cyclopent-2-enone was chemically reasonable, especially the double bond in 2-position.

NMR measurements in $CDCl_3$ gave the following results: ^{1}H-NMR (600MHz): $\delta = 0.96$ (t, *J* = 7.7Hz, 3H), 1.14 (d, *J* = 7.5Hz, 3H), 2.02 (s, 3H), 2.06 (dm, *J* = 1.1, 18.0Hz, 1H), 2.17 (q, *J* =7.6Hz, 2H), 2.33 (quint.d, *J* =2.4, 7.5Hz, 1H), 2.71 (ddm, *J* =0.9, 6.8, 18.0Hz, 1H). – ^{13}C-NMR (151MHz): $\delta = 12.9$ (+), 16.2 (-), 16.5 (+), 16.8 (+), 39.5 (+), 40.6 (-), 140.6 (quart., C=C), 167.6 (quart., C=C), 211.9 (quart., >C=O).

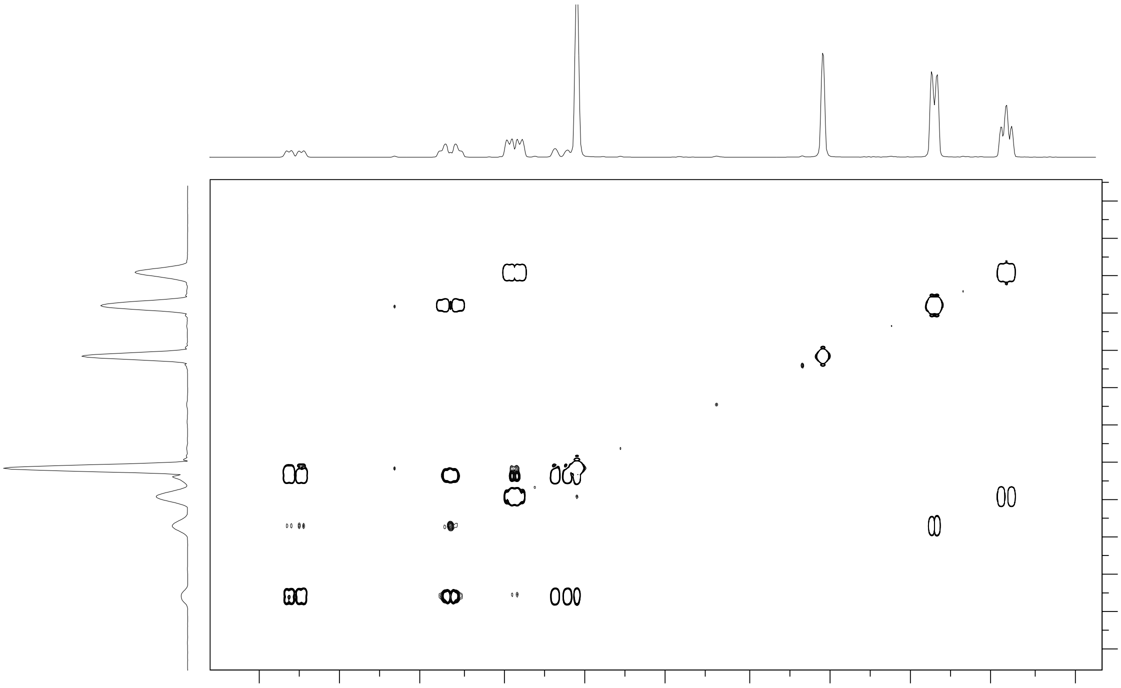


Figure 3.11: COSY-spectrum of the cyclopent-2-enone derivative.

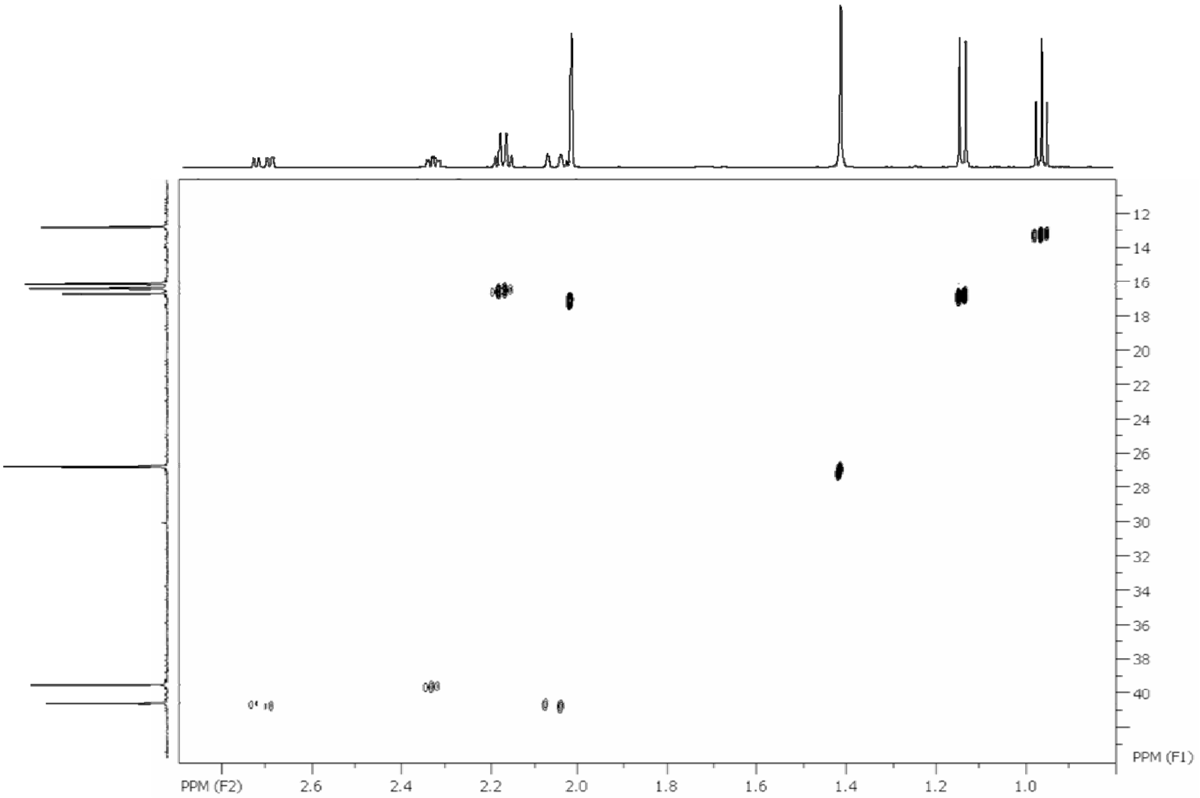


Figure 3.12: HSQC-spectrum of the cyclopent-2-enone derivative.

With Figure 3.11 and Figure 3.12 neighbored atoms were identified. Thus, the exact structure of the derivative of cyclopent-2-enone was determined. The result, 2-ethyl-3,5-dimethyl-cyclopent-2-enone, is shown in Figure 3.13. The attribution of chemical shift and corresponding atom is shown in Table 3.6. The atoms C3 and C4 are differentiated by a HMBC-spectrum.

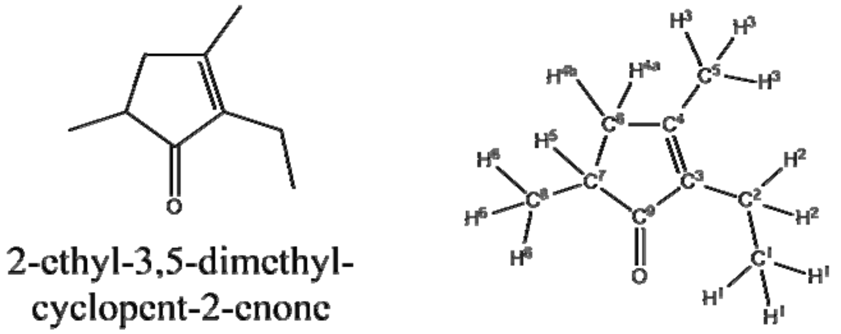


Figure 3.13: Structure of 2-ethyl-3,5-dimethyl-cyclopent-2-enone (left) and numbered atom positions for the identification (right).

Chemical shift (H-atom)	H-atom	neighbored C-atom	Chemical shift (C-atom)
0.96	H^1	C^1	12.9
1.14	H^6	C^8	16.5
2.02	H^3	C^5	16.8
2.06	H^4	C^6	40.6
2.17	H^2	C^2	16.3
2.33	H^5	C^7	39.6
2.71	H^4	C^6	40.6
-	-	C^3	140.7
-	-	C^4	167.6
-	-	C^9	211.9

Table 3.6: Mapping of the atoms of 2-ethyl-3,5-dimethyl-cyclopent-2-enone in NMR.

3.6.2.5.Main mechanism

With the result that the main products were 2-methyl-2-pentenal (A), 2-ethyl-3,5-dimethyl-cyclopent-2-enone (B), and mesitylene (C), these products and their formations are illustrated in Figure 3.14.

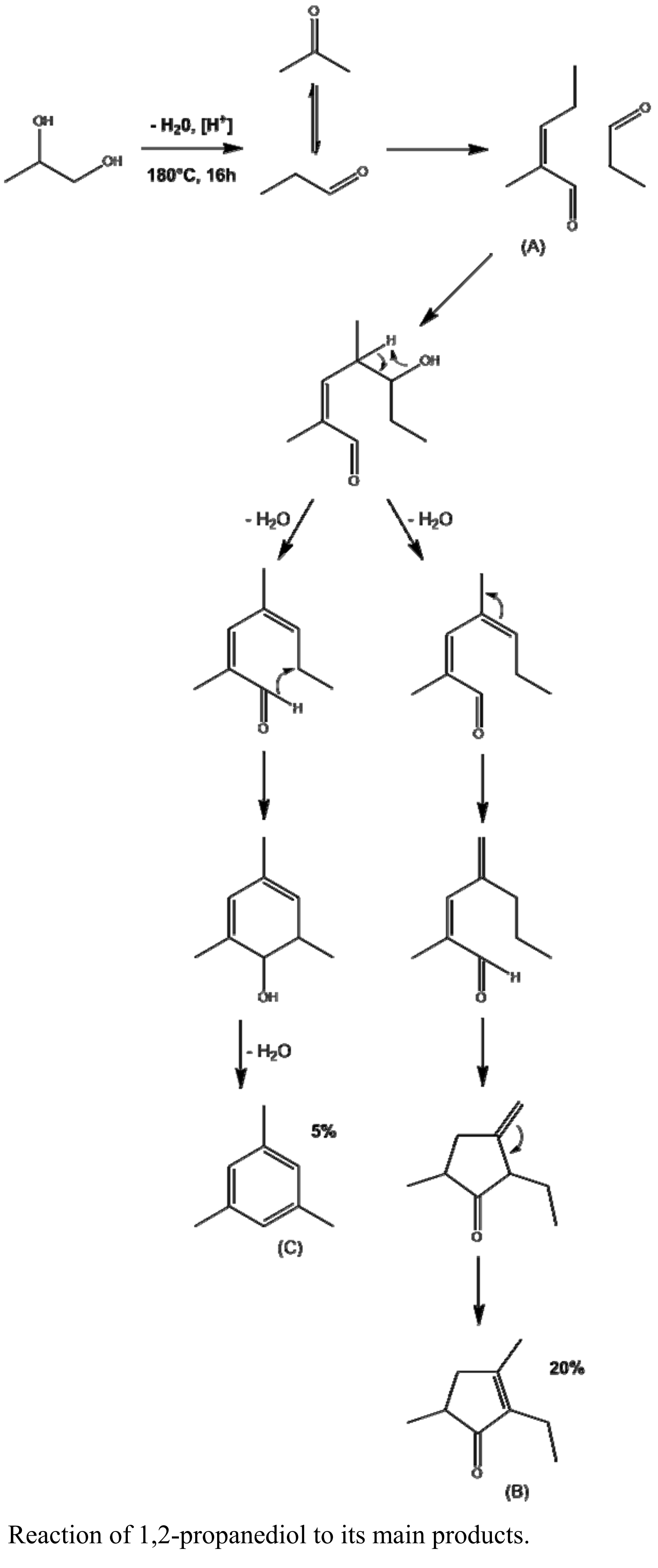


Figure 3.14: Reaction of 1,2-propanediol to its main products.

Important for the formation of (B) instead of (C) is the change of the position of the double bond after adding the third 3-carbon compound. This repositioning is shown in the right part of the second haft of the mechanism.

In 2010 Heck et al. published reactions with catalysts based on phosphorous. Among others they reported the cyclization of propanal to 2-ethyl-3,5-dimethyl-cyclopent-2-enone in dichloromethane [102]. Thus, the proposed mechanism was confirmed. Moreover, a possible catalyst for the cyclization of ethylene glycol (see chapter 3.2) was identified.

3.6.2.6.Alternative reaction conditions

That the recycling of the aqueous phase would be advantageous and so the reuse of the aqueous phase was studied by removing the organic phase and re-adding starting material. It was to declare for the avoidance of doubt that this was repeatable as long as the concentration of hydrochloric acid did not fall below a certain threshold. If this was the case, the reaction time increased and, thus, the advantage was exhausted.

Figure 3.15 and Figure 3.16 show the conversion of 1,2-propanediol as a function of the number of cycles re-using the aqueous phase. The difference between them is that Figure 3.15 compares the obtained mass of organic phase with the employed mass of 1,2-propanediol, whereas Figure 3.16 sets the amount of organic phase in relation to the amount of 1,2-propanediol which was added after the preceding cycle. Thus, the conversion in Figure 3.15 approaches to a certain limit which is obtainable in an ideal case and Figure 3.16 converges to zero conversion. The reason for this difference is that only the organic phase is considered. By contrast, the amount of formed water is not negligible and causes that less and less organic phase is replaced after a cycle by new 1,2-propanediol. That is why the amount of used 1,2-propanediol decreases which each cycle while the HCl concentration also decreases and lowers, therefore, the conversion rate. Besides, if a complete dehydration reaction is assumed, a yield of 58wt% of organic phase corresponds to a 100% molar conversion.

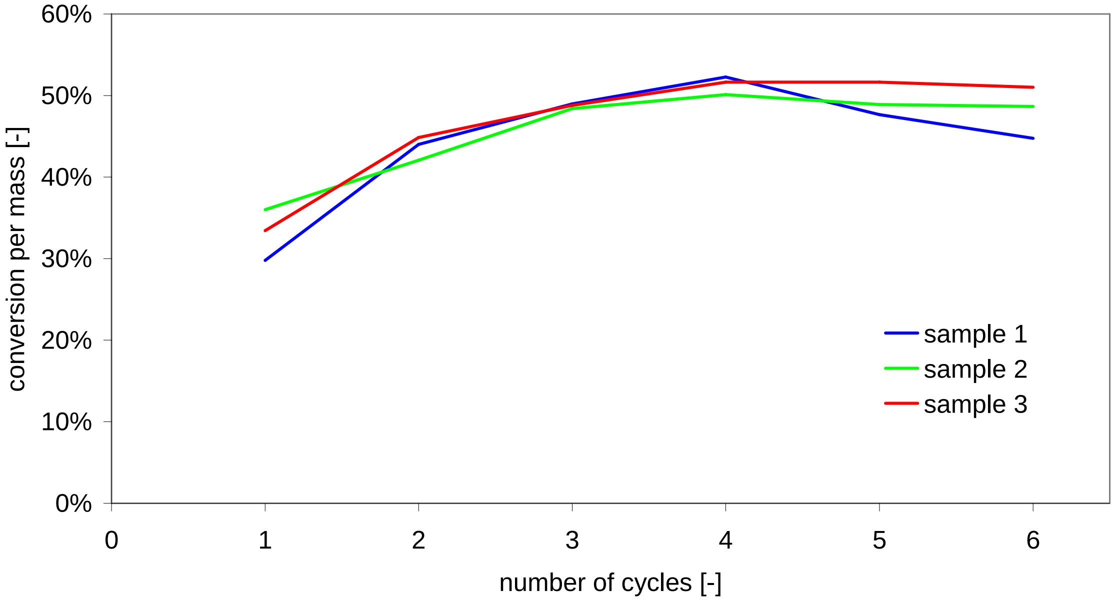


Figure 3.15: Conversion per at whole added mass of 1,2-propanediol as a function of cycles re-using the aqueous phase.

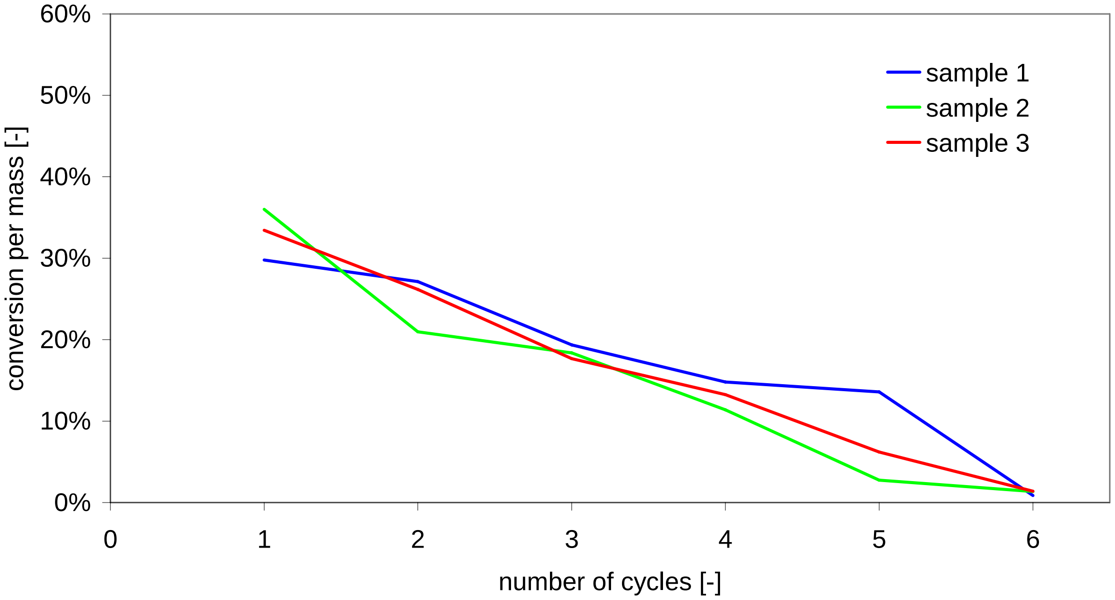


Figure 3.16: Conversion per mass of recently added 1,2-propanediol as a function of cycles re-using the aqueous phase.

Further investigations showed that the hydrochloric acid could be replaced by sodium hydroxide and that the self-made 1,2-propanediol could be used to produce the biofuel. In the case of using NaOH as catalyst, the chromatogram showed the same products, but with different ratios. This could be very interesting for the biodiesel industry as glycerol is produced in an aqueous alkaline solution with excess-methanol from the transesterification. Thus, the purification of glycerol might be unnecessary as the conversion of glycerol to 1,2-propanediol did not need acid as catalyst. Thus, it is to investigate, if crude glycerol from biodiesel production can be used without purifying. If this is the case, the aqueous phase from biodiesel production could be converted directly into a further organic phase. The advantage would be that the volume of liquid, from which the catalyst must be recovered, was divided by a factor above two. So to say the concentration would have been more than doubled. The disadvantage would have been that the excess-methanol from the esterification process of the biodiesel-production as well as the water in the aqueous phase had to be heated up to 220°C without any positive impact. Even if base-catalyzed aldol reactions are not new and the pOH is known to be increased at higher temperatures (see chapter 2.3), the practical use might be enormous.

Even though, an equilibrium between 1,3-propanediol and 1,2-propanediol was thought to be probable under hydrothermal conditions via dehydration and re-hydration. But the replacement of 1,2-propanediol by 1,3-propanediol gave different product compositions employing the same conditions on both reaction mixtures. This was also valid for acetone. It was likely to be in equilibrium with 1,2-propanediol as it could be received by dehydrating 1,2-propanediol followed by a keto-enol tautomerism. Even if the compositions of the mixtures after reaction were much more similar to the one for 1,2-propanediol in the case of acetone than in the case of 1,3-propanediol, the mixtures were not the same. Amongst others, this was due to some other isomers. Correspondingly, there was a mixture of these products in the case of taking a mixture of acetone and 1,2-propanediol as starting materials.

The synthesis of this biofuel is also possible in a microwave oven. Anyhow, the progress of the reaction depends only on the time for which the elevated temperature is hold. Thus, in this case the kind of heating has no influence on the result of the reaction. That is why heating by microwave is possible, but there is no advantage for the reaction time and, therefore, heating in a compartment dryer is adequate.

However, this hydrothermal reaction of 1,2-propanediol offers biomass-based access to aromatic compounds which are still commonly products from fossil sources.

1,2-Propanediol was formed out of glycerol. The reaction of 1,2-propanediol was optimized for higher conversion rates and the main products were separated and identified. A mechanism and alternatives were described.

3.6.3 Possible ways to valorize the obtained products

As stated before, it is not sufficient to produce molecules from biomass, these molecules also have to be useful. This chapter shows ways how the obtained reaction mixture from 1,2-propanediol, or parts of it, can be used. Exploitations without treatment, after hydrogenation and after separation are mentioned.

3.6.3.1.Exploitation without treatment

The not purified mixture of the organic phases was studied as some product molecules had the same composition as diesel or a near diesel composition with C_9H_{12} and $C_9H_{14}O$, respectively. Even if it was evident that the mixture had to be conditioned before an eventual use as fuel in diesel engines or as additive in diesel, some properties were examined.

Therefore, the specific enthalpy of combustion had been determined by own measurements to be 39MJ/kg for the water saturated mixture. Compared to 40MJ/kg for biodiesel and 45MJ/kg for diesel it seemed that this mixture made from biomass could help to reduce the fossil content of nowadays fuels.

Measurements made by means of Differential Thermal Analysis (DTA) showed that the mixture of the organic phase had a certain similarity to diesel, but, however, it was obviously not the same. On the contrary, gasoline showed a completely different behavior as it evaporated before the DTA could tare. The DTA-curve showed that the biofuel started to evaporate earlier than diesel, but, on the other hand, evaporating finished later. So the boiling range of diesel was narrower than the one for this untreated biofuel, but both mean evaporating temperatures of the fuels were comparable.

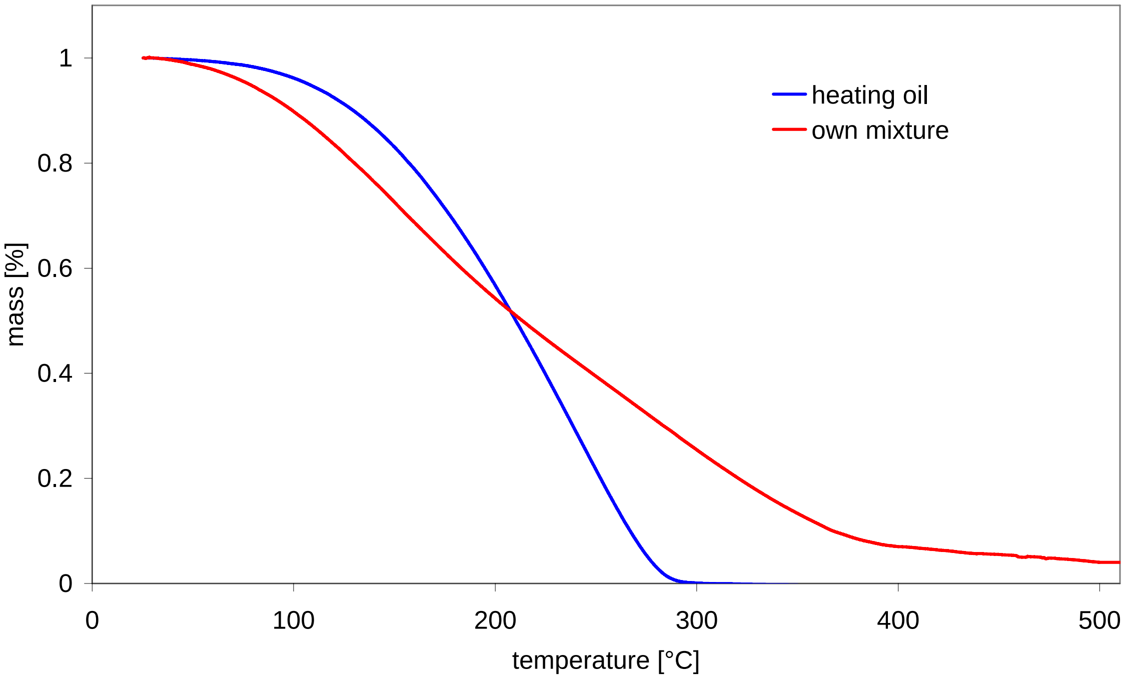


Figure 3.17: DTA-measurements comparing heating oil and the product mixture obtained from 1,2-propanediol.

Nevertheless, the color and the viscosity would not have supported the direct use as fuel. Especially the viscosity had to be changed in order to facilitate the pumping and the injection of the fuel. For these reasons the use of this untreated biofuel would have been limited to adapted applications. There are some applications to use or co-use glycerol as fuel in power plants [103-105], but due to its high viscosity and the formation of more residue some modifications are needed. Here the viscosity was not as high as for glycerol, but it was still higher than for diesel and the formation of residue had to be considered as the DTA-measurements showed a non-evaporated content of 6mass-% at 450°C. Therefore a modification of the application was indispensable.

In any case, this potential biofuel offered the potential to store energy due to its high specific energy density. The production of the biofuel was an endothermic reaction and therefore energy was needed. In general this is an unfavorable property, but on the contrary, actually this property brought forth the high energy content per mass and, thus, the biofuel was usable for energy storage. The intake of energy in form of heat favored this use as energy could be taken in times of an energy excess. In times of lack of energy the biofuel could be used. A further application would be to use the stored energy locally independently of its production site. So energy excesses could be buffered in place and time and would also be available for mobile applications.

3.6.3.2.Exploitation after hydrogenation

From the three main products 2-methyl-2-pentenal, mesitylene and 2-ethyl-3,5-dimethyl-cyclopent-2-enone only mesitylene had yet applications. The other two main products could be useful as starting materials for several reactions forming carbon-carbon bonds due to their conjugated double bonds. Besides, cyclopentanone derivatives might be useable as solvents.

Therefore, the distilled biofuel was hydrated over palladinated carbon in methanol at 80°C during 16h under 10bar hydrogen pressure. This caused that 2-methyl-2-pentenal was completely converted into 2-methyl-pentanal and 2-methyl-pentanal dimethyl acetal. 2-Ethyl-3,5-dimethyl-cyclopent-2-enone was converted almost completely into three isomers of 2-ethyl-3,5-dimethyl-cyclopentanol. Mesitylene was not hydrogenated.

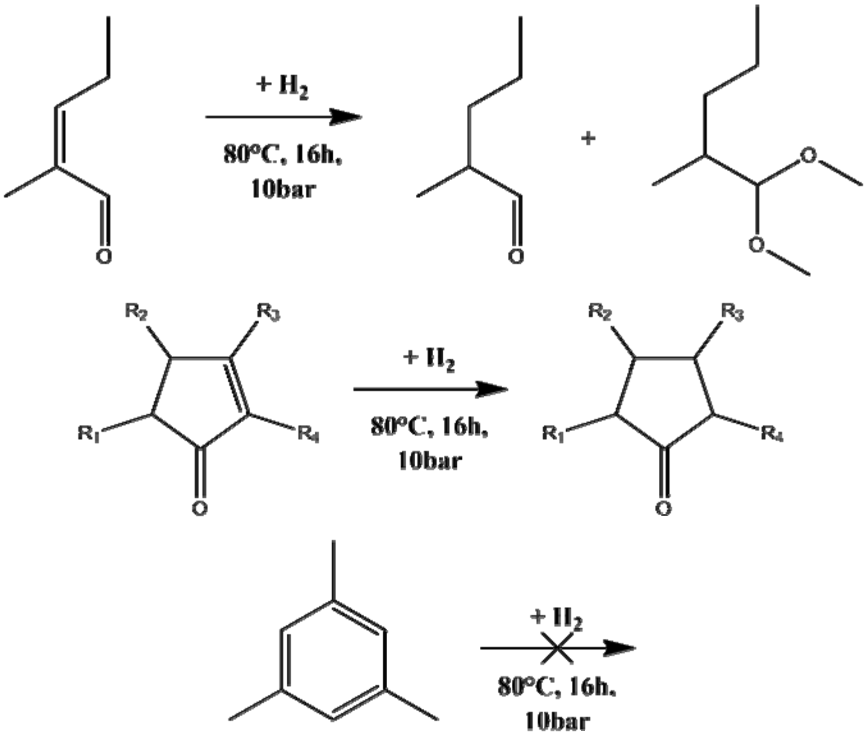


Figure 3.18: Hydrogenations of the main products.

These observations corresponded to pretests which were made under the same conditions. Those showed 1,1-dimethoxycyclopentane and cyclopentanol when cyclopent-2-enone was the starting material. The hydrogenation of 2,3,4,5-tetramethyl-cyclopent-2-enone led to five peaks of 2,3,4,5-tetramethyl-cyclopentanone. Thus, at both cyclopentenones only the double bonds were hydrogenated, but not the carbonyl groups. Pure mesitylene was not hydrogenated.

Concluding, mesitylene did not lose its value and the other main products could be used for further applications after hydrogenation. Furthermore, the distilled mixture became simplified and lost its color. Therefore it was expected that the properties of the hydrogenated mixture were different from the original ones. Probably, also a better combustion performance came along as further compounds were hydrogenated and high boiling compounds disappeared almost completely from the chromatograms of GC-MS and GC-FID.

3.6.3.3.Exploitation after separation

The separation of the potential biofuel was of interest as there were several compounds in exploitable quantities. Due to the added value of some products as to be mentioned the mesitylene or the 2-ethyl-3,5-dimethyl-cyclopent-2-enone a separation could be advantageous. 2-Ethyl-3,5-dimethyl-cyclopent-2-enone might be applicable for reactions of Diels-Alder or Michael. The same is valid for 2-methyl-2-pentenal.

The mixture could be distilled to several fractions with different quantities of compounds. Table 3.7 summarizes the results. Additionally, the color changed from bright yellow of the first fractions to brownish yellow before ending in dark olive for the last fractions. The viscosity increased with a higher darkness of the fraction.

fraction number	lowered pressure	mass-% of fraction	main product(s)
1	no	12.80%	2-ethyl-4-methyl-1,3-dioxolane, 2-methyl-2-pentenal
2	no	15.40%	2-ethyl-4-methyl-1,3-dioxolane, mesitylene, 2-methyl-2-pentenal
3	no	4.90%	2-ethyl-3,5-dimethyl-cyclopent-2-enone
4	yes	9.60%	2-ethyl-3,5-dimethyl-cyclopent-2-enone
5	yes	8.00%	2-ethyl-3,5-dimethyl-cyclopent-2-enone
6	yes	1.40%	-
7	yes	2.30%	-
8	yes	6.50%	-
9	yes	2.90%	-
10	yes	0.80%	-

Table 3.7: Amount of fraction and their main products.

As mesitylene was minor to 2-ethyl-3,5-dimethyl-cyclopent-2-enone yet in the mixture, it could not easily be received as a pure fraction by distillation. Both would be usable as solvents. Anyhow, a good separation would need several steps of distillation or other methods in addition.

The use as fuel seemed to be more appropriate for the distilled mixture than for the crude mixture (see Figure 3.19). This was verified by an analysis of a distilled mixture due to DIN 51 453. The result was the mixture contained volatile compounds as well as compounds with boiling points above 210°C. Therefore, it consisted of gasoline and diesel like fractions. For a use as fuel in conventional engines a further separation would be necessary.

Figure 3.19: Crude mixture (left) and distilled mixture (right).

Ways to exploit the mixture without or after treatment as biofuel or for biorefinery have been explored. The mixture is hydrogenated rather selectively. In combination with distillation or other separations several compounds of added value are accessible.

3.6.4 Conclusion and perspectives for the reaction of 1,2-propanediol

In this chapter we confirmed that 1,2-propanediol could effectively be obtained from glycerol. In a second step 1,2-propanediol was converted into 2-methyl-2-pentenal, mesitylene and 2-ethyl-3,5-dimethyl-cyclopent-2-enone as interesting main products. The latter one caused yet 27% of the molar conversion. Thus, an aromatic compound was accessible out of glycerol by a two-step conversion.

Optimizations of the hydrothermal reactions lead to the use of 0.05mol/L HCl as solvent and then to a reduction of the solvent volume so that 1,2-propanediol was converted in presence of low amounts of HCl. As could be expected, time dependence showed that 2-methyl-2-pentenal was formed before 2-ethyl-3,5-dimethyl-cyclopent-2-enone was obtained.

Separating the mixture by evaporation and using columns allowed identifying 2-ethyl-3,5-dimethyl-cyclopent-2-enone with means of MS and NMR.

With the data from the time dependence of the reaction and the identification, a mechanism could be postulated. In the beginning, an aldol condensation led to 2-methyl-2-pentenal and then this was converted into 2-ethyl-3,5-dimethyl-cyclopent-2-enone and mesitylene by a second aldol condensation which was followed by a ring closure. Just one double bond needed to shift in order to change the final product.

Two of the mentioned main compounds were of the compositions C_9H_{12} and $C_9H_{14}O$, respectively, which corresponded to the average composition of diesel. Thus, the mixture or parts of it were interesting for the use as biofuel. Their high specific energy density supports this idea. Nevertheless, a treatment was necessary to adapt physical properties, especially the viscosity, and to improve further requirements. Otherwise, the usage would be limited to adapted applications. In any case, this obtained reaction mixture could be used to store energy based on biomass with a need for lower storage capacities as the energy density was higher per mass as well as per volume in comparison to other biomass feedstocks.

Hydrogenation offered the possibility to receive a mixture of brighter color and a diminished amount of high-boiling compounds. Mesitylene was not hydrogenated, but the other two main products were hydrogenated and therefore deactivated. Thus, they assure a higher level of security for people with low chemical knowledge such as most car drivers.

The distillation of the mixture led to several fractions with higher purity of the one or of the other compound. Therefore, the exploitation of pure chemicals could be advantageous. Nevertheless, the distillation had to be combined with a second step of purification.

Taking everything into consideration, this application of a hydrothermal reaction has the potential to be used as energy storage or for biorefinery in order to have products based on biomass. Further investigations are useful, especially for the adaptation of the fuel for mobile applications.

3.7 Conclusion and perspectives

The reports found in literature before starting this work underline that functional diols can react under harsh hydrothermal conditions. The aim of this chapter was to extend these reactions to milder reaction conditions and simple diols when using diluted acids.

The reaction of ethylene glycol in dependence of the temperature and of the solvent demonstrated the flexibility of the reactions of simple diols. Therefore, the choice of the reaction conditions was very important. A single product could be the main product in high yield and high purity or it was a byproduct or even not detectable. Thus, one reaction could be taken for two different purposes. In order to synthesize 2-methyl-1,3-dioxolane or 1,4-

dioxane the solvent had to be chosen at low temperature and 6-, 8- and even 9-carbon compounds were received at higher temperatures.

1,2-Propanediol reacted to a similar high number of compounds as ethylene glycol, but the main products were generated in higher amounts so that they stuck out from the rest of the products. Especially the syntheses of the 9-carbon compounds mesitylene and 2-ethyl-3,5-dimethyl-cyclopent-2-enone seemed to be interesting as the molecular formulae were comparable to the ones of fuels. Likewise, the feasibility of optimizing the yield for one or another compound was given. The application of 220°C for 16h and 1.0mol/L NaCl yielded much 2-methyl-2-pentenal in high purity. Besides two isomers of 2-ethyl-4-methyl-1,3-dioxolane and 2-ethyl-3,5-dimethyl-cyclopent-2-enone were the only byproducts. Compared to some other reaction mixtures this was very pure. The mentioned fuel-like compounds were formed efficiently in HCl containing solvents, especially at high temperatures.

Interestingly, there were similarities between the reaction of acetone and 1,2-propanediol, but the similarities were limited. On the one hand, acetone and 1,2-propanediol could interconvert under hydrothermal conditions by hydrations, dehydrations and keto-enol tautomerism. On the other hand, not all the products were the same as it would be expected, if acetone and 1,2-propanediol achieved to be in equilibrium. Thus, they were not in equilibrium. Nevertheless, the selectivity to form some identical products and some other products was interesting.

The reaction of 1,2-propanediol was optimized. Thus, the main products could be produced in higher quantities, separated and identified. Also the mechanism of the main reaction pathway was discovered. Further information can be found concluded in chapter 3.6.4

Taking everything into consideration, the idea to obtain aromatic compounds by trimerization was not confirmed in general, but this was possible to a certain extent. Mesitylene was obtained from 1,2-propanediol in an amount of several percent, whereas ethylene glycol led only to traces of benzene. Further investigations are necessary for augmenting the yields.

4. Hydrothermal Friedel-Crafts type reactions

The observation of an intramolecular Friedel-Crafts type reaction for 1-phenyl-1,2-ethanediol (see chapter 2.5) under hydrothermal conditions prompted to consider this reaction in more details, especially because an alcohol was the alkylating agent. Therefore, we decided to investigate the use of hydrothermal chemistry to promote intermolecular Friedel-Crafts type reactions with alcohols.

4.1 Literature review

The Friedel-Crafts reaction used in its form reported in 1877 an at least equimolar amount of dry aluminum chloride as promoter, an alkyl chloride as the alkylating agent and the desired aromatic compound as solvent at room temperature [106]. This results in the formation of about 88mass-% of waste products [8]. This was not acceptable, and because of its industrial relevance, numerous paths have been investigated to make this type of alkylation greener.

Various approaches to a less harmful reaction were studied. Many homogeneous and heterogeneous catalysts such as $Re_2(CO)_{10}$ [107], iron-containing aluminophosphate molecular sieves [108], superacids [109, 110] or tin-containing catalysts [85, 111, 112] are published. Furthermore, zeolites [113-117] and mesoporous oxides [118-120] gained also their place in the appropriate literature.

More interesting for the hydrothermal approach is that Sato et al. focused on supercritical water without any added catalyst. And indeed, supercritical water replaced an organic solvent for the alkylation of phenol [121-124]. But the use of supercritical water implicates harsh conditions and, therefore, strong requirements on the materials both for mechanical and for corrosion resistance. At the expense of the yield, also water at temperatures below the critical point can be used [125].

Another disadvantage of the classical form of Friedel-Crafts reactions besides the catalyst is the alkylating agent. The use of a halogenated alkane leads to an equimolar formation of the corresponding hydrohalogenic acid. This does, due to its hazardous potential for the environment, not count as the greenest possibility. Therefore, several working groups already used alcohols as alkylating or acylating agents, but mainly only benzyl alcohol or allyl alcohol are reported [126-129]. Additionally, alcohols which are known to alkylate ketones, malonates or nitrils [130-133] are promising agents [85]. Instead of producing HCl, water would be the byproduct. An example for this pathway is given by Yadav et al. in combination with superacids as catalysts [134].

You et al. report intermolecular Friedel-Crafts reactions for imines [135] comparable to the reactions of 1-phenyl-1,2-ethanediol yet reported in chapter 2.5. For heteroaromatic compounds such as indoles a highly efficient stereoselective hydroxyalkylation was presented. The attacking 3,3,3-trifluoropyruvate led to high yields and enantioselectivities [136]. Nevertheless, chiral catalysts for simple benzene derivatives are not yet known, but desirable [135].

The Friedel-Crafts reaction is one of the very important reactions in the chemical industry. Hence the reaction is well studied and optimized for different aspects, but hydrothermal conditions still offer a field for studies.

Except from the classic, aprotic form of the Friedel-Crafts reaction, the concentration, respectively the activity, of H^+-ions has the main impact on the reaction [123]. Thus, diluted acids under hydrothermal conditions may reduce technical requirements caused by the use of concentrated acids or supercritical water.

4.2 Reaction conditions

The Friedel-Crafts type reactions were investigated for different temperatures and several solvents in chapter 4. Therefore, 0.25g alcohol and 0.25g aromatic compound reacted during 16 hours in 10mL solvent. The combinations of temperature and solvent are illustrated in Table 4. and followings for the tested pairs of alcohol and aromatic compound.

	125°C	150°C	180°C	200°C	220°C
Water	+	+	+	+	+
1.0mol/L NaCl	+	+	+	+	+
0.5mol/L NaCl, 0.5mol/L HCl	+	+	+	+	+
0.5mol/L HCl	+	+	+	+	+
1.0mol/L HCl	+	+	+	+	+

Table 4.1: Investigated reaction conditions for the benzylation of naphthalene (0.23mol/L benzyl alcohol, 0.24mol/L naphthalene).

	125°C	150°C	180°C	200°C	220°C
Water	+	+	+	+	+
1.0mol/L NaCl	+	+	+	+	+
0.5mol/L NaCl, 0.5mol/L HCl	+	+	+	+	+
0.5mol/L HCl	+	+	+	+	+
1.0mol/L HCl	+	+	+	+	+

Table 4.2: Investigated reaction conditions for the benzylation of phenol (0.23mol/L benzal alcohol, 0.27mol/L phenol).

	180°C
Water	+
1.0mol/L NaCl	+
0.5mol/L NaCl, 0.5mol/L HCl	+
0.5mol/L HCl	+
1.0mol/L HCl	+

Table 4.3: Investigated reaction conditions for the benzylation of toluene (0.23mol/L benzyl alcohol, 0.27mol/L toluene).

	180°C
Water	+
1.0mol/L NaCl	+
0.5mol/L NaCl, 0.5mol/L HCl	+
0.5mol/L HCl	+
1.0mol/L HCl	+

Table 4.4: Investigated reaction conditions for the reaction of benzaldehyde (0.24mol/L) with acetophenone (0.21mol/L).

Then, 0.05mol/L HCl was the solvent and different combinations of alcohol and aromatic compound were tested during 16h at 180°C. The tested combinations are given in Table 4.5.

	phenol	naphthalene	toluene	p-xylene
2-propanol	+	+	+	+
2,3-butanediol	+	+	+	+
sec-phenethyl alcohol	+	+	+	+
benzyl alcohol	+	+	+	+
4-methyl-benzyl alcohol	+	+	+	+
4-hydroxy-benzyl alcohol	+	+	+	+

Table 4.5: Investigated combinations of alcohol (0.30mol/L) and aromatic compound (1.5mol/L).

4.3 Alkylation of naphthalene

At first, naphthalene was selected as substrate for Friedel-Crafts type alkylation by alcohols under hydrothermal conditions. The expected reaction with benzyl alcohol is given in Figure 4.1 with both isomers of the product molecule.

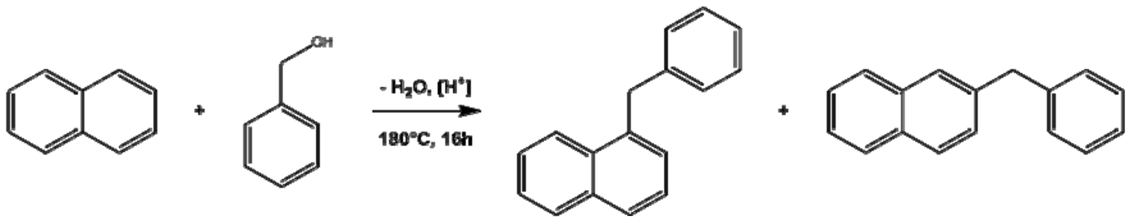


Figure 4.1: Expected Friedel-Crafts type reaction of naphthalene and benzyl alcohol.

4.3.1 Benzylation of naphthalene as a function of temperature and solvent

In the beginning of these studies, the reaction conditions were modified for the alkylation of naphthalene by benzyl alcohol. Therefore, the impacts of reaction temperatures from 125°C to 220°C and of five aqueous mixtures as solvents were investigated.

There was no reaction observable in pure water as solvent at 125°C. Traces of benzyl alcohol were formed at 150°C and 180°C. Dibenzyl ether and both isomers of benzylnaphthalene were obtained in low amounts at 200°C and at 220°C.

Using 1.0mol/L NaCl led to the same results as for pure water. Only at 200°C there was additional benzyl ether.

The mixture with 0.5mol/L NaCl and 0.5mol/L HCl as well as 0.5mol/L HCl and 1.0mol/L HCl led to both alkylation products yet at 125°C. Main product was dibenzyl ether and benzylbenzyl alcohols were byproducts. Applying temperatures of at least 150°C resulted in a complete conversion and the Friedel-Crafts products were the main products in high purity.

In general, higher temperatures led to higher amounts of benzylnaphthalene. HCl in the solvent decreased the reaction temperature which is necessary to achieve a quantitative conversion. Among the studied HCl containing solvents, the chloride concentration had more influence on the product amounts than the acid concentration.

The reaction is in good coherence with the expected reaction shown in Figure 4.1.

4.3.2 Benzylation of naphthalene using different amounts of starting material

Changing the amounts and the ratio of the two starting materials was also investigated. The reaction of 0.1g naphthalene (0.09mol/L) with 0.4g benzyl alcohol (0.31mol/L) at 200°C caused an almost complete conversion of benzyl alcohol and naphthalene as long as the solvent contained HCl. In pure water and in 1.0mol/L NaCl the conversion was incomplete and the impurities were already known.

In comparison, the series with 0.25g benzyl alcohol (0.23mol/L) and 0.25g naphthalene (0.20mol/L) resulted in higher purity. Anyhow, the latter studies showed complete conversion of both starting materials.

4.3.3 Benzylation of naphthalene as a function of the concentration of HCl

With this knowledge the temperature was set at 180°C, the duration was kept at 16h and the impact of the concentration of hydrochloric acid on the reaction was studied for the reaction of 0.25g naphthalene (0.20mol/L) with 0.25g benzyl alcohol (0.23mol/L).

Figure 4.2 shows the quantities of the Friedel-Crafts products after reacting. Apparently, the dependence on the concentration of HCl in the solvent changed. At high concentrations there was almost no effect connected to a change of the concentration of the acid and there were almost only the Friedel-Crafts products and the excess of the starting material naphthalene. But at low concentrations less benzyl alcohol was converted and the amount of dibenzyl ether decreased. In order to looking for an optimum, the optimal conditions were defined as those which almost led to the highest achievable amount of Friedel-Crafts product in relation to the concentration of HCl. This was the case between 0.05mol/L and 0.1mol/L hydrochloric acid. Hence, there was a factor of two in the concentration and therefore the lower concentration was favored despite a moderate loss of purity and yield. In addition, a rather low conversion rate is accompanied by a higher percentage of aromatic compounds alkylated in 1-position. This changes with higher acid concentrations to an excess of alkylations in 2-position.

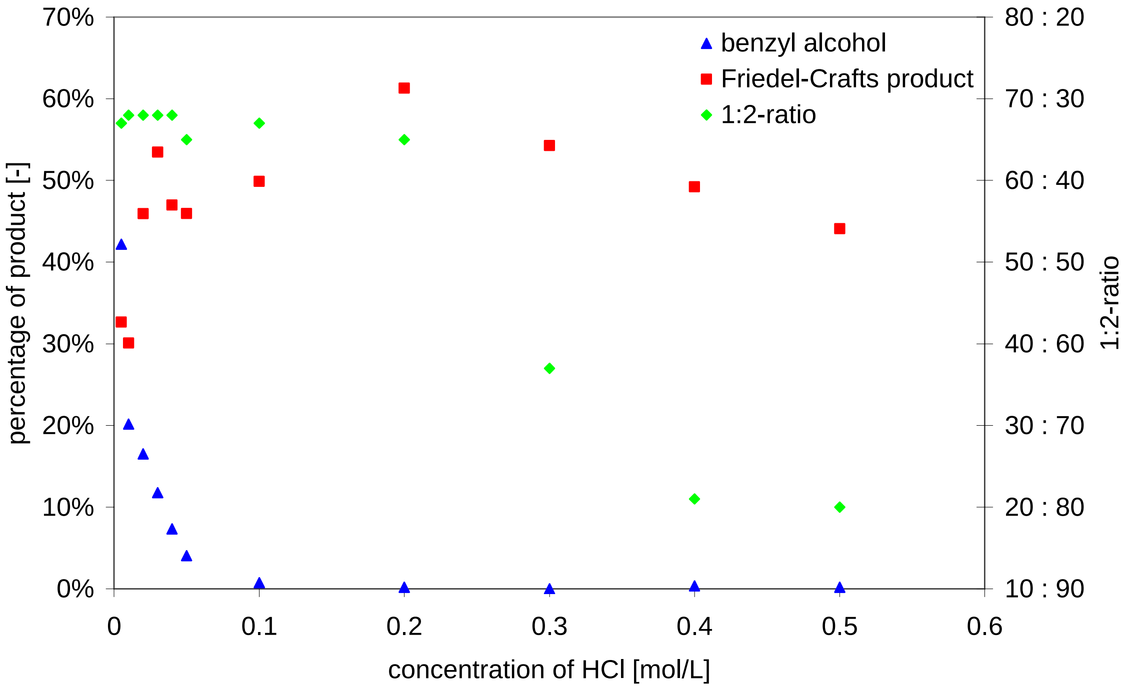


Figure 4.2: Amounts of products of the benzylation of naphthalene as a function of the concentration of HCl.

The 1:2-ratio is defined as the ratio of the amounts of 1-benzylnaphthalene to 2-benzylnaphthalene.

4.3.4 Benzylation of naphthalene in different acids

Subsequently, the substitutability of the mineral acid HCl by organic acids was investigated. Especially very simple carboxylic acids seemed to be interesting and, thus, acetic acid and formic acid were studied in dependence on their impact on the given Friedel-Crafts type reaction of benzyl alcohol on naphthalene. For both acids the tested concentrations ranged from 0.05mol/L to 2.0mol/L, but the highest concentrations are not shown in the figures so that the other measurements are better separated from each other.

Besides, the results for the concentrations of 2.0mol/L do not differ much from results for the ones of 1.0mol/L.

The studies with acetic acid showed a clear influence of the concentration on the reaction as it could be expected. At rather high concentrations of acetic acid the result of the reaction was almost independent of a further increase of the concentration of acetic acid. The positive influence dropped down at lower concentrations of HOAc. Nevertheless, high concentrations of acetic acid had the same effect as 0.005mol/L HCl. However, the conversion of benzyl alcohol remained below 60%.

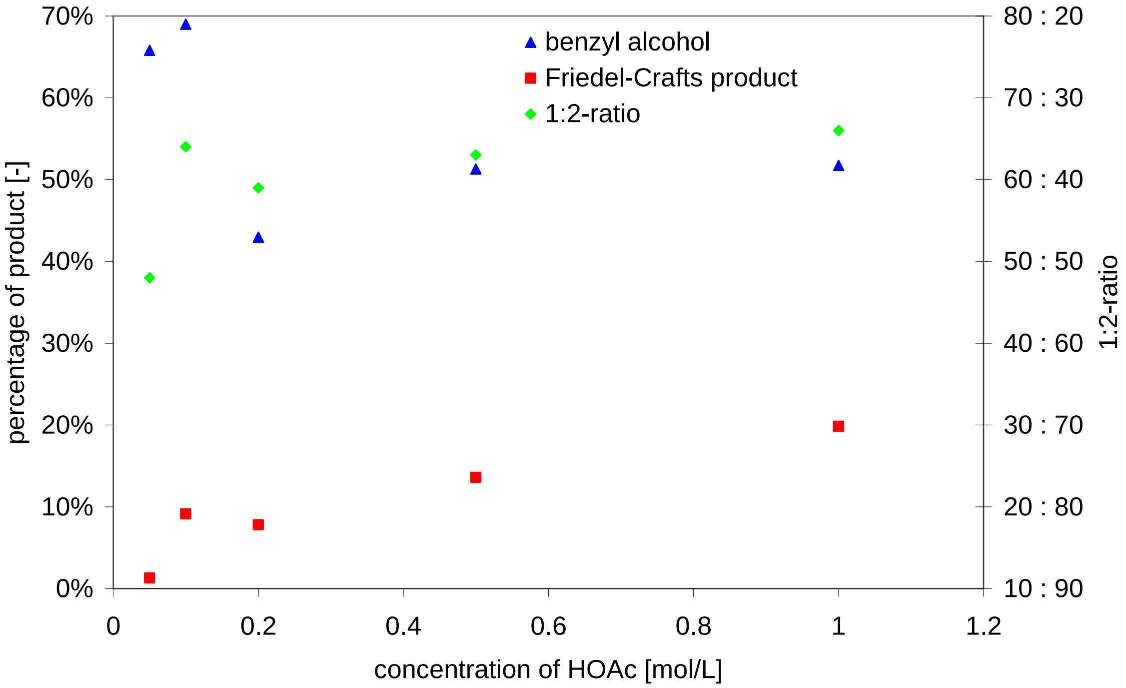


Figure 4.3: Amounts of products of the benzylation of naphthalene as a function of the concentration of HOAc.

The 1:2-ratio is defined as the ratio of the amounts of 1-benzylnaphthalene to 2-benzylnaphthalene.

Formic acid gave similar results as higher concentrations provoked higher purities of the Friedel-Crafts product and lower concentrations led to worse conversions. Also comparable is the fact that low concentrations of hydrochloric acid had results comparable to high concentrations of formic acid. However, the effect of formic acid is better than the one of acetic acid.

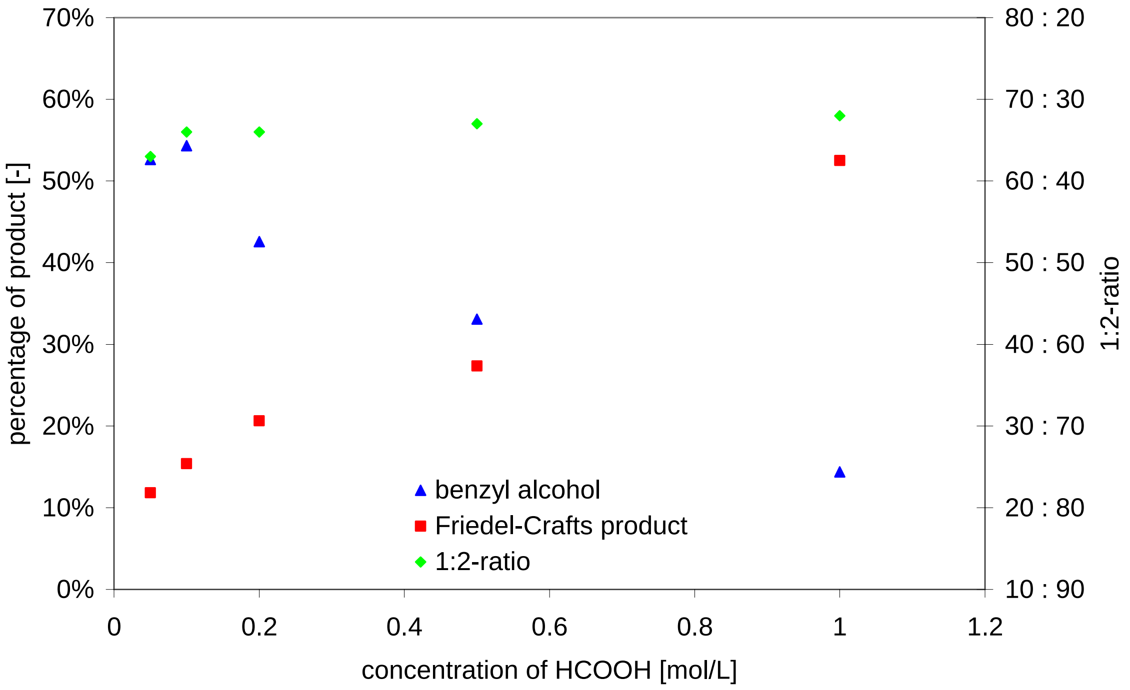


Figure 4.4: Amounts of products of the benzylation of naphthalene as a function of the concentration of HCOOH.

The 1:2-ratio is defined as the ratio of the amounts of 1-benzylnaphthalene to 2-benzylnaphthalene.

The fact that hydrochloric acid is more efficient than formic acid ($pK_a = 3.8$) which is still more efficient than acetic acid ($pK_a = 4.8$) is in coherence with the proposed mechanism of an acid catalyzed reaction and with the observation that the dissociated acid HCl is more efficient than the less dissociated formic acid. In this line, acetic acid has the lowest degree of dissociation and, therefore, it has the lowest catalytic influence on the Friedel-Crafts type reaction. Anyhow, a higher dissociation degree can be expected for both organic acids at higher temperatures.

Thus, a substitution of HCl could be favored because of ecological reasons and for a better biodegradability. Meanwhile, green chemistry does not only regard the kind of used products, but also their amounts and, therefore, it has to be decided, if 0.05mol/L HCl is worse for green chemistry than a 2.0mol/L acetic acid or a 2.0mol/L formic acid, respectively, with elevated requirements on the reactor material. This is especially important as the conversion and the yield are not the same for these three options. For this thesis 0.05mol/L HCl was considered to be more advantageous and that is why the following tests were made in 0.05mol/L HCl.

4.3.5 Alkylation of naphthalene with different alcohols

The following experiments were carried out in order to study which alcohols were able to alkylate naphthalene at 180°C during 16h in 0.05mol/L HCl. Primary alcohols, secondary alcohols and a tertiary alcohol were tested. Within the primary alcohols some derivatives of benzyl alcohol were also investigated. The results are summarized in Table 4. and Table 4.7.

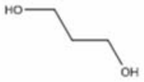
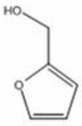
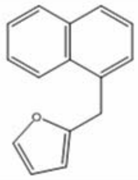
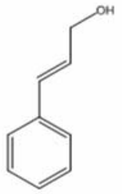
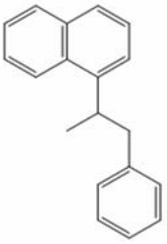
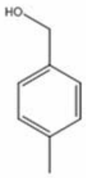
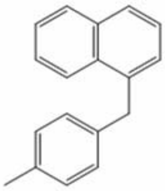
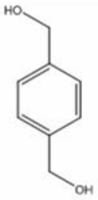
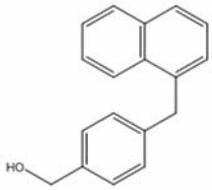
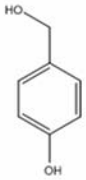
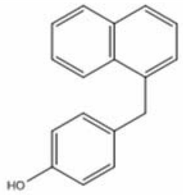
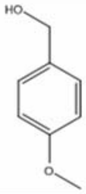
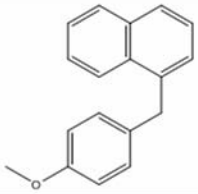
name of alcohol	structure of alcohol	kind of alcohol	structure of Friedel-Crafts product (1-position)
ethylene glycol		primary	
1,3-propanediol		primary	
furfuryl alcohol		primary	
cinnamyl alcohol		primary	
4-methylbenzyl alcohol		primary	
1,4-benzenedimethanol		primary	
4-hydroxybenzyl alcohol		primary, aromatic	
4-methoxybenzyl alcohol		primary	

Table 4.6: Friedel-Crafts type reactions of naphthalene with primary alcohols.

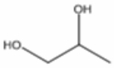
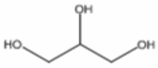
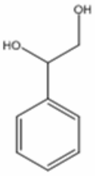
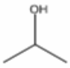
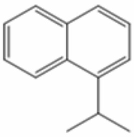
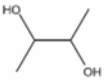
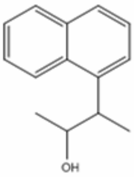
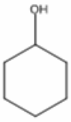
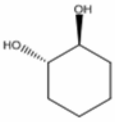
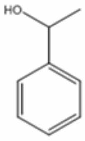
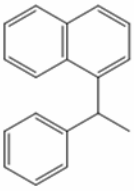
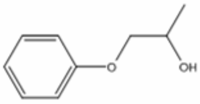
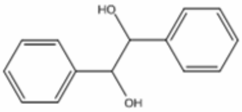
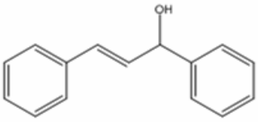
name of alcohol	structure of alcohol	kind of alcohol	structure of Friedel-Crafts product (1-position)
1,2-propanediol		primary, secondary	
glycerol		primary, secondary	
phenyl-ethanediol		primary, secondary	
2-propanol		secondary	
2,3-butanediol		secondary	
cyclohexanol		secondary	
trans-1,2-cyclohexanediol		secondary	
sec-phenethyl alcohol		secondary	
phenoxy-2-propanol		secondary	
meso-hydrobenzoin		secondary	
1,3-diphenyl-2-propen-1-ol		secondary	
pinacol		tertiary	

Table 4.7: Friedel-Crafts type reactions of naphthalene with secondary and tertiary alcohols.

Considering these results, primary alcohols next to delocalized systems of electrons alkylated naphthalene very well. This was also valid for the secondary alcohols 2-propanol, 2,3-butanediol and for sec-phenethyl alcohol. The other tested alcohols did not alkylate naphthalene.

Thus, activation was especially necessary for primary alcohols. Secondary alcohols showed good reactivity, except for sterically hindered alcohols.

The Friedel-Crafts type alkylation of naphthalene by benzyl alcohol was very efficient with 0.05mol/L HCl at 180°C within 16h. Acetic or formic acid can replace HCl, but much higher acid concentrations are necessary.

The Friedel-Crafts type alkylation of naphthalene can also be carried out with activated primary alcohols or with some secondary alcohols.

4.4 Alkylation of phenol

Secondly, another target molecule for the Friedel-Crafts type reaction, namely phenol, was investigated under hydrothermal conditions. The same reaction mechanism can be expected, but it is known phenol is not easy to alkylate. Therefore, these studies focus on the transferability of the hydrothermal Friedel-Crafts type alkylation.

4.4.1 Benzylation of phenol as a function of the temperature

The same reaction conditions as for the benzylation of naphthalene were also applied for the benzylation of phenol. The temperature was changed in a range from 125°C to 220°C and five aqueous mixtures were used as solvents. These were pure water, 1.0mol/L NaCl, 0.5mol/L HCl, 1.0mol/L HCl and a solution of 0.5mol/L NaCl and 0.5mol/L HCl.

There was no reaction in pure water until 150°C. At 180°C low amounts of ethers were formed. At least 200°C were necessary to obtain the Friedel-Crafts product as main product. Ethers remained byproducts of low amounts and further impurities occurred after reaction at 220°C. Anyhow, the conversion was not complete.

Also 1.0mol/L NaCl as solvent did not lead to products at 125°C. At 150°C and at higher temperatures two ethers were formed in low amounts. 200°C and 220°C led to the Friedel-Crafts products as main products.

Solvents with HCl led to the Friedel-Crafts products from 125°C to 220°C as main products. Ethers were byproducts and also alkylated ethers were observed. At temperatures of at least 150°C the ethers were alkylated. The conversion of the benzyl alcohol was quantitative not till 180°C. 1.0mol/L HCl led to higher yields of benzyl phenol, whereas the solvent with NaCl and HCl led to a higher amount of alkylated ethers than 0.5mol/L HCl or 1.0mol/L HCl.

NaCl showed advantages compared to pure water as higher product amounts were obtained at the same temperature. Complete conversions in combination with high purities were caused by HCl containing solvents yet at 180°C.

Therefore, a solvent based on HCl is chosen for further investigations.

The results of the reaction of phenol and benzyl alcohol were treated in further detail and the result is a view on the impact on the stereochemistry and the conversion rates. This is displayed in Table 4.8.

Solvent	Temperature (°C)	Conversion (%) [a]	Yield of mono-substituted Friedel-Crafts product (%)[b]	o/p-ratio
Water	125	0	0	-
	150	0	0	-
	180	1	1	-
	200	7	7	61 : 39
	220	14	14	59 : 41
0.5M HCl	125	100	89	50 : 50
	150	99	72	52 : 48
	180	100	66	53 : 47
	200	100	67	53 : 47
	220	100	63	53 : 47
1.0M HCl	125	84	71	48 : 52
	150	100	75	50 : 50
	180	100	69	51 : 49
	200	94	65	51 : 49
	220	100	62	52 : 48

Table 4.8: Alkylation of phenol with benzyl alcohol in aqueous media.

Reaction conditions: 0.5mmol benzyl alcohol, 15mmol phenol, 10mL solvent, heated to the desired temperature for 16h. a) The conversions were determined as 100% less the ratio of final to initial amount of benzyl alcohol, b) Yields were determined as the ratio of the amount of mono-alkylated products to the initial amount of benzyl alcohol.

As it could be expected according to Katritzky et al. [125], the ortho-products were especially preferred in pure water, but the obtained amounts of mono-alkylated Friedel-Crafts products were limited. The ortho- and para-products were synthesized almost equimolar in 0.5mol/L or in 1.0mol/L hydrochloric acid, but at higher yields than in pure water. Thus, 125°C and 0.5mol/L HCl were the most efficient conditions which were tested. Probably, changes of the temperature, the time and the acid concentration reach further optimizations. At least, the optimal condition has to be found in dependence of the question which product or product mixture has to be synthesized and which ratio of starting material is chosen.

4.4.2 Benzylation of phenol as a function of the concentration of HCl

After these experiments on the temperature dependence, the dependence on the kind of acid and its concentration were studied. The concentration of HCl was decreased until 0.005mol/L at 180°C for a reaction time of 16h.

Diminishing the concentration of HCl in the solvent had no great effect until a concentration of 0.1mol/L HCl was reached. At 0.05mol/L HCl a very low amount of benzyl alcohol remained non-converted. At concentrations not exceeding 0.03mol/L HCl, which corresponds to the pH value of gastric acid, greater amounts of benzyl alcohol remained non-converted in the product mixture. However, at 0.005mol/L HCl the yield of Friedel-Crafts products was still good, but the byproducts yet lost importance. Therefore this concentration could still be interesting, if the purity had a higher importance than the conversion rate. In contrast to the observations for naphthalene, the ortho/para-ratio is almost independent of the acid concentration.

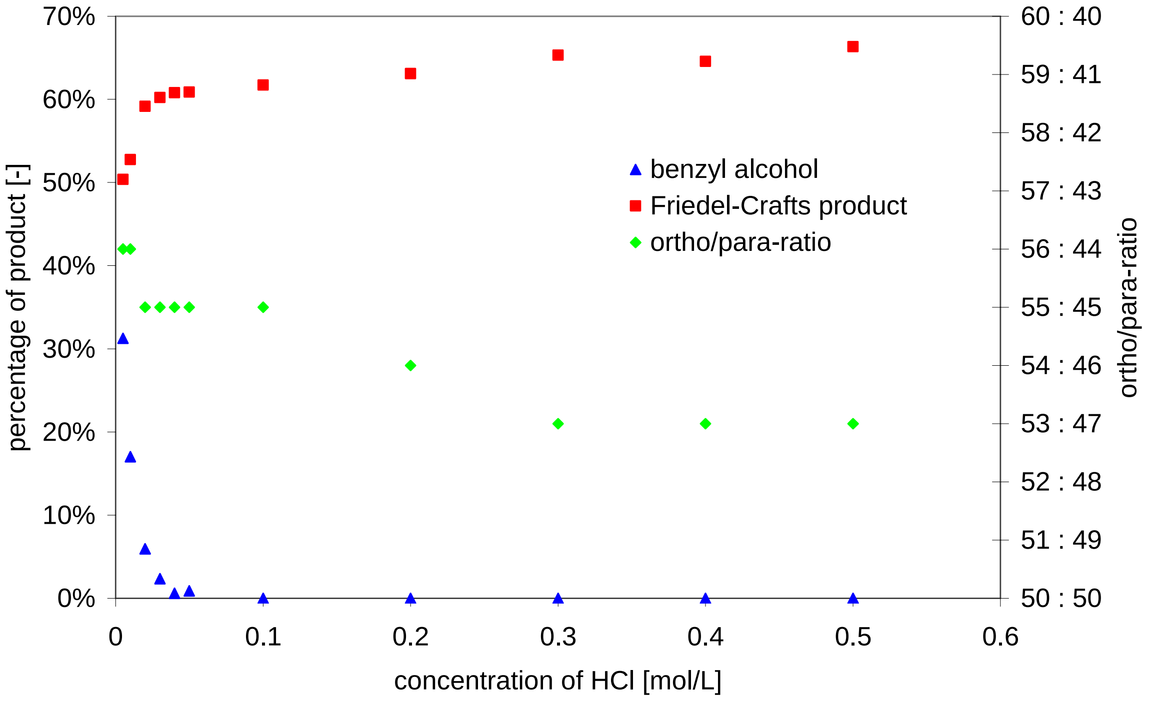


Figure 4.5: Amounts of products of the benzylation of phenol as a function of the concentration of HCl.

Percentages of non-converted starting material and formed mono-alkylation product (both: left axis) as well as the ortho/para-ratio (right axis) as a function of the concentration of HCl, after reaction at 180°C for 16h.

4.4.3 Benzylation of phenol in different acids

As previously shown, organic acids such as acetic acid and formic acid can be considered as alternatives for the mineral acid HCl.

During the studies acetic acid showed even at an elevated concentration of 2.0mol/L less efficiency than hydrochloric acid at a concentration of 0.005mol/L. Besides that, there was a good conversion toward the Friedel-Crafts products with a low amount of dibenzyl ether and phenylbenzyl ether. Decreasing the concentration of acetic acid until 0.1mol/L decreased also the conversion rate, but did not show any positive side effect.

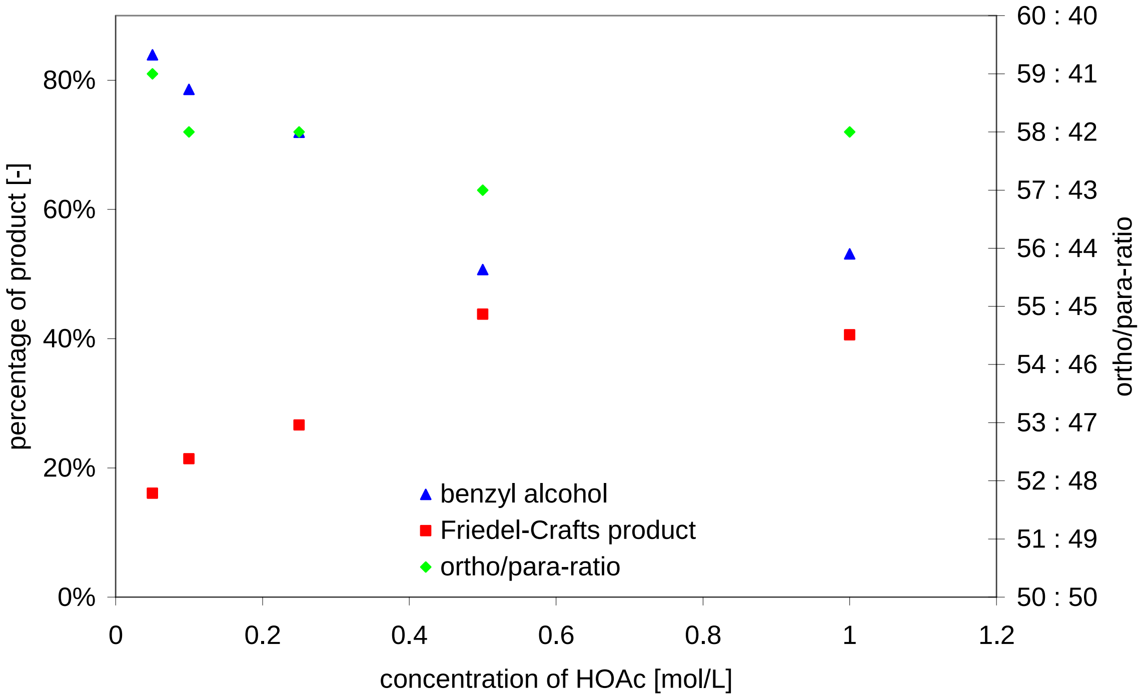


Figure 4.6: Amounts of products of the benzylation of phenol as a function of the concentration of HOAc.

Percentages of non-converted starting material and formed mono-alkylation product (both: left axis) as well as the ortho/para-ratio (right axis) as a function of the concentration of HOAc, after reaction at 180°C for 16h.

The same results were obtained for formic acid by repeating the series with concentrations from 2.0mol/L down to 0.1mol/L. Formic acid resulted in a higher conversion rate than acetic acid, but its effect on the yield was nevertheless lower than the one of HCl. In comparison to acetic acid, formic acid was more efficient at the same concentration. This was yet observed for the benzylation of naphthalene. More quantitatively, the concentration of acetic acid could be decreased by a factor of ten for formic acid in order to observe similar effects for the reaction. This could be verified for the range of 1.0 to 2.0mol/L acetic acid and 0.1 to 0.2mol/L formic acid, respectively.

The influences on the yield of mono-alkylated Friedel-Crafts product as well as on the ortho/para-ratio are summarized in Figure 4.6 and Figure 4.7.

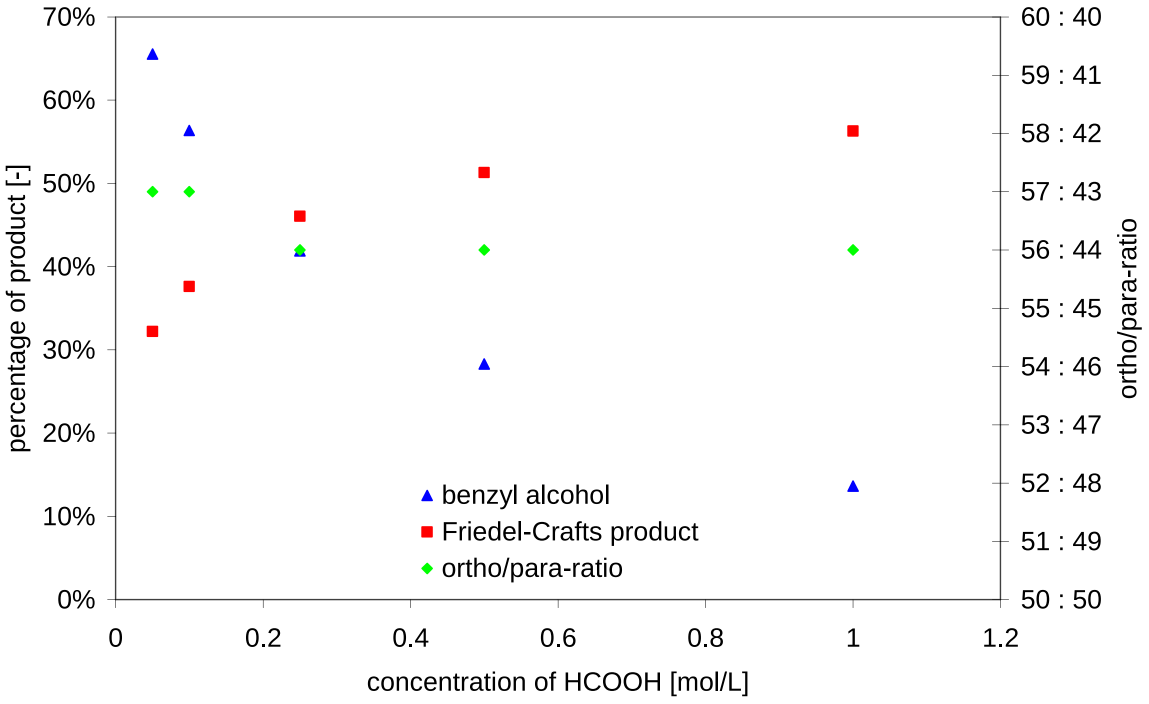


Figure 4.7: Amounts of products of the benzylation of phenol as a function of the concentration of HCOOH.
Percentages of non-converted starting material and formed mono-alkylation product (both: left axis) as well as the ortho/para-ratio (right axis) as a function of the concentration of HCOOH, after reaction at 180°C for 16h.

All in all, neither acetic acid nor formic acid was as efficient as HCl at comparable concentrations. Therefore the lower amount of hydrochloric acid was favored instead of the lower toxicity of the biodegradable acids. The standard conditions were confirmed to be 180°C for 16h in 0.05mol/L HCl.

4.4.4 Alkylation of phenol with different alcohols

In the following, the reactions of several alcohols with phenol were studied under these standard conditions. In the beginning, primary alcohols were taken und then secondary alcohols and a tertiary alcohol followed. Table 4.9 and Table 4.10 display the observations. Then, the following paragraphs note observations which are important, but did not or not only lead to the expected Friedel-Crafts products.

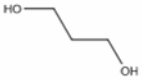
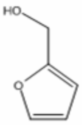
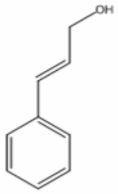
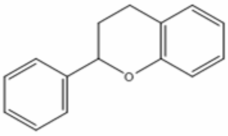
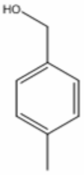
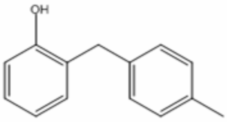
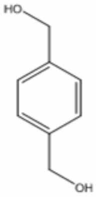
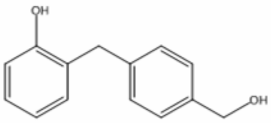
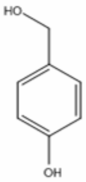
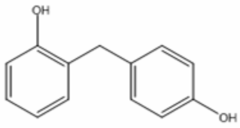
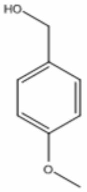
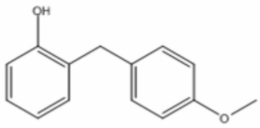
name of alcohol	structure of alcohol	kind of alcohol	structure of Friedel-Crafts product (ortho-position)
ethylene glycol		primary	
1,3-propanediol		primary	
furfuryl alcohol		primary	
cinnamyl alcohol		primary	
4-methylbenzyl alcohol		primary	
1,4-benzenedimethanol		primary	
4-hydroxybenzyl alcohol		primary, aromatic	
4-methoxybenzyl alcohol		primary	

Table 4.9: Friedel-Crafts type reactions of phenol with primary alcohols.

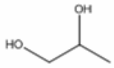
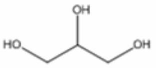
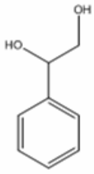
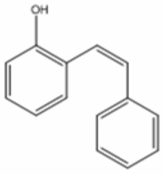
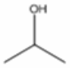
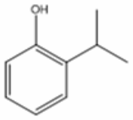
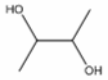
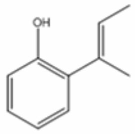
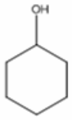
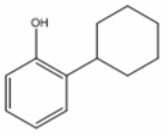
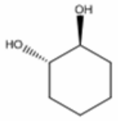
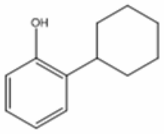
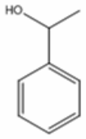
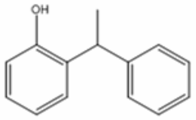
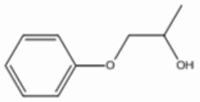
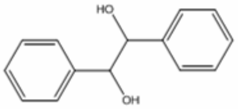
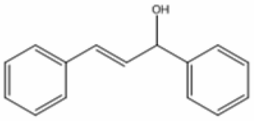
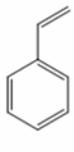
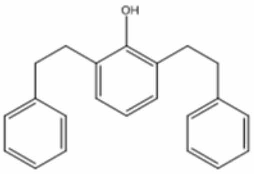
name of alcohol	structure of alcohol	kind of alcohol	structure of Friedel-Crafts product (ortho-position)
1,2-propanediol		primary, secondary	
glycerol		primary, secondary	
phenyl-ethanediol		primary, secondary	
2-propanol		secondary	
2,3-butanediol		secondary	
cyclohexanol		secondary	
trans- 1,2-cyclohexanediol		secondary	
sec-phenethyl alcohol		secondary	
phenoxy-2-propanol		secondary	
meso-hydrobenzoin		secondary	
1,3-diphenyl- 2-propen-1-ol		secondary	
pinacol		tertiary	
styrene		alkene, no alcohol	

Table 4.10: Friedel-Crafts type reactions of phenol with secondary and tertiary alcohols.

Furfuryl alcohol showed reactions in the presence of phenol, but no Friedel-Crafts product.

The product of phenol with cinnamyl alcohol suggests a Friedel-Crafts type reaction which was followed by a ring closure. This reaction is in congruence with the reaction of phenyl-ethanediol on itself and the formation of 2-phenylnaphthalene (compare with Figure 2.6). Whereas a second primary alcohol caused the ring closure there, here the double bond of the side chain of cinnamyl alcohol closed the ring with the aromatic alcohol of phenol forming a cyclic ether.

Derivatives of benzyl alcohol, especially 4-methylbenzyl alcohol and 1,4-benzenedimethanol, did not only form monosubstituted Friedel-Crafts products with phenol. In the case of 1,4-benzenedimethanol the mass spectrum proves that one molecule alkylated two different phenol molecules.

For the reaction of trans-1,2-cyclohexanediol with phenol to cyclohexyl-phenol one hydroxyl functional group reacted as awaited and the other one has to be hydrogenated formally. Hydrogenations like this are already known under hydrothermal conditions, but the formally dehydrogenated molecule is unknown.

Pinacol did not react with phenol, but showed the pinacol rearrangement.

Taking everything into consideration, activated primary alcohols alkylated phenol very well. Also rather small secondary alcohols were able to do so. Nevertheless, only 2-propanol, phenylethanediol and sec-phenethyl alcohol reacted to the Friedel-Crafts products in high yield.

4.4.5 Alkylation of phenol using different amounts of starting material

Changing the reaction conditions a little had an influence on the reactions. For example, this could be observed when phenol reacted with cyclohexanol. The use of 0.25g of each starting material led to a higher yield of the Friedel-Crafts products, but also to a lower conversion rate. However, a molar ratio of 5 : 1 for phenol to cyclohexanol resulted in a much higher yield of cyclohexene. For sec-phenethyl alcohol, the molar ratio of 5 : 1 showed a much lower amount of the Friedel-Crafts product which resulted from two attacks of the alcohol on phenol and the purity of the mono-substituted Friedel-Crafts product increased. Besides, there were fewer quantities of byproducts in comparison to the experiment with 0.25g of each starting material.

Applying a molar ratio of phenol to alcohol of 30 : 1 influenced the product amounts, too. In Table 4.11 the quantified results for the yield and the ortho/para-ratio are compiled.

Alcohol	Yield of mono-substituted Friedel-Crafts product (%)[a]	ortho/para-ratio[b]
benzyl alcohol	78	56 : 44
sec-phenethyl alcohol	93	34 : 66
4-hydroxybenzyl alcohol	68	18 : 82
cinnamyl alcohol	47	-
cyclohexanol	3	59 : 41
n-hexanol	0	-
2-propanol	3	64 : 36

Table 4.11: Friedel-Crafts type alkylation of phenol with different alcohols.

Reaction conditions: 0.5mmol alcohol, 15mmol phenol, 10mL solvent, heated to 180°C during 16h. a) The yield was determined as the ratio of the amount of mono-alkylated products to the initial amount of benzyl alcohol. b) The ortho/para-ratio was determined by means of GC-FID.

As could be expected from reported and from own results [137], only strongly activated alcohols yielded substantial amounts of the awaited alkylation product such as 93% for phenylethanol. Interestingly, cinnamyl alcohol formed the expected Friedel-Crafts product (molecule A in Figure 4.8) in a first step, but underwent a ring-closure yielding flavan in a second step (molecule B in Figure 4.8). GC data of the reaction product indicated that 35% of flavan derivatives and 13% of the desired Friedel-Crafts products were formed. This observation opens new opportunities for the production of biologically relevant flavonoids.

Besides, the reaction of cinnamyl alcohol with phenol was also carried out in a microwave oven. Within 3min the result was comparable to the reaction at standard conditions within 16h. Anyhow, the microwave oven caused a higher yield for the ortho-product.

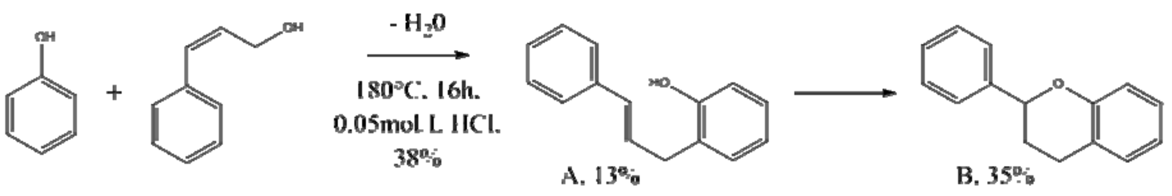


Figure 4.8: Reaction scheme with ring-closure for cinnamyl alcohol with phenol.

Cyclohexanol and iso-propanol are typical activated aliphatic alcohols. They led only to very limited amounts of Friedel-Crafts product under these conditions.

4.4.6 Alkylation of phenol re-using the aqueous phase

The possibilities to change the system were unlimited, but also other more basic aspects should be discussed. Therefore, the study on Friedel-Crafts type alkylations of phenol was round up by a short study on the recyclability of the HCl containing aqueous phase of the reaction. After the reaction, the products were extracted and the initial amounts of both starting materials were added in the aqueous phase, which is reused. The formed amounts of Friedel-Crafts products and of two flavan isomers using cinnamyl alcohol as alkylating agent are illustrated in Figure 4.9.

It was observed that the aqueous phase, which is the diluted hydrochloric acid, can be reused. As the amounts of received products increase with the number of cycles passed, the reuse is not only possible, it is also favorable. It seems the reaction has an induction period or it is autocatalytic. However, the augmentation of the amount of products can also be caused by the formation of water-soluble intermediates. These could remain in the aqueous phase and they can take part in the reaction yet in the beginning of the next cycle.

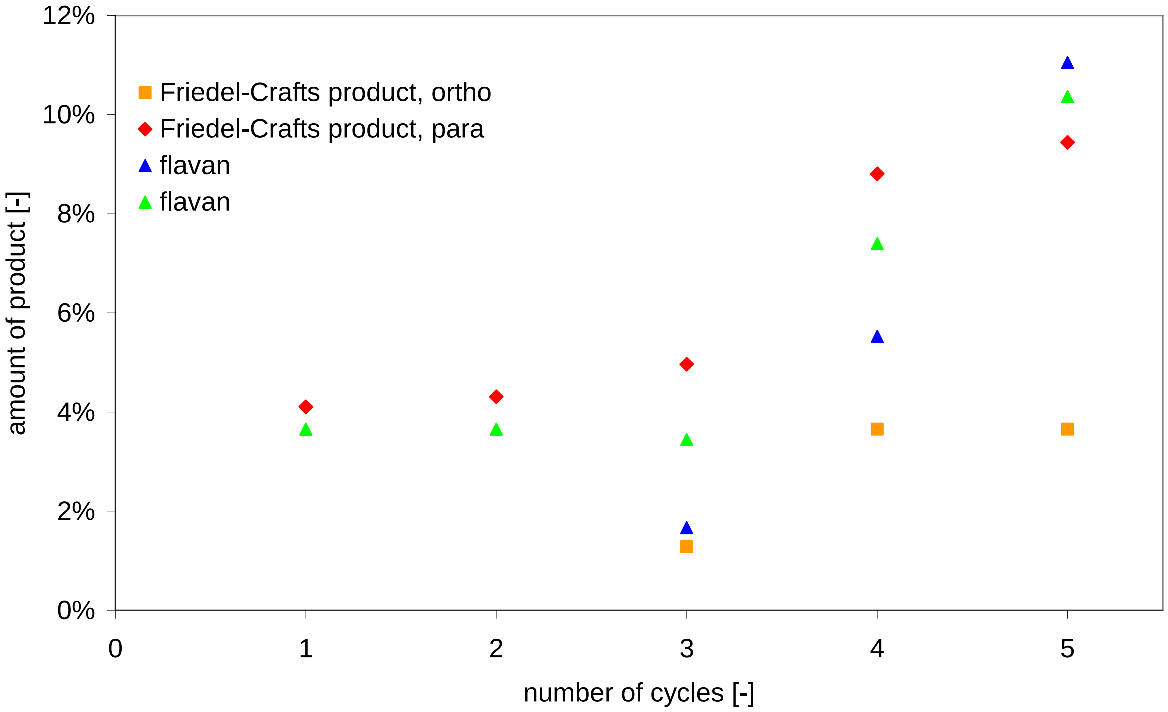


Figure 4.9: Product amounts for two isomers of flavan and two isomers of Friedel-Crafts products after recycling the aqueous phase.

Obviously, reactive compounds are enriched in the water phase. This would be an argument for the formation of intermediary chloroalkanes which alkylate the aromatic compounds as long as they would be soluble in water.

Benzyl alcohol alkylated phenol very efficiently during 16h at 180°C in 0.05mol/L HCl. Higher concentrations of acetic or formic acid gave no better result.

Especially activated primary alcohols alkylated phenol efficiently.

The reuse of the aqueous phase of the reaction mixture was advantageous.

4.5 Reactions of substituted aromatics

Thirdly, the Friedel-Crafts type reactions of some aromatic compounds were studied under hydrothermal conditions. The conditions were set to a standard of 16h at 180°C. The use of diluted acids was not always applied.

4.5.1 Benzylation of toluene

Toluene showed no reaction on benzyl alcohol in pure water. In 1.0mol/L NaCl solution there was a bit of dibenzyl ether, but besides that the starting materials did not react. When using an aqueous solution which had 0.5mol/L HCl and 0.5mol/L NaCl, the result was that all three mono-alkylated Friedel-Crafts products were formed and the benzyl alcohol was converted quantitatively. These three isomeric benzyl toluenes were accompanied by a bit of dibenzyl ether and low amounts of benzylbenzyl alcohol. Furthermore, there were other traces such as for diphenyl ethane and a trimer of benzyl alcohol. The observation after reaction in 1.0mol/L HCl was the same as in 0.5mol/L HCl. Additionally, there were two peaks probably for two ethers which were produced when a benzyl alcohol attacked on the ring of another benzyl alcohol.

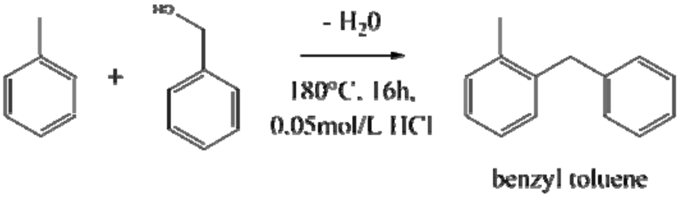


Figure 4.10: Friedel-Crafts type alkylation of benzyl alcohol and toluene.

4.5.2 Friedel-Crafts type reaction of benzaldehyde and acetophenone

The second step was to repeat this study with benzaldehyde and acetophenone. In pure water the main product was benzylidene acetophenone which could be formed when benzaldehyde and acetophenone made an aldol reaction, followed by a dehydration. In addition, there was a bit of ethylphenyl ether. In 1.0mol/L NaCl solution the results were the same, but the yield of benzylidene acetophenone was higher and the yield of ethylphenyl ether was much increased so that the amount was in the range of the amount of benzylidene acetophenone. The use of HCl, as it was the case for 0.5mol/L HCl, 1.0mol/L HCl and the solution of 0.5mol/L HCl and 0.5mol/L NaCl, respectively, increased the conversion so that the amounts of starting materials decreased obviously. All the HCl containing solvents also caused a low quantity of 1,3,5-triphenyl-1,5-pentanedione which could be explained by two aldol reactions of two acetophenones on the side chain of one benzaldehyde. Other byproducts were not observed.

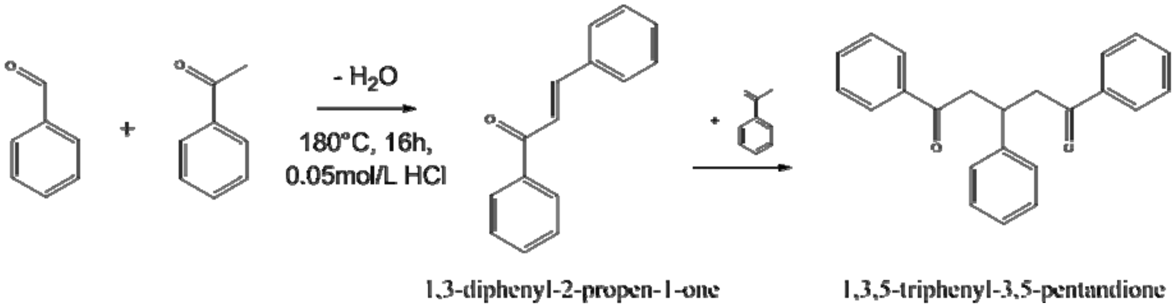


Figure 4.11: Benzylaldehyde, acetophenone and their products.

4.5.3 Alkylation of aromatic compounds

Furthermore, the reactions of some alcohols with four aromatic compounds were studied at 180°C during 16h. The alcohols were 2-propanol, 2,3-butanediol, sec-phenethyl alcohol, 4-hydroxybenzyl alcohol, 4-methoxybenzyl alcohol and benzyl alcohol. Phenol, naphthalene, toluene and p-xylene were the aromatic compounds. They are chosen in order to compare the reactivities of the compounds. Here, a molar ratio of 1 : 10 was applied for the amounts of alcohol to aromatic compound.

2-Propanol alkylated phenol so that two Friedel-Crafts products were reported. Neither with naphthalene nor with toluene the Friedel-Crafts product was obtained and with p-xylene only a trace. Thus, the reaction of 2-propanol was possible with exception for naphthalene and toluene, but the yields were not high with phenol and p-xylene.

No Friedel-Crafts product was detected for the alkylation of phenol with 2,3-butanediol. Products were found neither in the case of naphthalene nor with toluene. p-Xylene did not react with 2,3-butanediol, but showed a trace of 2-(p-tolylmethyl)-p-xylene which would be the product when p-xylene alkylated p-xylene. In conclusion, 2,3-butanediol did not react with the here tested aromatic compounds under these conditions. Reactions reported before gave evidence that changing the conditions might help to improve the reactivities.

Two isomers of (1-phenylethyl)-phenol were the products of the Friedel-Crafts type reaction of sec-phenethyl alcohol with phenol. A very low amount of phenol was attacked by two sec-phenethyl alcohol molecules and, besides, no byproducts were found. The reaction of sec-phenethyl alcohol with naphthalene led to two Friedel-Crafts products and a dimer of the alcohol as well as to the detection of some other byproducts in low amounts. No product besides the dimer of sec-phenethyl alcohol was obtained with toluene. p-Xylene did not react with sec-phenethyl alcohol, but two products after dimerization of the alcohol were found and also a bit of the dimer of p-xylene in form of the 2-(p-tolylmethyl)-

p-xylene. Thus, sec-phenethyl alcohol received higher yields of Friedel-Crafts products with the tested aromatic compounds, except for p-xylene.

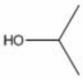
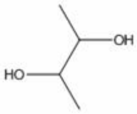
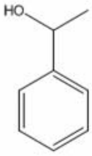
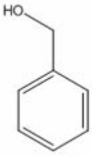
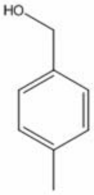
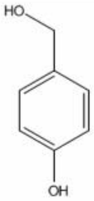
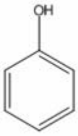
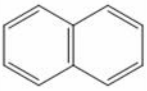
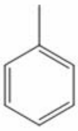
						
	+	-	+++	++	++	++
	-	-	+	+++	++	-
	-	-	+	++	++	-
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Table 4.12: Combinations of aromatic compounds and alcohols and their amount of Friedel-Crafts products.

As already known, the reaction of benzyl alcohol with phenol led to two Friedel-Crafts products and no byproducts were observed. Furthermore, naphthalene was alkylated by benzyl alcohol very selectively and without byproducts. Toluene showed three Friedel-Crafts products with benzyl alcohol and dimers were formed for benzyl alcohol. p-Xylene was also attacked by benzyl alcohol and showed only one product of benzyl xylene as expected. Thus, benzyl alcohol alkylated all the tested aromatic compounds in good yields and confirmed its position as standard alcohol.

The next alcohol with aromatic system to be tested was 4-methylbenzyl alcohol. There were two products with phenol which might had been the Friedel-Crafts products due to the molar mass and some characteristics of the mass spectra. The same reaction with naphthalene caused two Friedel-Crafts products. Neither dialkylated nor other byproducts were found. Toluene reacted with 4-methylbenzyl alcohol to all the three possible mono-alkylated products, but the data from GC-MS suggested also some dialkylated products due to the maximal mass and a similarity to the mass peaks for the mono-alkylated products. 4-Methylbenzyl alcohol formed 2-(p-tolylmethyl)-p-xylene with p-xylene and did not show any byproduct. Considering these results, 4-methylbenzyl alcohol reacted extremely well with the four tested aromatic compounds by a Friedel-Crafts type reaction. Usually, the selectivity was very high.

Last but not least, 4-hydroxybenzyl alcohol was tested as alkylating agent for the four aromatic compounds. It formed two mono-alkylated Friedel-Crafts products with phenol and no byproducts were found. With naphthalene, toluene and p-xylene, respectively, no products were observed. This meant that no products were formed or that the formed products could not be detected. The selective alkylation of phenol in rather high yield suggested that the other aromatic compounds also reacted with 4-hydroxybenzyl alcohol. The lack of the alcohol after the reaction confirmed that. If the alkylation was preferred to be a di-alkylation or an oligo-alkylation, the analyzing method might have not been able to detect the products due to their boiling points above the maximal temperature of the GC. Therefore, it could not be said for sure, if 4-hydroxybenzyl alcohol was a good alkylating agent or not.

These results are summarized in Table 4.12. The indications for the amounts range from “-“ for a very bad conversion over “+” and “++” until “+++” for a very high yield.

All in all, 2-propanol reacted with phenol and p-xylene, but not with naphthalene or toluene and never gave a high yield for the Friedel-Crafts products. 2,3-Butanediol did not react with the tested aromatic compounds. The secondary alcohol sec-phenethyl alcohol and most derivatives of benzyl alcohol reacted mainly in high selectivity and gave a high yield. p-Xylene was predestinated for lower yields and the deactivated 4-hydroxybenzyl reacted only with phenol.

4.5.4 Benzylation of aromatic compounds

In a last step, the reactions of phenolic derivatives with benzyl alcohol were studied at 180°C with reaction times of 16h. Table 4.13 shows the obtained and quantified results.

Aromatic compound	Yield[a]	Selectivity[b]
Catechol	66%	3-benzyl catechol 44% 4-benzyl catechol 56%
p-cresol	89%	2-benzyl-4-methyl phenol 82% 3-benzyl-4-methyl phenol 18%
4-hydroxybenzoic acid	<1%	-
4-hydroxyphenyl acetic acid	41%	4-hydroxy-3-benzylphenyl acetic acid > 98%

Table 4.13: Benzylation of hydroxyl aromatic derivatives with benzyl alcohol. Reaction conditions: 0.5mmol benzyl alcohol, 15mmol phenolic compound, 10mL solvent, heated to 180°C during 16h. a) The yield was determined as the ratio of the amount of mono-alkylated products to the initial amount of benzyl alcohol. b) The ratio of the isomers was determined by means of GC-FID.

The reaction of benzyl alcohol on catechol (Table 4.13) yielded an amount of 66% for the alkylation product. Catechol could not form para-products because of its high symmetry. Therefore a mixture of 3- and 4-benzyl catechol (see Figure 4.12) was obtained. A slight excess of 4-benzyl catechol is detected.

p-Cresol led to 89% mono-alkylated product and a high excess of 2-benzyl-4-methyl phenol is observed with a 73% overall yield for this compound.

4-Hydroxybenzoic acid appeared to be a very weak electron donor for the Friedel-Crafts reaction, probably because of the electron attracting properties of the carboxylic group. Thus, the molecule could not react until it lost this carboxylic group via an already observed decarboxylation reaction [138] in order to yield phenol in a first step, and the usual benzylphenol isomers in a second step.

4-Hydroxyphenyl acetic acid (Table 4.13), on the contrary, proved to be more reactive and obtained 41% of mono-alkylated product. Interestingly, the alkylation was very selective towards the addition in ortho-position – with respect to the hydroxyl group.

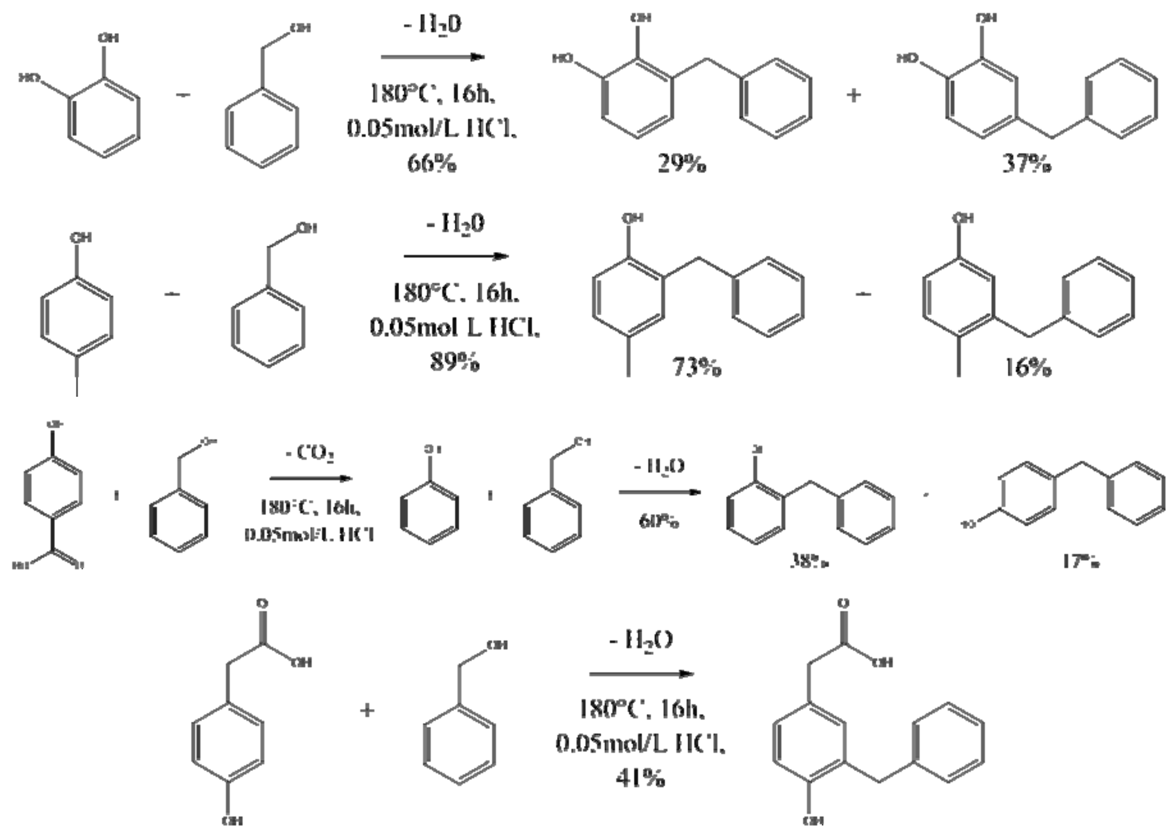

Figure 4.12: Alkylation of catechol, p-cresol, 4-hydroxy-benzoic acid and 4-hydroxyphenyl acetic acid with benzyl alcohol.

It was confirmed that the choice of reaction conditions, namely the solvent, is a way to induce or to avoid a reaction. This is also valid for substituted benzene derivatives.

The combination of alcohol and aromatic compound is important for the reactivity.

The benzylation of aromatic compounds showed that weaker electron donors become alkylated to a lower percentage.

4.6 Polybenzyl alcohol

As it was observed as a side reaction in the chapters 4.2 and 4.5, benzyl alcohol can dimerize through Friedel-Crafts type reactions. This is especially observable, when there is another aromatic compound in the mixture which is not activated enough to be attacked by benzyl alcohol. If the self-alkylation can be repeated on the benzylbenzyl alcohol, a polymerization is started. Such a polymerization has already been documented for benzyl alcohol in presence of tungsten oxide nanoparticles which act as catalysts for the polymerization [139].

4.6.1 Calibration of the Size Exclusion Chromatography (SEC)

In the beginning, six standards of polystyrene were analyzed using chloroform as solvent. Polystyrene was chosen because of its similarity to the expected polybenzyl alcohol. Other standards which were less similar would not have been comparable as the retention during a SEC-run is not only influenced by the molar mass, but also by the shape of the molecules. Figure 4.13 shows the different chromatograms for the standard samples. The three lighter standards, 208g/mol, 580g/mol, and 950g/mol are of interest, while the other three standards of 1490g/mol, 2050g/mol and 2500g/mol are out of the range of the tested polybenzyl alcohols. Besides, the latter are hardly separated.

To mention is that small molecules pass the detector after the big ones as the small ones enter into the pores and, thus, they have a longer effective way. Big molecules do not enter into the pores – or at least into fewer pores – and therefore they leave the column earlier. That is also the reason why there is a minimum for the retention time. This minimum, which is determined by the time which is necessary to pass the column without any retention, the so called dead time, is reached for all molecules which are too big for any separation by this column. After this the difference of retention times increases while keeping equal differences in the molar mass. Thus, only the molecules with low masses are separated clearly one from another.

Anyhow, there were challenges connected to the analysis of the chromatograms. In some cases oligomers had an elevated retention time so that their maxima were too late for the one and too early for the other species. It seemed that in these cases especially the trimers and tetramers were eluted several seconds later. The monomers could not be well detected by the RID, but therefore the diagrams of the RID are completed by the one of a UV-detector of 254nm of wavelength. The UV-signals must not be compared with molar amounts. The short, but provable divergence of the retention times is owing to the physics as the UV-detector is passed before the RID. As this causes a divergence of about two seconds, it was kept in mind, but not regarded in detail. However, the exactness of quantifications based on the RID-signal is limited, especially compared to the GC measurements. They have to be seen rather in a comparative context with the other predictions of these series.

The standard of 208g/mol shows a clear maximum at a retention time of 8.5min for the dimer and a shoulder at 9.0min probably represents the monomer. Then, at 7.9min the standard of 580g/mol shows a first maximum which represents the trimer, followed by the tetramer at 7.5min, the pentamer at 7.2min and than, at about 7.0min, the hexamer is no more clearly separated from higher oligo- and polymers. The standard of 950g/mol shows only a maximum at 6.5min without any finer structure which would allow determining further details. The other standards with molar masses of 1490g/mol, 2050g/mol and 2500g/mol with maxima at 6.2min, 6.1min and 5.9min, respectively, give no additional information.

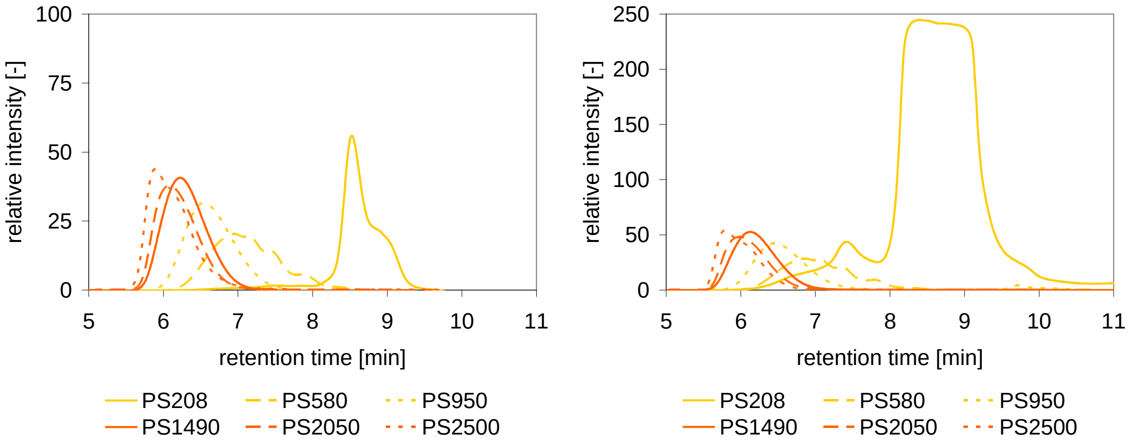

Figure 4.13: Standards of polystyrene, RID-signal (left) and UV-signal (right) per mass.

4.6.2 Polymerization of benzyl alcohol

The effect of a polymerization of benzyl alcohol was studied in further detail under hydrothermal conditions. Therefore, different amounts of benzyl alcohol were heated in hydrochloric acid. The temperatures and the durations of heating were varied. The products of these tests were analyzed by means of SEC which was calibrated by polystyrene standards (see chapter 4.6.1). According to the nature of these analyses, a quantification of the result was not possible for single compounds.

In the following, some chromatograms visualize the data from SEC. Here, the results of the Refractive Index Detector (RID) are presented as the refractive index is proportional to the molar mass. This property was not ensured for the other two detectors which were UV-detectors. The signals at 254nm are shown, too, in order to get an idea of the amount of remained benzyl alcohol. The diagrams use the same axes in order to facilitate the comparison between them. The parameters of each single run of the SEC were exactly the same. Only the concentrations of polymers varied within a low range. Therefore, the chromatograms show the intensities per mass.

At 160°C the reaction of different amounts of benzyl alcohol in 0.5mol/L hydrochloric acid during 24h showed changes in the composition of the product mixture. Starting with 0.5g benzyl alcohol the main product was the trimer at a retention time of 7.9min. Dimers (8.5min) and tetramers (7.5min) were formed at comparable amounts. Pentamers (7.2min) were obtained only in very low amounts. Increasing the amount of starting material to 2.0g and further to 5.0g led to a strong increase of the amount of dimer. However, the amounts of the other oligomers decreased. As the intensity per mass is shown in Figure 4.14, the absolute mass of, for example, trimers might have increased, but the amount of trimers per product mass decreased. This is due to a strong increase of the amount of dimers which dilutes the other oligomers in the product mixture.

Taking 2.0g benzyl alcohol, but increasing the reaction time from 8h over 24h to 40h diminished the amount of dimers hardly. By contrast, the amount of the other oligomers increased.

Thus, at 160°C the highest amount of longer oligomers was obtained at long reaction times for low amounts of starting material.

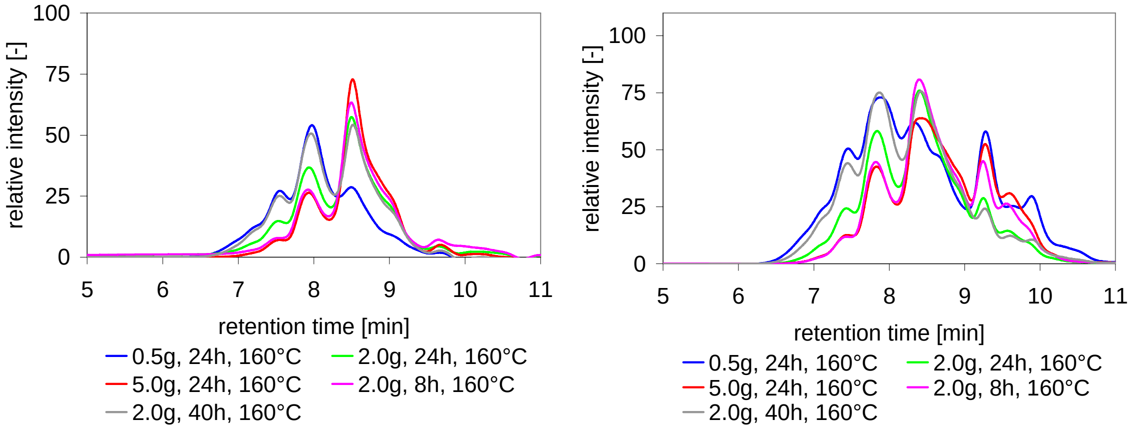

Figure 4.14: Product quantities for the reaction of benzyl alcohol at 160°C, RID-signal (left) and UV-signal (right) per mass.

The same experiments at 180°C gave the results visualized in Figure 4.15. Augmenting the quantity of starting material led to an increase of the amount of dimer after the reaction. However, the amount of higher oligomers decreased, although the amount of trimers diminished only slightly. The UV-signal gave evidence for a higher conversion of the monomers.

The reaction time was also changed from 8h via 24h to 40h for a constant amount of benzyl alcohol. Doing like that, in a first step the amount of dimers decreased and then the oligomers longer than tetramers increased in quantity.

Summing up, also at 180°C low amounts of benzyl alcohol and long reaction times led to higher amounts of longer oligomers.

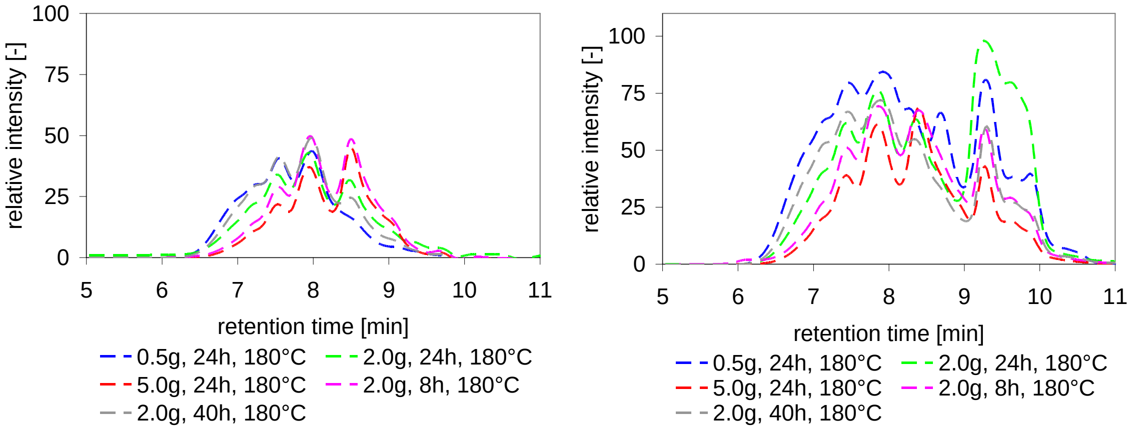

Figure 4.15: Product quantities for the reaction of benzyl alcohol at 180°C, RID-signal (left) and UV-signal (right) per mass.

After showing the data for 160°C and 180°C, Figure 4.16 summarizes the obtained data for 200°C. It was observed that different amounts of benzyl alcohol polymerized almost identically when keeping the other reaction conditions unchanged. Increasing the duration of the reaction led to the same result. The only differences were observed for a high amount of starting material and for a short reaction time as these conditions led to slightly shorter oligomers in average.

To conclude, using high amounts of benzyl alcohol or short reaction times led to higher quantities of formed dimers and trimers than in the other cases and the oligomers did not reach the same maximal length.

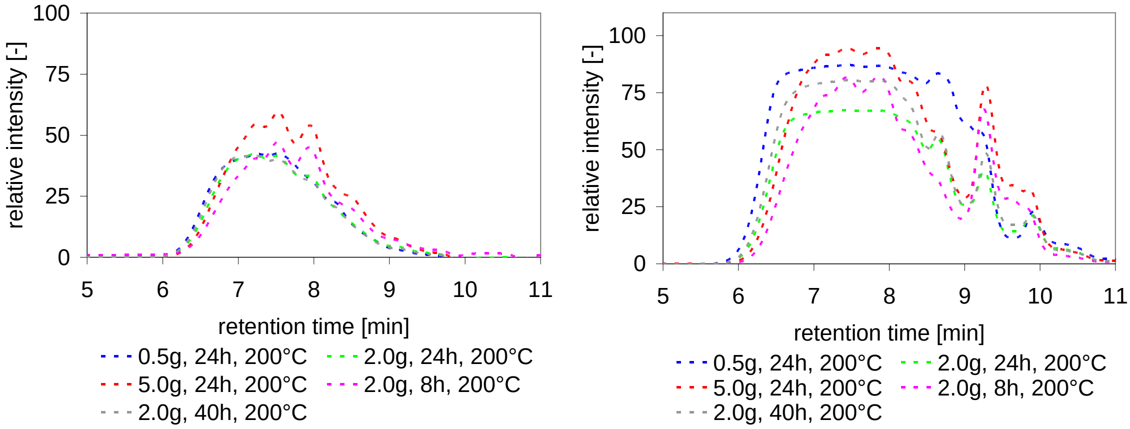

Figure 4.16: Product quantities for the reaction of benzyl alcohol at 200°C, RID-signal (left) and UV-signal (right) per mass.

Repeating the same polymerization reactions at 220°C led to the spectra displayed in Figure 4.17.

An increase of the amount of benzyl alcohol in the beginning led to a slight decrease of the amount of dimers and trimers, while the amount of pentamers and hexamers increased.

Similar observations were made when the reaction time was increased for a constant mass of monomers.

Thus, changing the reaction conditions did not lead to greater differences to the results at 220°C. However, a preference for short oligomers was observed for short reaction times and high amounts of starting material.

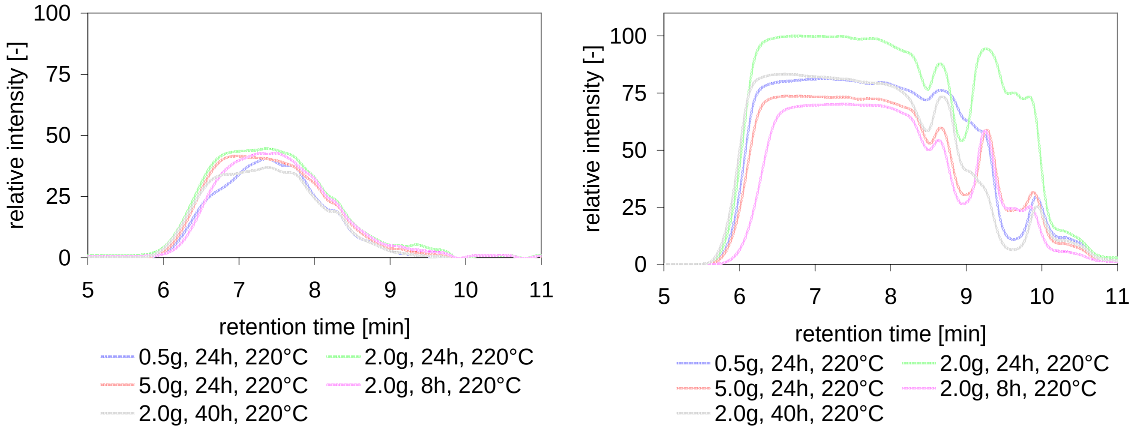

Figure 4.17: Product quantities for the reaction of benzyl alcohol at 220°C, RID-signal (left) and UV-signal (right) per mass.

The temperature dependences must not be neglected as the temperature's influence was very important. A higher temperature led to longer oligomers. While there were hardly any oligomers longer than pentamers in the reaction mixture after heating to 160°C, heptamers and octamers were obtained at 220°C. Dimers and trimers were the main fraction of oligomers after the reaction at 160°C, but they hardly were detected after conversion at 220°C.

Taking these results into consideration, a higher temperature has the main influence and results in a higher polymerization degree, while lower amounts of short oligomers are obtained. The impacts of a higher amount of starting material and a shorter reaction time are less, but lead to higher amounts of obtained short oligomers.

Thus, taking more of the starting material causes more initial polymerizations. But the conversion of all the monomers needs more time. During this time, the initial polymers grow and longer polymers are formed. This can be done by combining a monomer and an oligomer or by combining two oligomers. The fact that the length of the oligomers increases with the temperature gives evidence that the reaction takes place between monomers and oligomers, but not of two oligomers. In addition, the need for a higher temperature is due to the higher activation energy of the oligomer, because the activation energy of benzyl alcohol does not change. Thus, the oligomer becomes more and more stable with increasing length until a further growth becomes improbable. This results finally in a limit for the degree of polymerization.

4.6.3 Characterization of polybenzyl alcohol and its discussion

Analyses were carried out in order to get information of the nature about this yellowish polymer. Therefore, IR-, UV/Vis- and fluorescence measurements were made.

Benzyl alcohol and the mixture with the oligomers were characterized by IR-measurements. Their comparison showed especially the lack of OH-bonds after the polymerization. Other peak intensities changed, too, but to a much lower extent.

Thus, the oligomers had no hydroxyl groups or at least not many. This confirms the image of a Friedel-Crafts type alkylation.

While preparing the samples in chloroform for the SEC-analyses, sometimes a blue fluorescence was observed, especially for the samples of higher reaction temperatures. Thus, a certain length of the oligomers is needed to show this effect intensively. This fluorescence was studied in more detail for the example of 2.0g benzyl alcohol reacting during 24h at 220°C. Therefore, in the beginning the absorbance of UV- and visible light was measured. Figure 4.18 lays out the spectra for the monomer and the mixture of oligomers. The mixture of oligomers is measured in high and in low concentration and, thus, differences to the spectrum for the monomer can be seen. Only the low concentrated polymer mixture shows a small local maximum of absorbance at 262nm. Additionally, the concentrated mixture led to a local maximum of absorbance between 350nm and 400nm. This maximum is also observable in less intensity for the diluted mixture, but not for the monomer. Thus, this absorption is caused by oligomers.

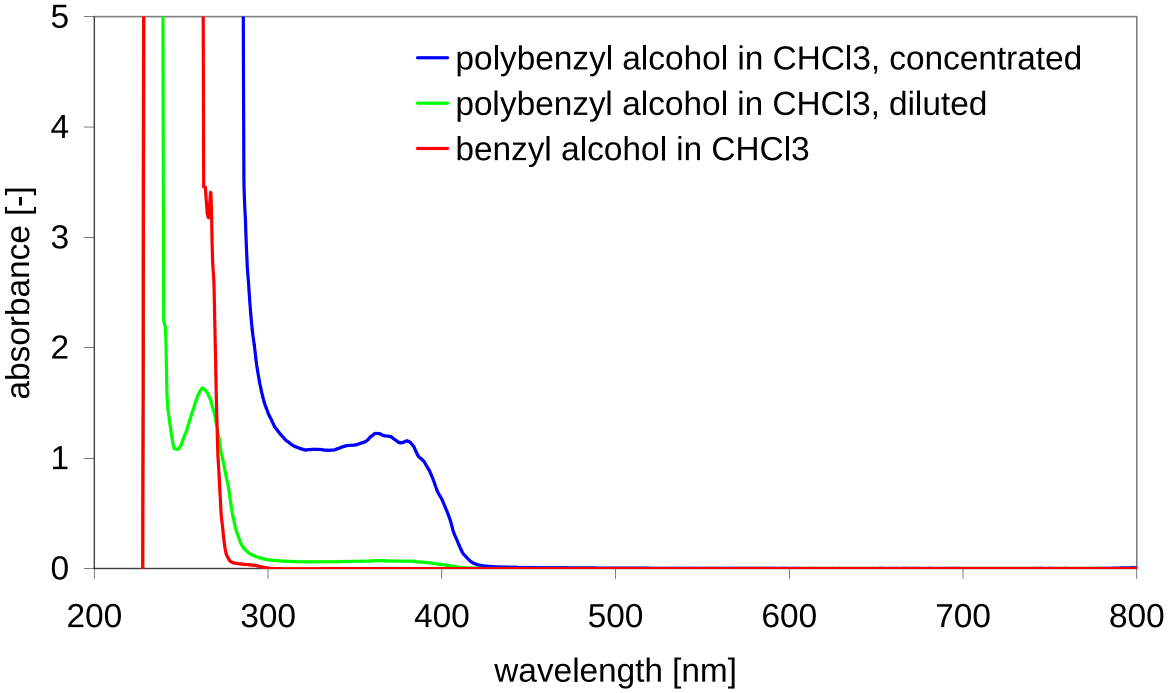

Figure 4.18: UV/Vis-spectra of polybenzyl alcohol in different concentrations and of benzyl alcohol.

After having a look on the UV/Vis-absorbance, the fluorescence measurement was carried out. Therefore, the molecules were excited with light of 350nm wavelength. Figure 4.19 sets up the fluorescence spectrum for the mixture in contrast to the one for the monomer.

The mixture of oligomers showed an intensive fluorescence in the range of 390nm to 470nm. The monomer did not show fluorescence. The signals of the lower diagrams show the Counts Per Second (CPS) while the upper ones display the signals corrected by a reference. This explains the increase of the average non-corrected signal for benzyl alcohol at higher wavelength.

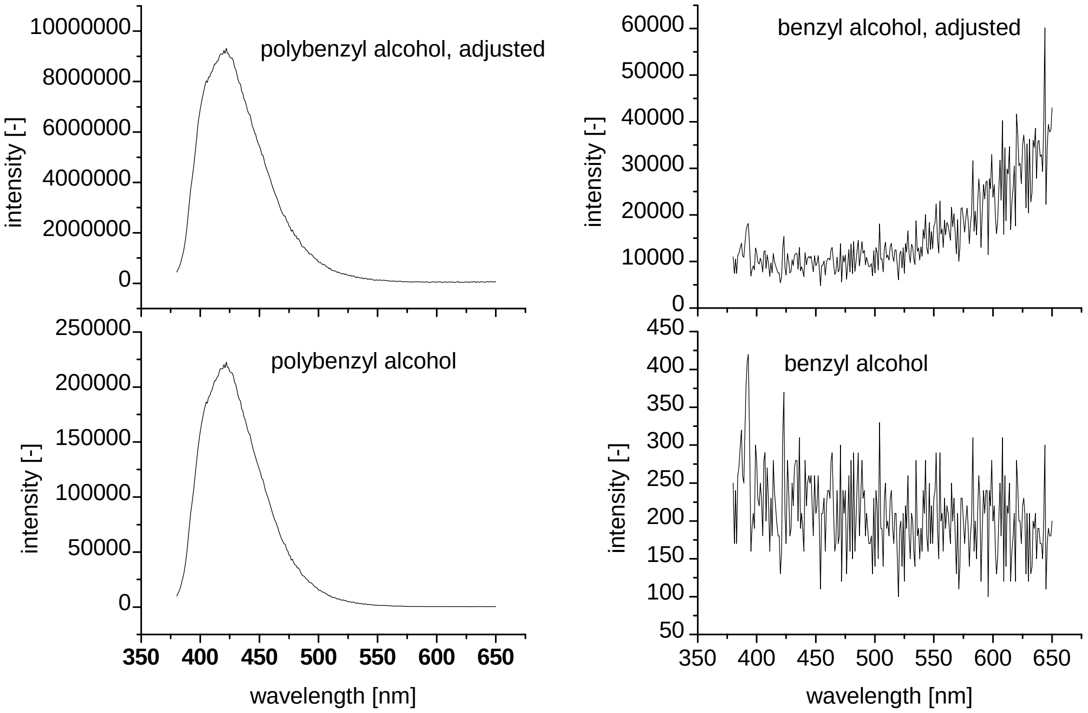

Figure 4.19: Fluorescence-spectra at 350nm for polybenzyl alcohol (left) and for benzyl alcohol (right).

Thus, with respect to the UV/Vis- and the fluorescence-spectra the oligomers are fluorescent. Even if the aromatic electron systems of polybenzyl alcohol are separated by single methylene groups in between, the delocalized systems influence one another. Otherwise fluorescence could not be possible. This influence can be intermolecular or intramolecular. Both types can be caused by parallel or orthogonal annealing of aromatic systems, but the intramolecular one would need a loop similar to the one of polypeptides. The third possibility is that the methylene groups do not separate strictly the aromatic systems.

Intermolecular interactions, maybe in a ravel like conglomeration, can be excluded in both cases of UV- and of fluorescence measurements. However, intermolecular annealing would not show great changes of the UV spectrum to the monomer. As fluorescence was also observed for samples containing only shorter oligomers, the formation of loops can be excluded. Consequently, the mesitylene groups do not separate the systems of delocalized electrons strictly. This causes the fluorescence.

This gives evidence that the activation energy for a further alkylation of an oligomer increases with the length of the oligomer. So, the temperature limits the length of the oligomers. This explanation allows also the inference that the electron system is slightly delocalized over the whole oligomer and causes on the one side the need for the higher activation energy and on the other side the fluorescence. The higher activation energy is due to the partial delocalization including the methylene groups and, thus, a lower electron density in the aromatic ring. Finally, the activation energy limits the growth of the oligomer. By contrast, the partial delocalization of the electrons over the whole molecule leads to fluorescence by a lower energy difference between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecule Orbital (LUMO).

Summing up, the polymerization of benzyl alcohol showed several dependences. The combination of low temperature and high amounts of starting material led to a high content of dimers. Low temperatures in general, for example 160°C, caused hardly any oligomers larger than tetramers, but a preference on dimers and trimers. Heating up to higher temperatures decreased the amount of dimers and the importance of trimers in favor of a fraction of tetramers to octamers.

Benzyl alcohol oligomerizes under hydrothermal conditions in 0.5mol/L HCl. Especially the temperature influences the length of the oligomers. These are fluorescent.

4.7 Conclusion and perspectives for hydrothermal Friedel-Crafts type reactions

Taking everything into consideration, diluted hydrochloric acid at 125°C to 220°C was employed for Friedel-Crafts type reactions under hydrothermal conditions.

In the beginning, Friedel-Crafts type alkylations of naphthalene were studied. Increasing the concentration of HCl showed no improvements above 0.1mol/L HCl, but at lower concentrations of HCl the conversion dropped down without a loss of purity. However, pure water needed about 40°C more to give similar results as hydrochloric acid. A solution of NaCl avoided the reactions even better than pure water and, thus, it showed less Friedel-Crafts products. Changing the temperature, the solvent, the amounts of starting materials and their ratios influenced the obtained reaction mixture.

The change from hydrochloric acid to acetic acid showed that acetic acid was less favorable as the yield of Friedel-Crafts product was lower even at high concentrations of acetic acid compared to low concentrations of hydrochloric acid. Formic acid gave a better result than acetic acid, but the results for hydrochloric acid were not reached. This might be caused by the formation of chlorinated, active intermediates. Comparing the environmental advantages of the use of acetic and formic acid to the disadvantage of the higher amount of used acid resulted in a preference for 0.05mol/L hydrochloric acid.

Alkylating naphthalene with other alcohols than benzyl alcohol led to different results. Derivatives of benzyl alcohol and 2-propanol worked very well, whereas 2,3-butanediol and sec-phenethyl alcohol gave limited yields. Other tested alcohols hardly alkylated naphthalene.

The Friedel-Crafts type reaction of phenol was carried out in the same way. The screening with benzyl alcohol at different temperatures and in different solvents proved that there was almost no reaction in pure water until 150°C. At higher temperatures the starting materials reacted to Friedel-Crafts products and ethers. In 1.0mol/L NaCl the results were almost the same, but from 200°C on the conversion rate increased. In an aqueous solution of 0.5mol/L hydrochloric acid the Friedel-Crafts products were the main products independent of any additions of NaCl or further HCl.

A lowered concentration of HCl not below 0.1mol/L showed not much effect on the reaction and its products compared to 1.0mol/L. At 0.03mol/L HCl and below the amount of not converted benzyl alcohol gained importance. The replacement of HCl by acetic acid was not favorable as even high concentrations of acetic acid gave a lower yield and less conversion than 0.005mol/L HCl, the lowest tested concentration of HCl. Anyhow, formic acid catalyzed the reaction better than acetic acid with a higher yield and a higher conversion rate at the same molar concentration. Nevertheless, it could not reach the efficiency of HCl.

The change from benzyl alcohol to other alcohols as alkylating agents was only successful, if the other alcohol was activated. Primary and secondary alcohols showed poor yields. sec-Phenethyl alcohol reached a yield for mono-alkylated Friedel-Crafts products of remarkable 93% without any optimization for exactly this reaction. However, 4-

hydroxybenzyl alcohol obtained a ortho/para-ratio of 18 : 82 for the mono-alkylated Friedel-Crafts products at a yield of 47%.

The recyclability of the aqueous, HCl containing solution of the Friedel-Crafts type alkylation of cinnamyl alcohol on phenol showed good results. The re-use was advantageous and gave evidence for an induction period like the formation of a water-soluble intermediate, which can participate at the reaction yet in the beginning of the next cycle, or an auto-catalytic process.

The comparison of alkylations of aromatic compounds showed that 2-propanol reacted with phenol and p-xylene, but neither with naphthalene nor toluene. 2,3-Butanediol did not react with the tested aromatic compounds. Benzyl alcohol confirmed its status as model compound as it alkylated most tested aromatic compounds well. Besides, 4-hydroxybenzyl alcohol formed two Friedel-Crafts products with phenol in high yield and very high purity, but no products with naphthalene, toluene or p-xylene.

Reactions of benzyl alcohol on hydroxyl aromatic compounds showed a slight preference of additions in the 4-position of catechol, whereas the ratio of alkylation in 2-position to 3-position was 82 : 18 in the case of p-cresol combined with a high yield of 89%. For 4-hydroxybenzoic acid the preference of the alkylated position was not determinable as the yield of alkylated compound was below 1%. 4-Hydroxyphenyl acetic acid was alkylated to 41% and with a selectivity of more than 98% in the 4-position.

Benzyl alcohol showed alkylation of other benzyl alcohol molecules. The logic result was the idea to polymerize benzyl alcohol under hydrothermal conditions. And indeed, benzyl alcohol formed oligomers in the range of dimers to octamers in 0.5mol/L HCl in the range of 160°C to 220°C during 8h to 40h. The mass of starting material was varied from 0.5g to 5.0g. Dimers to tetramers were preferred at low temperatures and at short reaction times. Longer reaction durations and higher temperatures resulted in longer oligomers, but octamers were not or not obviously exceeded. Higher temperatures, especially 200°C and 220°C, avoided oligomers shorter than tetramers and limited the impacts of other reaction parameters.

IR-analyses gave evidence for the Friedel-Crafts type alkylation as the intensity of the OH-band decreased drastically. Measuring the UV/Vis properties showed a difference between the monomer and the oligomer mixture at wavelengths of 250nm to 400nm. This was also confirmed by the fluorescence as the oligomer mixture showed this effect, but not the monomer. This is due to a partial delocalization of the electrons bridging methylene groups.

Anyhow, the exact mechanism of the Friedel-Crafts type reaction could not be investigated, but due to the expected lack of stereochemistry of HCl in water a reaction similar to the Friedel-Crafts reaction was probable, but a real Friedel-Crafts reaction was not sure. A transition state with a well defined transition complex with the catalyst can be excluded.

In effect, the expected intermolecular Friedel-Crafts type reactions were found in dependence of the combination of alcohol and aromatic compound.

5. Separation processes

Building on the above described results hydrothermal syntheses may find applications in the domain of separation chemistry.

On the one hand, in chapter 5.1 the Friedel-Crafts type reaction for polymerization will be transferred to the common solvent in nuclear industry, namely to nitric acid. In a second step the reducing properties of benzyl alcohol and the catalytic properties of the formed metallic particles will be combined for usage in the domain of metal separation.

On the other hand, a non-hydrothermal, biomass-based process will be developed in chapter 5.2 in order to separate metal ions out of solutions very selectively. The separability of the biomass ensures a low-cost process.

5.1 Selective separation of platinoids under hydrothermal conditions

5.1.1 Field of application

After the usage of fuel rods in nuclear power plants the spent nuclear fuels still contain unburned U235. In addition, fertile U238 has been converted into fissile Pu. Thus, a lot of energy is still not used. Therefore, some countries recycle spent fuel rods in order to recover this energy potential for further usage.

The burned fuel rods are dissolved in nitric acid, but a certain amount of solid remains. This residue contains platinoids in an alloy with molybdenum and technetium and is hard to be used as a source for platinoids.

In order to separate, the process of Plutonium and Uranium Recovery by EXtraction (PUREX) is the current state of the art. This process is a liquid-liquid extraction. Therefore, the extractant tributylphosphate is diluted by kerosene. In contact with the solubilized metal ions in nitric acid, plutonium and uranium are extracted. Other metals in the solution such as the noble metals palladium, rhodium and ruthenium are not separated. But separating and using them is in discussion since the Manhattan Project in the 1940s.

The obtained two fractions are the fraction with uranium and plutonium and the other one is called High-Level Liquid Waste (HLLW). Both fractions can be treated by hydrometallurgical separations or by pyrometallurgical separations.

PUREX as one of the hydrometallurgical processes is solvent extraction-based. In the beginning plutonium and uranium are separated. Besides, U(VI) and Pu(IV) would interfere with the separation of the platinoids. Furthermore, any formation of solids, e.g. of insoluble Pd containing compounds of the degradation products of the extractant of the PUREX process, would pose difficulties to the separation of the platinoids and has to be avoided. Thus, the platinoids should be separated from the HLLW before the evaporation of its solvent. The HLLW concentrate contains a complex solid mixture of metals and hydroxides which is vitrified nowadays. During the vitrification the platinoids can precipitate and cause a phase separation and, thus, they limit the performance of the vitrification.

Besides, fission platinoids might be useful products in order to reduce the dependence on exploitations of mines. Anyhow, ruthenium has a lower commercial value compared to platinum and rhodium. Radiorhodium also contains traces of isotopes with short half-lives so that it needs a decay time of several decades before being used. Platinum contains 17% of an instable isotope, a soft β-emitter with a half-life time of $6.5*10^6$ years and relatively low radiation intensity at the surface. Therefore it might be used in some applications where the remaining radioactivity is no problem. However, the applications will be very limited and the public opinion might opposite these plans.

Anyhow, many countries have their own ways to treat the waste. Other countries do not treat the waste as it is still cheaper to use new uranium from mines. In addition, the treatment decreases the amount of highly radioactive waste by a factor of about 30, but the amount of radioactive waste in general is increased as materials are added which should separate.

All in all, it is the aim to avoid the problems caused by platinoids and also to profit by the value of the platinoids. Additionally, no significant amount of additional waste should be obtained and none of the added compounds should disturb the vitrification in the end. [140, 141]

5.1.2 Literature review

In this context, in 2003 Kolarik et al. reviewed studies which have been published in order to have access to platinoids. The processes can be divided into hydrometallurgical and pyrometallurgical ones. The hydrometallurgical processes base on solvent extraction, ion exchange, sorption, precipitation or deposition.

In aqueous systems the behavior of platinoids depends, among others, on the concentration of the nitric acid. Besides, permanganate as a strong oxidant leads to RuO_4 which is gaseous and therefore its separation from a solution is very easy. By contrast, volatile radioactive ruthenium increases dangerousness in the case of an incident. That is why the formation of radioactive gases should be avoided.

Solvent extraction based processes have advantages such as a high throughput, a continuous operation method and the possibility to keep the contact time to the highly radioactive aqueous phase very limited in order to avoid degradation of the extractant. Some of the solvating extractants for palladium are tributyl phosphate (TBP), dialkyl sulfoxides, dialkyl sulfides, thioethers, sulfur donors, and nitrogen donors. They have variable efficiencies and, in addition, the studies have different parameters for contact times as well as for the concentrations of the solutions and the extractants. Diisoamyl methylphosphonate and dialkyl sulfides are employed for rhodium extractions. TBP and some phosphine oxides are reported for the solvent extraction of ruthenium. Acidic extractions use mixed nitrogen and oxygen donors, but also sulfur donors as extractants for palladium. Dinonylnaphthalenesulfonic acid in kerosene extracts rhodium under certain conditions in inverted micelles. bis(2,4,4-Trimethylpentyl)-dithiophosphinic acid in kerosene extracts ruthenium in low efficiency. Basic extractants for palladium ions as amines and quaternary ammonium bases show, partially, high selectivities. For rhodium special cation exchange resins and triisooctylamine as well as trioctylamine are usable basic extractants.

Ion exchange and sorption show the advantage that platinoids are separable from strongly acidic solutions. The disadvantages are the discontinuous process and a limited throughput which is caused by the longer contact time. Some of the anionic or, respectively, cationic exchangers show high performances. For palladium anion exchangers are much better, while rhodium is extracted better by cation exchangers. Nevertheless, the cation exchangers are rather a Russian domain and many anion exchangers are from an American company.

Another way is the sorption on active carbon. Pd^{2+} sorbs, while Rh^{3+} sorbs weakly. Ru(III)NO forms different species. These sorb as weak as Rh^{3+} or even stronger than Pd^{2+}. Anyhow, the sorption of Tc^{7+} is similar to the sorption of Pd^{2+} and can cause difficulties.

Precipitation out of the solution can show high selectivities, but in general the separation is less complete and less clean compared to liquid-liquid extractions.

Further depositions such as electrochemical depositions are expected to be easy with regard on the equipment and the scale-up, but only palladium deposits suitable fast. In contrary, the presence of U^{4+} decelerates the deposition of palladium. Chemical reduction by ascorbic acid seems to be applicable in the case of palladium also from HLLW. Metallic palladium and rhodium can be obtained by adding formic acid. Photoreduction to the metallic platinoids is supported by TiO_2 as photocatalyst, but Ru^{3+} can hardly be separated starting from its nitrosyl form.

Pyrochemical separations have the great advantages of a higher radiation stability of the used materials, the much lower quantities handled with, and the resulting higher compactness. The disadvantages are discontinuous processes, the conversion of a nitrate solution to an oxide or chloride solid, and the fact that after all, the platinoids have to be cleaned up by a hydrometallurgical process after re-dissolving to an acidic nitrate solution. For example the extraction of palladium and rhodium can be carried out by a molten salt mixture of LiCl : KCl (50 : 50, n : n). By changing to agents forming borosilicate type glass and adding reductants and scavengers a metal phase is obtained above the glass phase. A metal phase of platinoids with molybdenum can be separated from the oxides of the other metals by heating up to 1800°C under an argon atmosphere. [140, 141]

The tables 5.1 and 5.2 summarize the separation methods which are presented by Kolarik.

Method	agent	metal	yield	distribution factor	(optimal) conditions / remarks
solvating ex-tractants	tributyl phosphate (TBP)	Pd(II)	-	max. 1.3 (neat TBP); max. 0.23 (30% TBP in decane)	0.6-0.7mol/L HNO_3
	Trialkyl-phosphine oxides	$Pd(NO_3)_2$	-	better than TBP	< 1mol/L HNO_3
	bifunctional phosphoryl extractants	Pd(II)	-	not noteworthy	-
	dialkyl sulfoxides	$Pd(NO_3)_2$	-	16.5	better than other oxygen donor extractants, strong dependence on extracting compound and on concentrations
	mixed nitrogen/ oxygen	Pd(II)	-	90	below 4mol/L HNO_3

	donor pyridine-based extractants				
	pyridine-based extractants	-	-	depends on the diluent	only with halogenated diluents
	pure oxygen donors	$Pd(NO_3)_2$	-	very weak	-
	diheptyl sulfide	$Pd(NO_3)_2$	-	Several hundred	0.25mol/L extractant in benzene, > 1mol/L HNO_3
	dihexyl sulfide	Pd(II)	-	1000-5000	10vol-% extractant in dodecane, after 30min, 0.1-6mol/L HNO_3
	sulfide extractant	Pd(II)	-	10-100	2-3mol/L HNO_3, high selectivity
	Triisobutyl-phosphine sulfide	Pd(II)	-	0.64-1.60	0.1-6.0mol/L NO_3, 0.0001mol/L extractant in Solvesso 100, equilibrium after 45min
	straight chain and macrocyclic thioesters	Pd(II)	-	1.08-42	dependent on the species and the concentrations
	sulfur donor extractants	$Pd(NO_3)_2$	-	-	0.0025mol/L in dichloroethane, equilibrium after 1h, solubility problems
	nitrogen donor extractant	$Pd(NO_3)_2$	-	1.7	0.0001mol/L in Solvesso 100, 2mol/L HNO_3
	phosphoryl extractants	Rh(III) nitrate	-	0.1-0.01	2min contact time, 1-15mol/L HNO_3
	diisoamyl methylphosphonate	Rh(III) nitrate	-	-	< 5mol/L HNO_3, 50% extractant in diethylbenzene, salting-out agents
	trioctylphosphine oxide	Rh(III) nitrate	-	Very weakly	2min contact time, extractant in xylene
	dialkyl-sulfides	Rh(III) nitrate	-	0.001-0.002	30min contact time, 10vol-% extractant in dodecane
	tributyl phosphate (TBP)	$RuNO(NO_3)_3$	-	63	30% TBP in dodecane, 0.1mol/L NO_3, 30s contact time, decrease with increasing HNO_3-concentration, decrease with time

acidic extractants	oxygen donor extractant	Pd(II)	-	-	pH0.5-1.5
	mixed nitrogen/ oxygen donor extractant	Pd(II)	> 50%	-	1mol/L HNO_3, 0.0004mol/L initial concentration, equilibrium after < 20min
	sulfur donor extractant	Pd(II)	practically 100%	-	> pH0.8, 30min contact time, V(org.) : V(aqu.) = 1 : 2, 0.2mol/L extractant in kerosene
	bis(2,4,4-trimethyl-pentyl)-dithiophosphinic acid	Pd(II)	-	selective	extraction chromatography, extractant encapsulated in Ca alginate gel, distribution equilibrium after 3 days
	2-hydroxy-5-nonyl-benzophenone	Pd(II)	-	40	0.01mol/L extractant in heptane : chloroform = 9 : 1 (vol : vol), 1mol/L HCl, equilibrium after 25h, equilibrium after 4h with phase transfer catalyst Aliquat 336
	dinonyl-naphthalene-sulfonic acid	Rh(III)	-	-	0.1-1.0mol/L HNO_3, extractant in kerosene, equilibrium after < 15min
	bis(2,4,4-trimethyl-pentyl)-dithiophosphinic acid	nitrosylruthenium	-	4-0.2	pH4.0-1.1, 0.2 mol/L extractant in kerosene
basic extractants	trioctyl-amine	$Pd(NO_3)_2$	-	1.6	0.33mol/L extractant in benzene, 1.2mol/L HNO_3
	quarternary ammonium bases	$Pd(NO_3)_2$	-	-	maximal distribution ration at rather low HNO_3-concentrations
	Methyl-ammonium nitrate	Pd(II)	-	20	0.042mol/L extractant in benzene, 0.5mol/L HNO_3
	Amberlite LA-1 and triisooctyl-amine	Rh(III) nitrate	-	< 0.01	2min contact time, extractant in xylene, 1-14mol/L HNO_3
	trioctyl-amine	Rh(III)	-	-	0.5mol/L extractant in xylene, > pH2

	Aliquat 336	Rh(III)	-	moderate	extractant in benzene, pH0.3-9.5
anion ex-changers	4-(N,N-dimethyl-benzimid-azole)-phenol	Pd(II)	-	-	strong affinity at 6mol/L HNO_3, equilibrium not after 20h at 60°C
	Dowex 1X8	Pd(II)	-	35	2-2.5mol/L HNO_3
	Amberlite INR-78	Pd(II)	-	95	2-2.5mol/L HNO_3
	AV-17X8	Pd(II)	-	64, 56, 200	0.5, 3.0, 8.0mol/L HNO_3, strongly basic resin
	VP-1AP	Pd(II)	-	64, 77, 35	0.5, 3.0, 8.0mol/L HNO_3, strongly basic pyridinium anion exchanger
	AN-104	Pd(II)	-	475, 350, 120	0.5, 3.0, 8.0mol/L HNO_3, weakly basic anion exchanger
	KhFO	Pd(II)	-	900, 500, 200	0.5, 3.0, 8.0mol/L HNO_3, strongly basic phosphonium anion exchanger
	Dowex 1X8	Rh(III)	-	13	2-3mol/L HNO_3, 20°C
	Amberlite INR-78	Rh(III)	-	8	2-3mol/L HNO_3, 20°C
	AV-17X8	Rh(III)	-	< 5	-
	AN1-4	Rh(III)	-	< 5	-
	VP-1AP	Rh(III)	-	< 5	-
	KhFO	Rh(III)	-	< 5	-
	AV-17X8	nitrosylruthenium	-	1.3	3mol/L HNO_3
	VP-1AP	nitrosylruthenium	-	6	3mol/L HNO_3
	KhFO	nitrosylruthenium	-	11	3mol/L HNO_3
	Amberlite IRA-401	Pd(II), Rh(III)	-	-	efficiently enough sorption from aged alkaline supernatant solution
cation ex-changers	Dowex 50W	Rh(III)	-	55, 9, 1	0.5, 1, 3mol/L HNO_3, 20°C
	KU-2X8	Pd(II)	-	9	3mol/L HNO_3, sulfonic acid resin
	KU-2X8	Rh(III)	-	0.5	3mol/L HNO_3, sulfonic acid resin
	KU-2X8	Ru(III)NO	-	5	3mol/L HNO_3, sulfonic acid resin
	KRF-20t-60	Pd(II)	-	9	phosphoric acid resin
	KRF-20t-60	Rh(III)	-	< 5	phosphoric acid resin

	KRF-20t-60	Ru(III)NO	-	3	phosphoric acid resin
	VPK	Pd(II)	-	850	3mol/L HNO_3, aminocarboxylic resin
	ANKB-2	Pd(II)	-	350	3mol/L HNO_3, aminocarboxylic resin
	ANKB-35	Pd(II)	-	150	3mol/L HNO_3, aminocarboxylic resin
	MS-50	Pd(II)	-	160	3mol/L HNO_3, aminocarboxylic resin
	VPK	Ru(III)NO	-	51	-
	ANKB-2	Ru(III)NO	-	45	-
	ANKB-35	Ru(III)NO	-	43	-
	MS-50	Ru(III)NO	-	55	-
	VPK	Rh(III)	-	230	-
	ANKB-35	Rh(III)	-	24	-
	MS-50	Rh(III)	-	5	-
	CS-346	Pd(II)	-	well	0.5-6mol/L HNO_3, chelating amide oxime exchanger
	CS-346	Ru (not specified species)	-	rather weakly	-
	CS-346	Rh(III)	-	very weakly	-
	FS-15	Pd(II)	-	100	3mol/L HNO_3, Cu hexacyanoferrate / silica gel
	FS-14	Pd(II)	-	74	3mol/L HNO_3, Ni hexacyanoferrate / silica gel
	GSM	Pd(II)	-	36	CuS
	hydrous $TiO_2 : ZrO_2$ (12 : 1 - 25 : 1)	Pd(II)	-	9	-
	FS-14	Rh(III)	-	10	-
	FS-15	Rh(III)	-	10	-
	GSM	Rh(III)	-	< 5	-
	$TiO_2 : ZrO_2$	Rh(III)	-	< 5	-
	FS-14	Ru(III)NO	-	4	-
	FS-15	Ru(III)NO	-	2	-
	$TiO_2 : ZrO_2$	Ru(III)NO	-	0.5	-
other sorbents	active carbon	Pd(II)	-	strongly sorbed	-
	active carbon	Rh(III)	-	weakly sorbed	-
	active carbon	Ru(III)NO	-	weak - strong	dependent on the species of Ru(III)NO, stronger than Pd(II) … weak as Rh(III)

precipitation	sucrose	Pd(II)	-	-	from HLLW, reflux
	oxidation and Cl^-	Pd(II)	-	-	not acceptable
	HCl and $SnCl_2$	Pd(II)	97-100%	-	> 2mol/L HCl, 0.1mol/L $SnCl_2$, hardly acceptable
	HCl and $SnCl_2$	Rh(III)	97-100%	-	> 2mol/L HCl, 0.1mol/L $SnCl_2$, hardly acceptable
	HCl and $SnCl_2$	Ru(III)NO	97-100%	-	> 2mol/L HCl, 0.1mol/L $SnCl_2$, hardly acceptable
	20wt-% acetate	Rh(III)	94-96%	-	pH8-12, separation from Mo at pH12
	20wt-% acetate	Pd(II)	< 10%	-	pH8-12
electro-chemical reduction	electricity	Pd(II)	-	-	Pt-cathode, -0.2-0.1V (vs. SCE), 8-70mA/cm^2
	electricity	Pd > Rh > Ru	-	-	Ta-cathode, -0.1V (vs. SCE), 40°C, deposition rate decreases with increasing HNO_3-concentration, U(VI) decelerates Pd-deposition
chemical reduction	ascorbic acid	Pd(II)	> 99%	-	0.03-0.06mol/L reductant at 0.5-4mol/L HNO_3, 0.04mol/L reductant at 2mol/L HNO_3, selective for Pd(II), 20min, redessolving after 14h
	ascorbic acid	Pd(II)	98-99%	-	0.25mol/L reductant, 0.5mol/L oxalic acid, 0.4-2mol/L HNO_3
	ascorbic acid	Pd(II)	10%	-	0.25mol/L reductant, 0.5mol/L oxalic acid, 4mol/L HNO_3
photo-reduction	2kW xenon lamp	Pd(II)	90%	-	60min, TiO_2 as photocatalyst, 3mol/L HNO_3, 20% ethanol
	2kW xenon lamp	Rh(III)	90%	-	60min, TiO_2 as photocatalyst, 3mol/L HNO_3, 20% ethanol
	2kW xenon lamp	Ru(III)	60-80%	-	60-90min, TiO_2 as photocatalyst, 3mol/L HNO_3, 20% ethanol
	2kW xenon lamp	Ru(III)NO	2-3%	-	60-90min, TiO_2 as photocatalyst, 3mol/L HNO_3, 20% ethanol

oxy-dation	electricity	Ru(III)NO	-	-	30°C, > 2V (vs. SCE), >12mA/cm^2, 0.4-1L/m^3 air flow, Pt-anode, bubbling ozone
	electricity	Ru(III)	98%	-	bubbling ozone, 3mol/L HNO_3

Table 5.1: Overview over the hydrometallurgical separation methods for platinoids, after [140].

method	agent	metal	Yield	distribution factor	conditions / remarks
extraction by molten metals and salts	$Zn_{(l)}$	Pd, Rh	100%	-	from LiCl : KCl = 50 : 50 (n : n), 800°C
	$Cd_{(l)}$	Pd, Rh	100%	-	from LiCl : KCl = 50 : 50 (n : n), 500°C
	$Cd_{(l)}$	Pd, Rh	100%	-	from LiCl : KCl = 50 : 50 (n : n), 650°C
	$Pb_{(l)}$	Pd, Rh	100%	-	from LiCl : KCl = 50 : 50 (n : n), 600°C
	$Bi_{(l)}$	Pd, Rh	100%	-	from LiCl : KCl = 50 : 50 (n : n), 800°C
	$Zn_{(l)}$	Ru	70-100%	-	from LiCl : KCl = 50 : 50 (n : n), 600-800°C
	$Cd_{(l)}$, $Pb_{(l)}$, $Bi_{(l)}$	Ru	5-40%	-	from LiCl : KCl = 50 : 50 (n : n), 500-800°C
	oxide scavenger and reductant	Pd, Rh	20-100%	-	cooling down after heating to 1100°C with metal oxide scavenger (Sb_2O_3, Bi_2O_3, PbO, SnO, CuO) and reductant (graphite, charcoal, flour, corn starch, sugar, silicon)
	oxide scavenger and reductant	Ru	30-100%	-	cooling down after heating to 1100°C with metal oxide scavenger (Sb_2O_3, Bi_2O_3, PbO, SnO, CuO) and reductant (graphite, charcoal, flour, corn starch, sugar, silicon)
	$Pb_{(l)}$ and $Na_2B_4O_7$ or B_2O_3	platinoids	85-100%	-	750-1100°C
	magnesium and uranium : chromium =	Ru	-	-	high selectivity over Pd, 900-950°C, separation factor 10^6

	19 : 1 (w : w)				
	magnesium and uranium : iron = 89 : 11 (w : w)	Ru	-	-	750-850°C, separation from Pd
	magnesium and aluminium : bismuth = 89 : 11 (w : w)	Pd, Ru	-	-	700-900°C
reactions involving solids	reactions involving solids	platinoids	-	-	argon atmosphere, 1800°C, separation as metal phase (including Mo), probably without reductant
	AlN, BN, TiN, Si_3N_4	platinoids	-	-	> 1600°C, formation of metal phase (platinoids and Mo) and oxide phase

Table 5.2: Overview over the pyrometallurgical separation methods for platinoids, after [140].

Anyhow, a patented electrochemical process to separate the platinoids from the other metal ions from the HLLW suffers from a complex installation [142]. Other patents deal with tricaprylmethyl ammonium [143] or dialkyl sulfide [144] as extractants in the liquid-liquid extraction. Besides, saccharose is proposed as chemical reductant, but the exothermal reaction can lead to an auto-inflammation [145] which threatens the applicability in nuclear industry.

Palladium can be extracted sufficiently well by numerous extractants. For an improved extractability of rhodium further investigations are to be done.

Electrochemical deposition of palladium is adaptable, but for rhodium it is too slow.

Pyrometallurgical separation is suitable for the separation of platinoids from solid residues, but purification by hydrometallurgical processes is needed.

5.1.3 Idea and first approach

5.1.3.1.Idea of separating PGMs by means of benzyl alcohol

The problem of the too high content of some metals such as the Platinum Group Metals (PGM) for the direct vitrification can be solved by separating them. Almost as a side effect the separated platinum group metals can be used.

As shown in the previous chapter, an electrolytic separation is possible, but hard to implement. However, an electrochemical process seems promising, because the reduction potentials of the PGMs are much lower than for most other fission metals. When the PGMs are reduced, they often form nanoparticles [146, 147]. These hardly precipitate nor can they easily be removed out of the liquid by filtration. To increase the size of the particles and, thus, to simplify the separation, an aggregation has to be enforced. As benzyl alcohol showed polymerization, it is a potential candidate to aggregate nanoparticles.

But even more important is the fact benzyl alcohol is known to be redox-active [148-150]. The idea is to add benzyl alcohol (0.48mol/L) in order to reduce the metal ions (0.02mol/L) to metallic particles. These cause the polymerization of benzyl alcohol which encloses the nanoparticles. Then the organic matrix with 1vol-% of metallic particles can easily be separated from the solution.

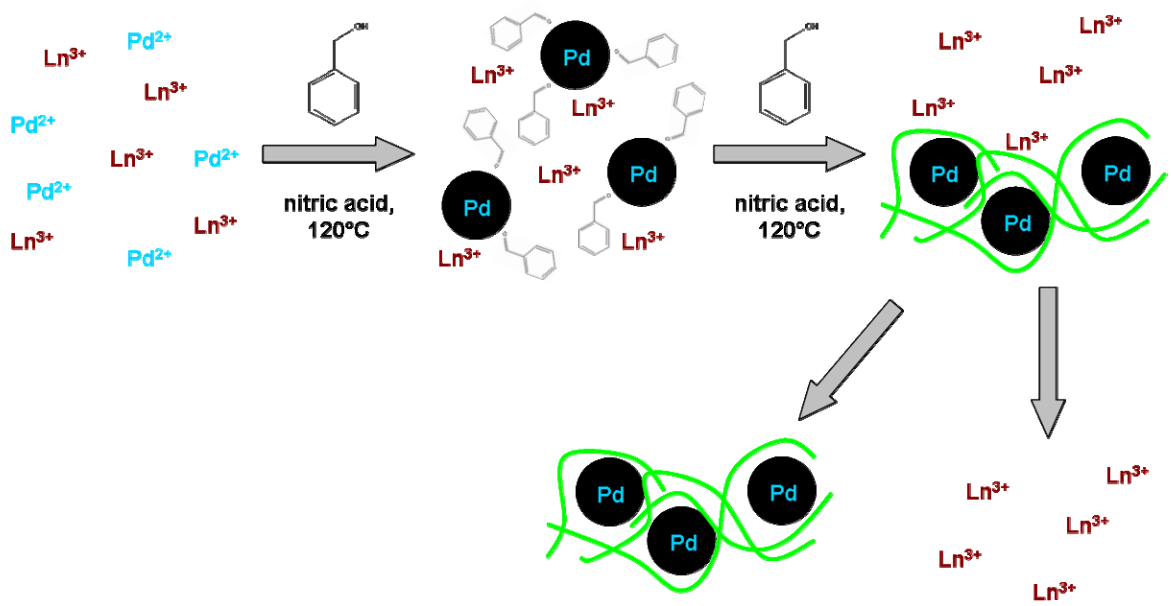

Figure 5.1: Theoretic process for separating 0.02mol/L Pd^{2+} from 0.02mol/L Ln^{3+} by means of 0.48mol/L benzyl alcohol under hydrothermal conditions.

As it is interesting to separate PGMs, it is not desirable to remove all kinds of metal ions. Thus, benzyl alcohol or another organic compound has to reduce PGM ions enough selectively. The chosen regulating screw was the reduction potential. The PGMs are easier to reduce than metal ions such of cerium. That is why the needed reduction potential should be between these two. Thus, the PGMs would be reduced, but not the cerium ions. This would cause the separation.

5.1.3.2.Adaptation of the polymerization of benzyl alcohol to separate PGMs

After first studies on the polymerization of benzyl alcohol in hydrochloric acid (see chapter 4.6), the reaction was carried out in nitric acid. HNO_3 was chosen as it is the dominating acid in nuclear fuel treatment and the metal separation should be applicated in this domain. 10mL of 0.7mol/L nitric acid were the solvent for the reaction of 2.0g benzyl alcohol during 24h. The received chromatograms are compiled in Figure 5.2.

160°C showed very low amounts of dimers and trimers. But there also was a peak with a retention time greater than the one of the solvent. This means that there was an attractive interaction between the sample and the material of the column. Otherwise, this effect is not possible. Besides, the reaction mixture was black instead of slightly yellow and the viscosity dropped off. The chromatograms for 180°C and 200°C showed less trimer, but besides that they did not show much difference compared to the chromatogram for 160°C. Just at 220°C the shoulder for the third species increased and became a further, local maximum.

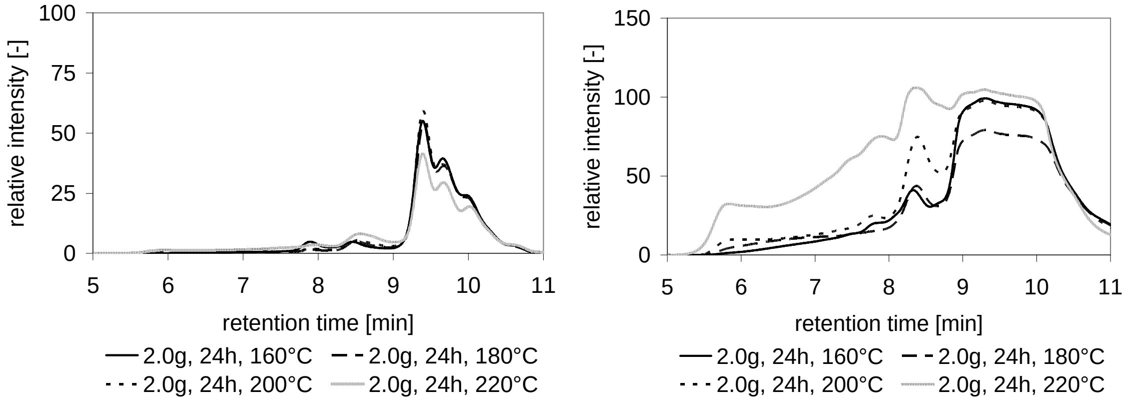

Figure 5.2: Reaction of 2.0g benzyl alcohol in 0.7mol/L HNO_3 during 24h, RID-signal (left) and UV-signal (right) per mass.

It seemed that the benzyl alcohol was partially nitrated. This influenced the interaction with the material of the column or the solubility in the solvent or both. With this assumed reaction the peak in the chromatogram with its two maxima and one shoulder indicated three species: Either the three mono-nitrated ortho-, meta- and para-products or the mono-, di- and tri-nitrated products or any combination in between.

An IR-spectrum (see Figure 5.3) of the dark mixture after the reaction shows both bands for nitro functional groups. The two bands for symmetric and asymmetric stretching are lowered by about 50cm^{-1} to 1496cm^{-1} and 1311cm^{-1} because of the aromatic system next to the nitro group. The band at 1700cm^{-1} stands for an aldehyde, probably next to an aromatic system. This is consistent with the intensive smell of benzaldehyde.

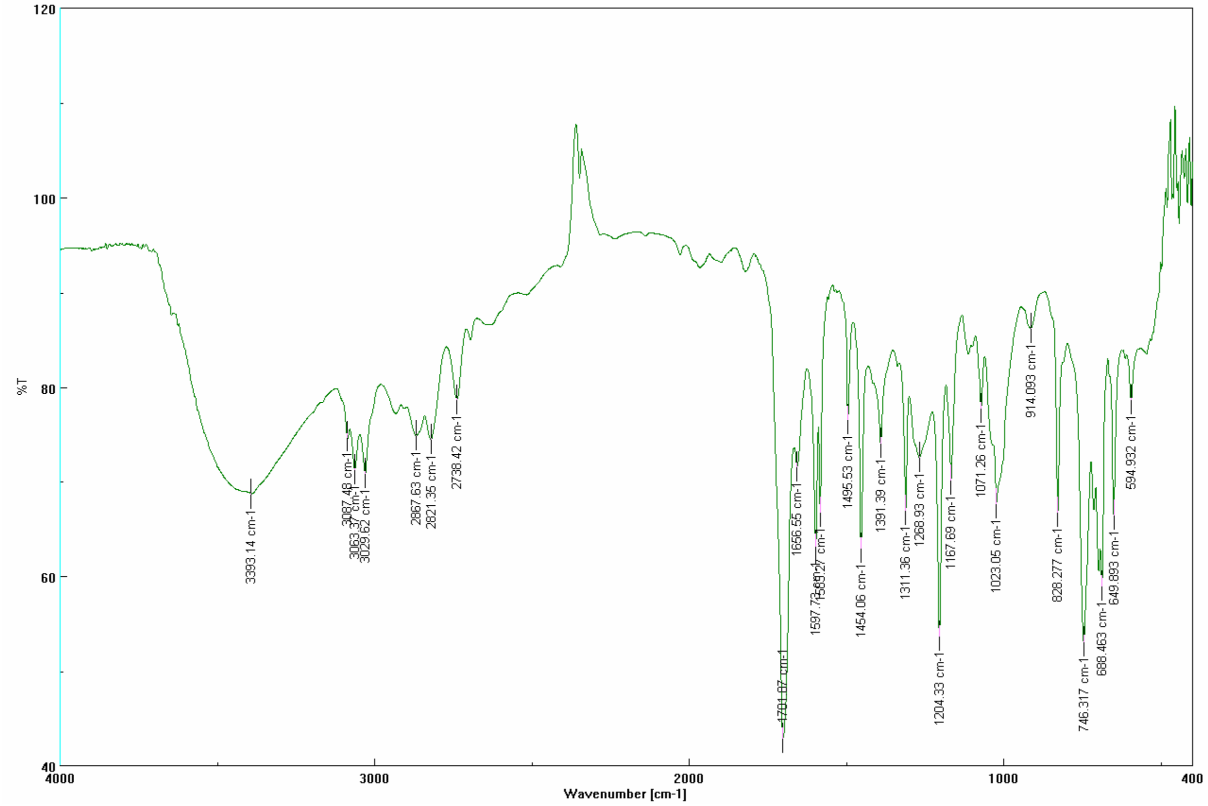

Figure 5.3: IR-spectrum of the organic phase after the reaction of benzyl alcohol in HNO_3.

In conclusion, the solvent HNO_3 changed the reaction apparently as the retention time of some products was longer than for the solvent. This was explained and proven by a nitration of the benzyl alcohol which caused an interaction with the material of the column or at least a lower solubility in the solvent. In this context, a lower solubility must not mean that the reaction mixture is no more soluble in the solvent. It is sufficient, if the partition coefficient for the compound is changed so that the distribution coefficient is more in favor of an adsorption on the solid phase in the column than of the solubility in the solvent.

All in all, changing the solvent of the polymerization of benzyl alcohol from HCl to HNO_3 was not successful, because benzyl alcohol was nitrated, but an oligomerization did not occur.

There is the aim to reduce the quantity of ions of PGMs from a solution. The tested method of resolution is to reduce the PGM ions chemically and to precipitate them by an organic matrix.

5.1.4 Optimization of the reaction conditions on model systems

Even if first tests for the polymerization of benzyl alcohol in HNO_3 were not satisfying, it was known that nanoparticles can support polymerization [139]. As the formation of especially metallic nanoparticles is expected in the case of separating PGMs, the polymerization might be preferred to the nitration of benzyl alcohol.

First tests were made with several organic compounds to have a look on different reduction potentials and their effects. Benzyl alcohol, glycerol, 4-hydroxybenzyl alcohol, 1,4-benzenedimethanol and phenol, gallic acid and hydroquinone were tested. So, just compounds with alcohol groups were examined as this functional group is expected to attach at metallic particles. With respect on first results, benzyl alcohol and its derivatives as well as glycerol and gallic acid were studied in further detail while the focus was on benzyl alcohol. Measurements by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) confirmed this selection. Owing to the efficiency of organic compound per price unit, benzyl alcohol was selected as the compound of choice. Nitration of benzyl alcohol in a metal ions containing solution based on nitric acid was not observed. Apparently, the metal ions suffice to avoid the nitrification of benzyl alcohol effectively.

To simplify the system as much as possible, the kinds of metal ions were limited to Pd and Ce. Palladium ions should be removed and cerium ions should remain in the solution. Therein palladium stood for all the PGMs and cerium represented the lanthanides.

Palladium was added in the form of $(NH_4)_2PdCl_4$ and cerium as $Ce(NO_3)_3 \cdot 6\ H_2O$. If ruthenium was in the solution, it was taken in the form of a solution of $Ru(NO_3)_3NO$.

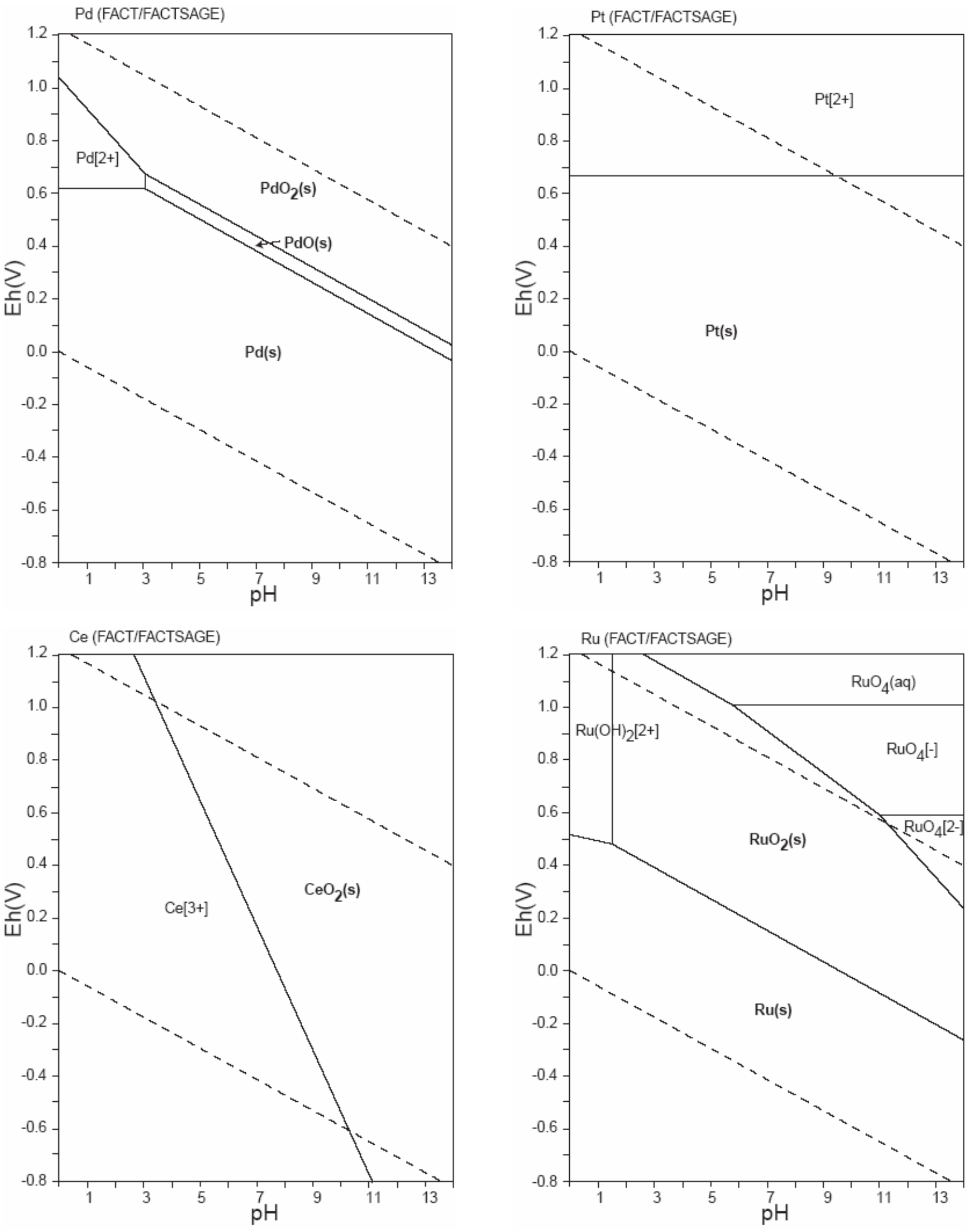

Figure 5.4: Pourbaix-diagrams for Pd, Pt, Ce and Ru, from [151].

With regard to the Pourbaix-diagrams shown in Figure 5.4 it has to be expected that palladium, platinum and ruthenium will form the metal for thermodynamic reasons as long as there is oxygen solved in the solution. Only cerium would exist in the cationic form, namely as Ce^{3+}. Anyhow, due to the equation of Nernst, $E_{red} = E^{o}_{red} - \frac{RT}{zF}\ln\left(\frac{a_{Red}}{a_{Ox}}\right)$, a higher temperature causes a higher reduction potential for every half cell. The corresponding reduction potential at 180°C was awaited to show an increase in the range of 80mV whereas the reduction potential of ruthenium, the most non-noble metal besides cerium, needs about 460mV to be oxidized under standard conditions at pH 0. Additionally, the model solution is more complicated than the calculated Pourbaix-diagrams. The solution is not only of nitric acid, it also contains several ionic species, especially anionic ones. Therefore, the transferability of the theoretic diagrams to the real solution of metal salt mixtures was investigated.

Halfreaction	E_0 [V]	E [V]
Pt --> Pt^{2+} + 2 e^-	1,18	1,26
Pd --> Pd^{2+} + 2 e^-	0,96	1,04
Ce --> Ce^{3+} + 3 e^-	-2,34	-2,26
Ru --> Ru^{2+} + 2 e^-	0,46	0,54

Table 5.3: Standard potentials and potentials under reaction conditions (pH 0, T=180°C, c($Me^{2+/3+}$)=0.02mol/L).

5.1.4.1.Dependences on mass of benzyl alcohol and on temperature

This simplified system was optimized for efficiency and selectivity. Several reaction parameters and their influences were investigated. In the beginning, the impacts of the amount of benzyl alcohol and of the temperature were studied. In Figure 5.5 blue points show the measuring points for palladium concentrations and the red lines connect their averages. The same was done with orange points and green lines for cerium. The axe in the right direction gives the temperature in °C, the vertical axe corresponds to the mass concentration β of metal ions which was found remaining in the solution after treatment and the axe in the left-down direction referred to the mass of added benzyl alcohol.

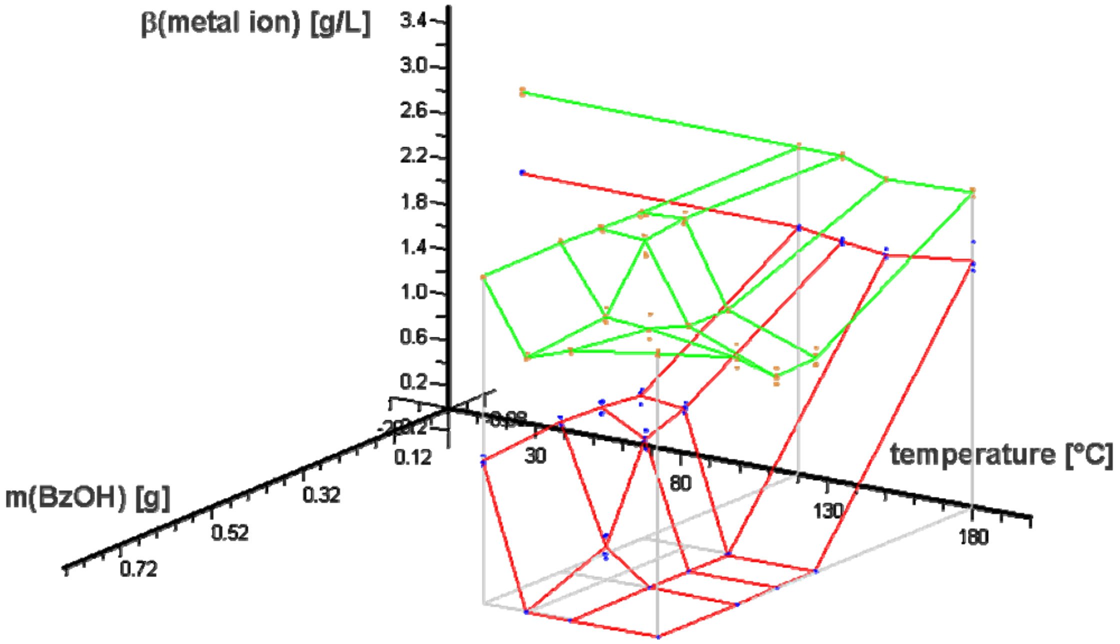

Figure 5.5: Amounts of Pd^{2+} and Ce^{3+} remaining in the solution.

The results of the ICP-OES showed that Pd^{2+} precipitated easier with increased concentration of benzyl alcohol. At 120°C the effect was not very great, but already at 135°C the effect was very important. The range of amount of added benzyl alcohol in which the effect depends much on the amount of added benzyl alcohol was in the studied one. At 150°C just the lowest studied amount of benzyl alcohol gave a result which was near the limit of detection. At 180°C all the remaining concentrations of palladium ions in the solution were below the limit of detection. Thus, the amount of added benzyl alcohol is to be lowered for studying the impact of benzyl alcohol at 180°C in dependence of its amount.

It is safe to say that 0.34g of benzyl alcohol in combination with 150°C were adequate for lowering the remaining concentration of palladium ions in the solution below 0.5% of the initial concentration. A higher amount of added benzyl alcohol did not lead to a measurable improvement of the results.

Due to these results there was further potential to precipitate palladium out of that solution. Thus, the concentration of palladium could be increased without the obligation to increase the amount of added benzyl alcohol.

For Ce^{3+} the situation was different. Heating without adding benzyl alcohol reduced the remaining concentration of cerium ions in the solution for maximal 6%. Heating to 120°C with different amounts of benzyl alcohol did not show any effect, whereas heating to 135°C with higher amounts of benzyl alcohol brought down the remaining concentration of cerium ions. At 150°C and at 180°C the situation was a bit more complex as the use of benzyl alcohol led to a shrinking concentration of cerium ions in the solution. By adding benzyl alcohol the remaining concentration of cerium ions in the solution shrunk, but at higher amounts of added benzyl alcohol the effect turned and more cerium ions remained dissolved. Thus, it was to expect that even higher temperatures in combination with not too high amounts of benzyl alcohol will precipitate more cerium out of the solution.

The reason for this behavior is not evident, but it might be due to a higher conversion rate in time of the benzyl alcohol. Probably benzyl alcohol polymerized too fast for reducing cerium or for precipitating with enclosed particles of cerium. As palladium was separated in very high efficiency the first argument was more probable. This could be due to the difference of the electric potential between palladium and cerium. This would say that at even higher temperatures palladium might remain dissolved, if the mechanism does not change. Nonetheless, higher temperatures were not interesting as it implicated an increased need for energy.

When using benzyl alcohol, the remaining concentration of palladium ions in the solution never exceeded the concentration of remaining cerium ions. Thus, the percentage of remaining palladium ions never exceeded 60%, while the concentration of cerium ions never fell below 64% of the starting concentration. Thus, a temperature of 135°C and 0.69g benzyl alcohol or 150°C and 0.34g benzyl alcohol were very efficient combinations as palladium was precipitated almost completely and cerium ions remained mainly in the solution. Starting at these points, every augmentation of temperature or of the amount of benzyl alcohol led to a complete precipitation of palladium.

Therefore, the reaction had been standardized with a temperature of 150°C for 16h and 519mg benzyl alcohol per 10mL solution. This led to a yellow solution and dark brown particles. No smell of nitrogen oxide was observable. This confirmed the absence of decomposition or only a very low decomposition rate for nitric acid.

5.1.4.2.Practical aspects for the separation

Not quantified, but nevertheless of high practical interest were some physical properties. The formation of foam was observed especially at 135°C, but also at 120°C and less intensive at 150°C. It was constituted that the surface-active agent is a derivative of benzyl alcohol whereas it was unclear, if it was a polybenzyl alcohol, benzoic acid, benzaldehyde, other derivatives, a polymer of the derivatives or a mixture of mentioned compounds. The precipitated particles acted as stabilizers of the foam and benzyl alcohol itself acts as co-surfactant. The gas used for the foam was caused by decomposing nitric acid. Its decomposition was supported by high acceleration rates as well as by scratching the solid from the inlet with a metal spatula. This could be justified by nuclei which provoke degassing of nitric acid as metallic palladium acts as catalyst for the decomposition of nitric acid. Thus, the volume could be doubled due to the stability of the foam. This effect increased with the amount of benzyl alcohol, but the correspondence with an increase of temperature was only valid between 120°C and 135°C. At 150°C the surface-active agents seemed to be destroyed as there was less foam at 150°C in combination with high amounts of benzyl alcohol. By contrast, there was no foam neither at 150°C with low amounts of benzyl alcohol nor at 180°C.

Besides, it was not to forget that the colors of the solutions did not correspond in every case to their concentration of metal ions. In general, the color was deeper, if the temperature had been higher. By contrast, as higher temperatures caused lower concentrations of remained metal ions in the solution, it was to expect that the color was less intensive. Additionally, there was a yellow compound which luminesced bright yellow in the presences of ultraviolet light. This is in congruency with the fluorescence of the polybenzyl alcohol.

On the other hand, the solid consisted of dark particles. At high temperatures additionally yellow particles of lower density were formed. Normally, all these particles precipitated very well during centrifugation for 5min at 2750g. Just in a few cases after high temperatures and at high amounts of benzyl alcohol some particles remained on the surface of the solution. The separation after using a high amount of benzyl alcohol and 180°C was not very well as the particles did not descend as well as the others. Maybe and especially in the first case was some flotation effect.

In the case of working without benzyl alcohol the separation was very easy, but, by contrast, there was not much precipitate and, thus, it was not very efficient. This corresponded to the remaining concentration of metal ions in the solutions found by ICP-OES.

Besides that, it will be important for industrial applications to optimize the point of lowest costs as a function of higher temperature and additional benzyl alcohol.

5.1.4.3. Dependence on the reaction time

Another way to reduce the costs would be to lower the duration of heating. This was studied for 120°C and for 150°C. The time dependence of the remaining concentration of metal ions in the solution is displayed in Figure 5.6.

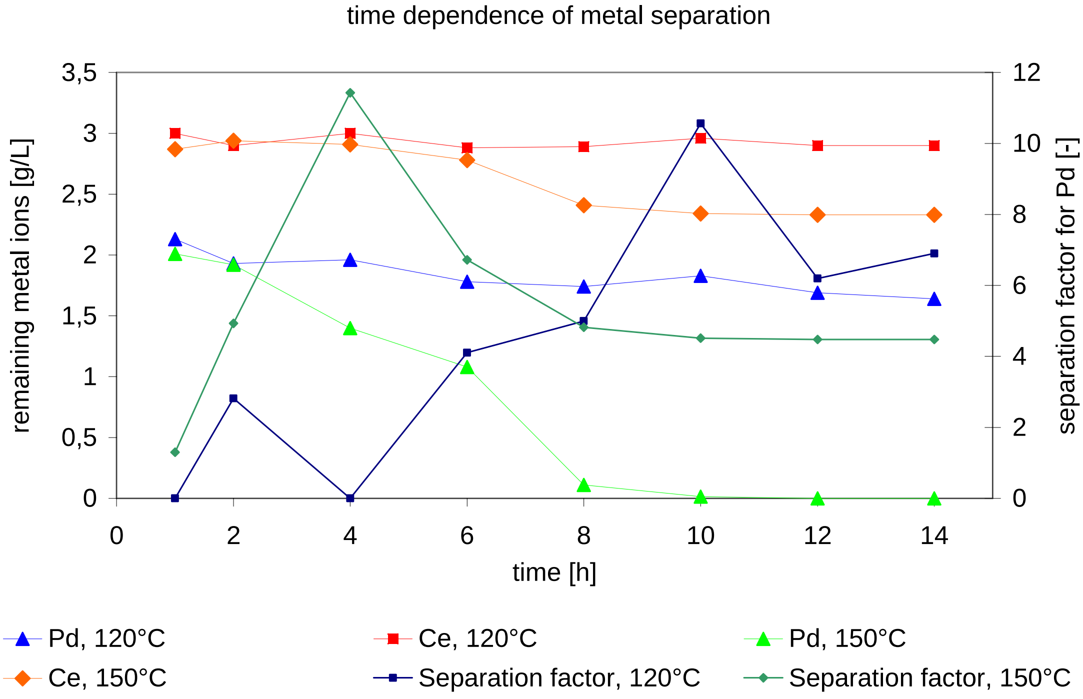

Figure 5.6: Time dependence of remaining concentrations of Pd^{2+} and Ce^{3+} and of separation factors using 519mg benzyl alcohol at 120°C and at 150°C.

The separation factor is defined as the ratio between the ratio of Pd to Ce in the liquid phase to the ratio of Pd to Ce in the solid phase. Table 5.4 gives the values for its calculation.

These measurements showed that the whole effect of adding benzyl alcohol in combination with heating was already reached after 12h and a heating time of 8h was almost sufficient. This allowed reducing the time by half which would lead to enormous savings in costs and time. It was also to recognize that 150°C were much better than 120°C. This might say that even less time at 180°C might have the same effect as mentioned above.

The separation factor depends a lot on the low changes of the concentration of cerium. Therefore, only its values for 150°C after 6 or 8 hours seem to be suitable, whereas the other values suffer from a lack of certitude. Thus, the separation factor for palladium from cerium approaches to 4.5 at 150°C under these conditions. This is according to the calculation in the used literature. Thus, no logarithmic law was taken which would have led to higher number. This separation factor allows a separation of palladium from cerium, but it is not adequate for purification.

temperature [°C]	time [h]	n(Pd(aq)) [mmol]	n(Ce(aq)) [mmol]	n(Pd(s)) [mmol]	n(Ce(s)) [mmol]	separation factor
120	1	0.200	0.214	0.000	0.000	-
	2	0.181	0.207	0.019	0.007	2.8
	4	0.184	0.214	0.016	0.000	-
	6	0.167	0.206	0.033	0.009	4.1
	8	0.164	0.206	0.037	0.008	5.0
	10	0.172	0.211	0.028	0.003	10.6
	12	0.159	0.207	0.041	0.007	6.2
	14	0.154	0.207	0.046	0.007	6.9
150	1	0.189	0.205	0.011	0.009	1.3
	2	0.180	0.210	0.020	0.004	4.9
	4	0.132	0.208	0.069	0.006	11.4
	6	0.101	0.198	0.099	0.016	6.7
	8	0.010	0.172	0.190	0.042	4.8
	10	0.001	0.167	0.199	0.047	4.5
	12	0.000	0.166	0.200	0.048	4.5
	14	0.000	0.166	0.200	0.048	4.5

Table 5.4: Values for the calculation of the separation factor (using 10mL solution).

5.1.4.4.Dependence on the type of alcohol

A possible way how to turn it even more attractive for industrial application might be the variation of the alcohol. Therefore, the influence of the type of alcohol was studied keeping the same molar amount of 4.8mmol alcohol. This corresponded to the standard of 519mg benzyl alcohol.

Figure 5.7 illustrates that different alcohols had different impacts. Ethanol showed only a slight impact whereas gallic acid, glycerol, 4-hydroxybenzyl alcohol and 4-methoxybenzyl alcohol had almost the same effect as benzyl alcohol. Anyhow, benzyl alcohol led to a complete separation of palladium ions and, additionally, it reduced the mass concentration of cerium ions more than the other alcohols did.

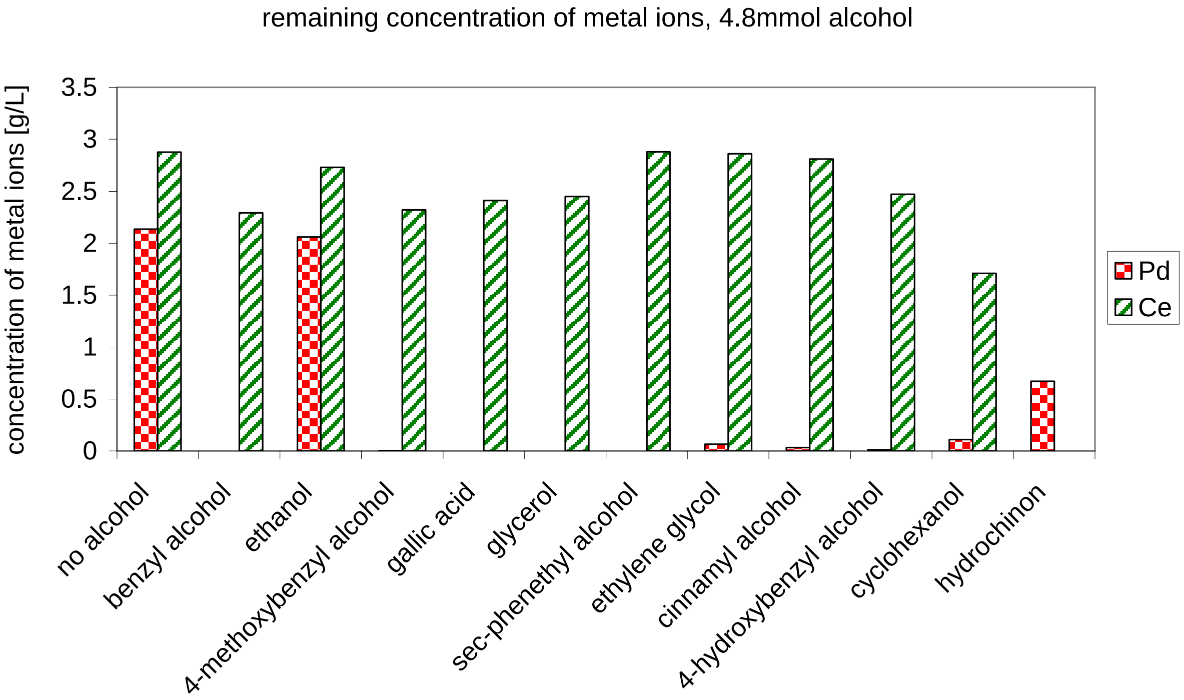

Figure 5.7: Remaining concentrations of Pd^{2+} and Ce^{3+} after reaction with 4.8mmol alcohol at 150°C for 16h.

sec-Phenethyl alcohol was the most selective alcohol as palladium ions were removed entirely and the concentration of cerium ions remained untouched. Under these conditions cinnamyl alcohol and ethylene glycol were also very selective, but it remained a low amount of palladium ions and a bit of cerium ions was removed. Cyclohexanol continued this direction and more palladium remained in the solution whereas more cerium was removed.

On the contrary, hydroquinone had an inverse effect due to the complete removal of cerium ions in combination with a remarkable, but obviously not entire diminution of the concentration of palladium ions in the solution. This was not appropriate to the problem which was handled here, but it might be extremely useful for other applications. Maybe it will get interesting not only to separate palladium, but also cerium or lanthanides out of the solution. If this had to be made separately and selectively, hydroquinone could be used in a second step – and ideally sec-phenethyl alcohol beforehand.

The studies with other alcohols suggested the assumption that different alcohols removed different metal ions from the solution. E.g. sec-phenethyl alcohol removed palladium ions quantitatively without touching the concentration of cerium ions. On the other hand, hydroquinone eliminated cerium ions entirely and decreased the concentration of palladium ions by a factor of about three.

5.1.4.5.Characterization of the precipitate

Moreover, the formed particles were studied. Figure 5.8 gives an image from a Scanning Electron Microscope (SEM) showing impressively the organic matrix in which the metallic particles were embedded. The forming of clusters could be seen in several scales: The shown particle as a whole with about 15µm of diameter seemed to be an agglomeration of five approximately round particles of 7µm of diameter and including one smaller particle. These particles of 7µm of diameter did not at all correspond to the size of the metallic particles. Thus, the metallic particles congregated in order to form the round particles of 7µm of diameter.

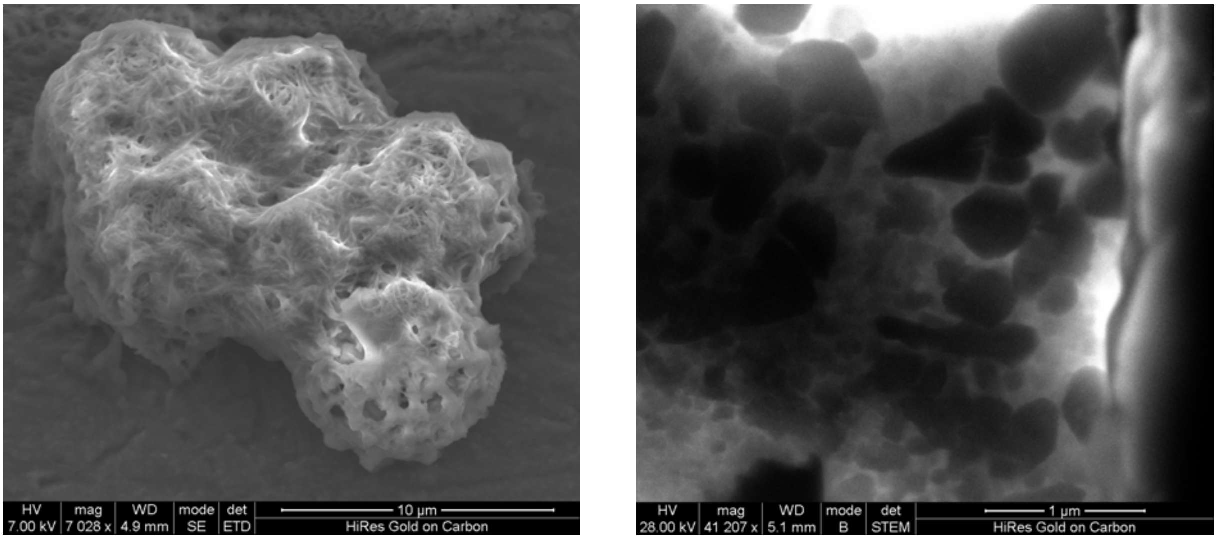

Figure 5.8: Images of precipitated particles taken by SEM (left) and STEM (right).

The size of the metallic particles is presented in Figure 5.8. It is a STEM-image (Scanning Transmission Electron Microscopy) which observed the electrons which passed a sample. Obviously, there is a distribution of particle sizes as there are smaller and bigger ones in the organic matrix. With this image the diameter of the metallic particles determined by X-Ray Diffraction (XRD) could be acknowledged to be in the range of about 200nm. Of course, this is neither valid for the smaller particles nor for the bigger ones. It has to be seen as an average.

As these particles do not occur in the absence of benzyl alcohol, the formation of the particles is not or not only caused by the Pourbaix-diagram, which would yet explain the formation of metallic palladium. Thus, the added benzyl alcohol participates in the formation of particles. This corresponds to the cited literature and Figure 5.1. Obviously, benzyl alcohol accelerates the kinetics and the metallic palladium is formed faster. By contrast, these analyses show neither the presence nor the absence of further elements in the particles. That is why metallic particles are awaited, but the formation of mixed metal and metaloxyde particles is possible. Only the organic matrix which embeds the particles is certain as the matrix appears when the SEM was used, whereas the STEM passes through.

Benzyl alcohol was tested for selectivity dependences on temperature, time and amount of benzyl alcohol. 0.34g benzyl alcohol in combination with 150°C for 8h are very efficient. Other organic compounds had other selectivities.

5.1.5 Validation by a simulated solution

After giving evidence for the feasibility of this separation, the validity was tested on a more realistic solution with a composition according to Table 5..

The results of tests with a more realistic model solution for reprocessing burned fuel rods of nuclear power plants of the current generation are shown in Figure 5.9 with indication of additional palladium containing compound. It shows that all the palladium was precipitated. Even further added palladium ions were removed completely. So there was enough benzyl alcohol to remove more palladium ions than demanded. This led to the idea that a certain amount of benzyl alcohol is necessary for the effect of precipitation, but a lower amount of benzyl alcohol would suffice for precipitating the present amount of palladium. In other words, the concentration of benzyl alcohol is important. Hence, it was the case that under these conditions the amount of palladium ions could be augmented without increasing the quantity of palladium ions after treatment, but the amount of benzyl alcohol could not be decreased without a negative impact. This impact could be compensated by a longer duration or a higher temperature.

Oxide	Amount of oxide [g/L]	Metal	Amount of metal ions [g/L]
Na_2O	18.739	Na	13.9
Al_2O_3	7.378	Al	3.9
ZnO	0.209	Zn	0.17
ZrO_2	9.479	Zr	7.02
TeO_2	1.272	Te	1.02
Cs_2O	5.757	Cs	5.43
SrO	1.703	Sr	1.44
BaO	3.632	Ba	3.25
SnO_2	0.128	Sn	0.1
Cr_2O_3	0.222	Cr	0.15
Fe_2O_3	1.698	Fe	1.19
MnO_2	1.997	Mn	1.26
La_2O_3	6.444	La	5.49
Nd_2O_3	14.878	Nd	12.75
Ce_2O_3	5.195	Ce	4.44
Pr_2O_3	2.821	Pr	2.41
MoO_3	9.413	Mo	6.27
P_2O_5	0.925	P	0.4
-	-	Pd	2.98
Total	91.89		70.61

Table 5.5: Compounds and concentrations of the model solution.

Moreover, when additional palladium was in the solution, the amount of cerium ions which remained in solution decreased a bit. To justify this observation, it could be helpful to regard the separation more globally. The palladium ions were reduced and the metallic palladium particles were kept in an organic matrix. Apparently, in the case of added palladium ions, more cerium ions followed this way. So there was no concurrence between palladium ions and cerium ions, there was a complementary effect. Either cerium prefers to be formed on metallic palladium or an intermediate compound was the key factor. The first possibility might result out of the higher number of formed palladium cores and the second one out of the higher number of reduced palladium ions and the thereby generated oxidized organic compounds, including their intermediates. Nevertheless, this effect was not very intensive, but because of the number of metals in the solution and further applications, it might become interesting in some future applications. Anyhow, if more palladium could be precipitated than there was in the solution reprocessing burned fuel rods of current nuclear power plants, this process needed not to be changed a lot in order to serve the reprocessing of burned fuel rods of the fourth generation of nuclear power plants which are in development.

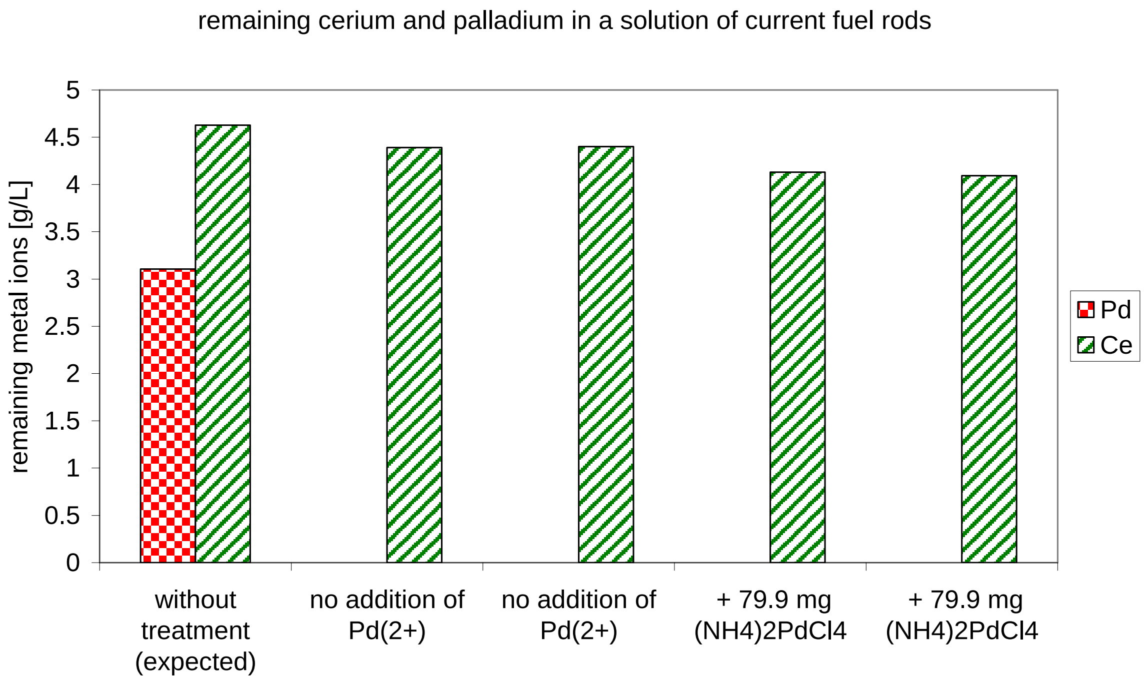

Figure 5.9: Remaining concentrations of Pd^{2+} and Ce^{3+} of the model solution after reaction with 519mg benzyl alcohol at 150°C for 16h, with or without adding further Pd^{2+}.

In general, the addition of benzyl alcohol did not change a lot the remaining concentration of cerium ions in the solution. The palladium ions were removed in a quantity so that their concentration was near or below 0.15g/L. Interferences of the signals in the ICP from other elements were observed in few cases as there were many other elements in the solution. So, if there was an interference with the signal for palladium, the signal could hardly be evaluated quantitatively. However, the ICP-signal was enough precise to detect, if there was a low amount of palladium ions in the solution or no palladium ions at all.

After removing the particles from the solution, it could be verified by Energy-Dispersive X-ray spectroscopy (EDX, see Figure 5.10) that particles which contained palladium atoms had been precipitated. Other results of EDX measurements also confirmed that there was much more palladium in relation to the other metal containing compounds in the precipitate than in the dried - and therefore extremely concentrated - solution. Nevertheless, the EDX-measurements showed many elements and therefore it was hard to quantify yet in the sample scale and especially in order to quantify the amount of precipitated palladium. These measurements showed a low variation, if the average of a wider field was measured. By having a closer look on some crystals and therefore relinquishing any greater average, the detected composition of elements differed from one measurement to another. In other words, the metals are not distributed homogeneously. This raised the idea it would be desirable to separate the crystals in dependence of their composition.

Figure 5.11 shows the precipitated solid where crystalline structures were embedded in an organic matrix. Yet here different crystal structures were identifiable and different sizes were obvious.

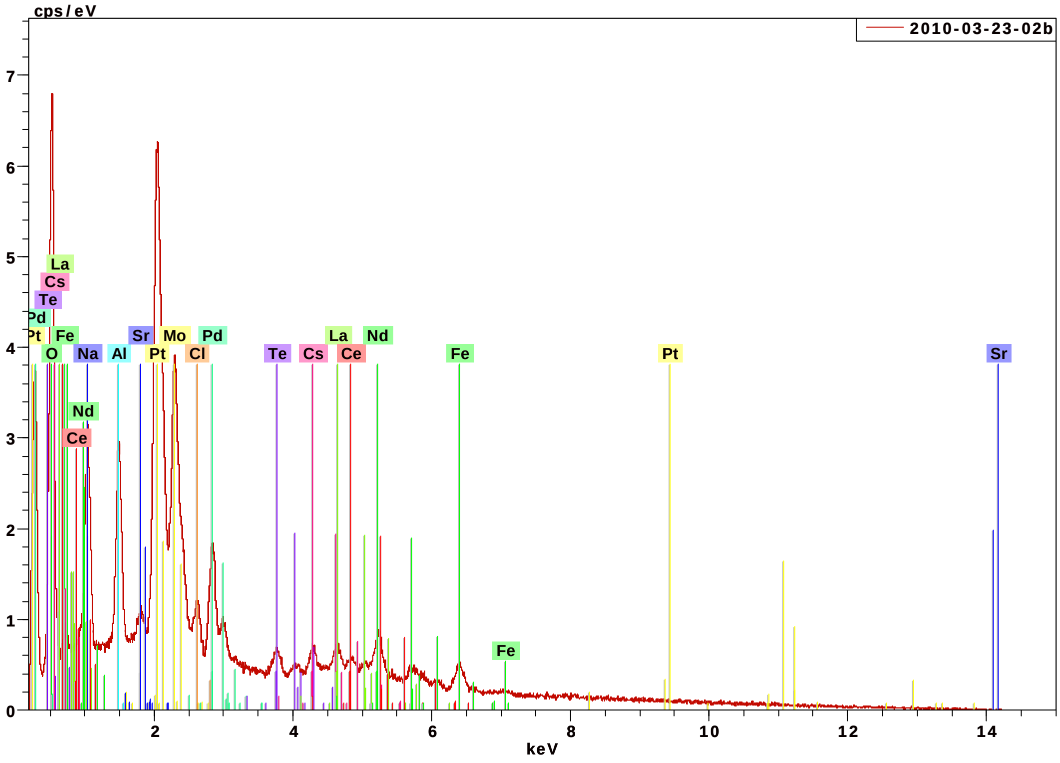

Figure 5.10: EDX-measurement of the precipitated particles.

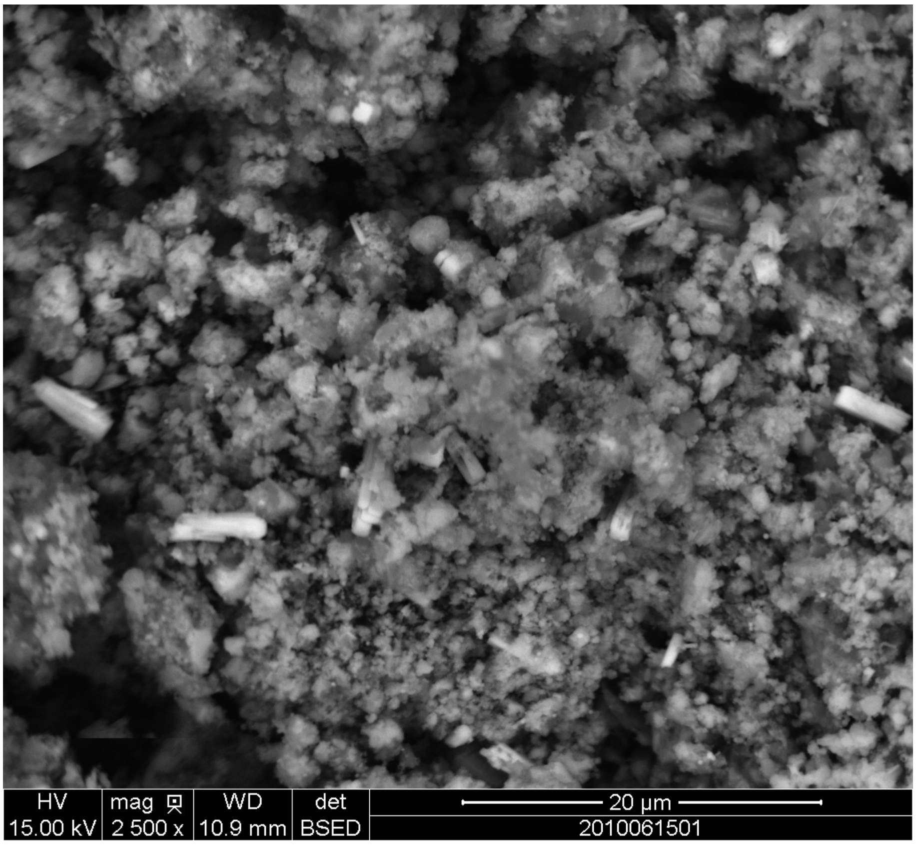

Figure 5.11: SEM-Image of treated model solution showing observed crystals.

The transfer of the results for the very simple system with Pd^{2+} and Ce^{3+} to a model solution of spent fuel rods from nuclear power plants of the current generation was successful. The selectivity of benzyl alcohol between Pd^{2+} and Ce^{3+} remained.

5.1.6 Further applications

This process was likely to be interesting also for other fields of applications. A huge market was seen in the recycling of catalysts. The recovery of PGMs from catalysts of the industry, but also from exhaust-gas catalytic converters as well, got more and more into mind as the prices for the catalytic active compounds rose and rose.

Platinum on alumina (1wt-% Pt) was used as example. As platinum is only soluble in nitrohydrochloric acid, the catalyst had to be dissolved in aqua regia. Complete dissolving of platinum was assumed and the color of the residue alumina confirmed the validity of this assumption. The concentration of platinum ions was lower than the concentration of palladium in the previous application, but with 1.0g/L still high enough to determine its diminution. However, the result was that the separation process could not be transferred to this system.

The amount of platinum remaining in the solution was not decreased under these conditions at 150°C during 16h. Thus, the precipitation of PGMs via the reduction by benzyl alcohol under hydrothermal conditions was expected to be helpful for the recycling of catalysts, but an adaptation is necessary.

Although benzyl alcohol formed a bright polymeric phase, no platinum was embedded. Maybe the higher acid concentration of the solvent had a negative impact on the separation. Anyhow, the difference of the electrochemical potential cannot be excluded as reason causing the difference as it is not well studied at elevated temperature in different acids and acid mixtures.

Further studies might grant access toward the recycling or the production of catalysts. But also in the mining of PGMs the separation would be useful as the PGMs have to be separated from associated materials. In combination with the yet mentioned selective separation in two or more steps, it also might simplify the purification of PGMs or the accessibility to further metals can be assured. In any case this method would be much less hazardous than a separation via multiple steps using hydrocyanic acid and other highly environmentally harmful substances.

The separation of PGMs could not be transferred to a model solution of catalyst recycling. Adaptations for catalyst recycling and mining are necessary.

5.1.7 Conclusion and perspectives

To sum up, in the context of a binary solution the use of benzyl alcohol under hydrothermal conditions aimed at lowering the concentration of palladium ions. Indeed, this concentration was lowered very much without limiting the concentration of cerium ions too much. 692mg benzyl alcohol for 10mL of a solution of 0.02mol/L $(NH_4)_2PdCl_4$ and 0.02mol/L $Ce(NO_3)_3 \cdot 6\ H_2O$ in 1.0mol/L nitric acid at 135°C had the same effect as the use of 346mg benzyl alcohol at 150°C, if the other parameters were not changed. According to that, the amount of benzyl alcohol could be replaced by temperature and vice versa. For practical reasons a process at 150°C was preferred instead of 135°C.

The time dependence shows that 8h were enough to remove the palladium ions almost quantitatively, if 519mg benzyl alcohol were combined with 150°C. For higher temperatures even lower durations might be applicable.

Other alcohols had other selectivities between palladium ions and cerium ions and therefore the alcohol was to be selected. The most selective alcohol was sec-phenethyl alcohol. Hydroquinone even changed the preference and decreased the concentration of cerium ions in the solution more than the concentration of palladium ions.

The result could be transferred from the sample including two metals to a model solution of burned fuel of the current generation of nuclear power plants which contained a various amount of different metal ions.

The separating process could not be applied on a model solution for catalyst recycling. Platinum was not separated from the solution. Probably the reaction conditions were not appropriate enough and further investigations have to be done. Also the separation in mining might become a field of application.

According to these observations, the application of hydrothermal reactions convinced to a far extent. The selectivity of the separation of metal ions and its variability was very promising.

5.2 Non-hydrothermal separation process

5.2.1 Field of application

The nuclear industry develops many processes which aim at separating metal ions either selectively or non-selectively. In some cases the treated solutions have low concentrations, but large volumes. Separating metal ions from these solutions has to be highly efficient and the price per treated volume must be low. Therefore, hydrothermal conditions are not always applicable. Besides, the application of these processes to other process solutions is also interesting.

One example for a separation of metal ions from large-scale volumes of liquid is the recycling of nitric acid from a solution which is obtained during the separation of uranium from its co-minerals (containing compounds with lanthanum, sodium, potassium, magnesium, calcium, aluminum, and iron). Therefore, it is not or not yet the aim to separate the metals, but to recover the nitric acid without the metal ions. In this case hydrothermal conditions are not applicable as heating would be too expensive and, in addition, it would destroy the nitric acid. Distillating the nitric acid would need lower temperatures than hydrothermal separation processes do, but due to the amount of volume it is not acceptable for energy cost-reasons. Also a decomposition of nitric acid and a recombination is not practicable. Thus, other conditions have to be employed.

In another context and as yet mentioned in the previous chapter, there are several metals which disturb the vitrification of nuclear waste. Besides the PGMs, also molybdenum may have to be separated, if burn up rates still grow. Indeed, upon vitrification, molybdates form a phase floating on the glass as can be seen in Figure 5.12. But as a floating phase is not vitrificated, this effect has to be eliminated.

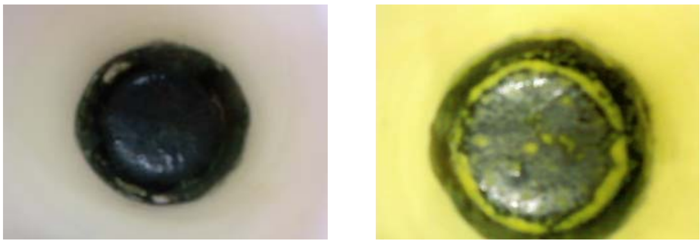

Figure 5.12: Glass for vitrification (left), glass with excess molybdenum (right), from [152].

These two aspects, an efficient separation out of large quantities of liquid and the elimination of molybdenum, were the basis for further investigations. These excluded hydrothermal reactions, but allowed the use of biomass.

5.2.2 Literature review

In the field of biomass-based separations which are highly selective for a group of elements or even for one single element, vegetable sources were yet investigated. It is known for a long time that some plants accumulate heavy metals [153, 154]. That is why they can be used for soil decontamination [155]. However, the irradiation intensity of wastes from nuclear industry is too elevated for living plants. Therefore, only dead plants or parts of plants can be used. One successfully implemented example is the use of tannin.

In 1997 a process has been installed in the Japanese nuclear industry for the treatment of waste of an ideal pH value in the range of 4 to 8. This process uses TANNIX, a tannin modified by formaldehyde. They modified the tannin to be insoluble in water so that it formed adsorption products with heavy metals which are easy to separate. The character of a polyoxyphenol is kept as this functional area is the key to adsorb heavy metals. They reported a high efficiency for the adsorption of actinides. For a liquid waste, containing 680ppb uranium, a volume ration of TANNIX to waste of 1 : 2000 is proposed. A further advantage is seen in the fact that no secondary radioactive waste is obtained and that TANNIX can be burned for metal recovery. Thus an adsorption rate of 99.5% for uranium and at least 96.1% for other actinides is combined with a volume reduction rate of almost 99% [156].

In 2011 Xiong et al. published a similar method. They also used tannin modified by formaldehyde, but in contrast to the Japanese they formed a gel. This gel was tested in batch mode as well as in a column for continuous flow. The studies on the pH dependencies showed a clear change in the range of 1mol/L HCl. In hydrochloric acids of lower acid concentrations the selectivity for molybdenum drops down with decreasing HCl concentration. Especially lead, iron and copper, but also nickel, zinc and manganese were also adsorbed below 1mol/L HCl while calcium and rhenium were separated from molybdenum in any case. Xiong et al. found an almost complete separation yet after 2h and with regard to measurements for different temperatures they postulated a pseudo-second-order rate law [157].

All in all, these two publications deal with the selective separation of metal ions out of a solution of several metal ions. In both cases the focus lies on the separation of a single element, but a group of elements can be separated. While Xiong et al. work in HCl, the Japanese worked in a liquid of pH 4 to 8. However, nuclear industry uses usually nitric acid at pH values below 4.

5.2.3 Idea and first approach

The idea for the task to recover nitric acid was to remove the metal ions unselectively by adding an organic compound at room temperature. By contrast, for the separation of molybdenum a very selective process was essential. Thus, modified tannic compounds were promising for both applications – once at low pH values and once in the range of neutral pH.

Yet existing results showed a good, unselective metal separation from the nitric acid with several organic compounds. Therefore, it was the aim to reproduce and to extend the yet studied examples which based on sugar and, respectively, a solution of chestnut bark.

Thus, it was started by adding succinic acid, tartaric acid, tannic acid, hydroquinone as well as a self-made extract of bark of chestnut in water to the nitric acid which should be purified from metal ions. 50g bark of chestnut were heated in 200mL water at 80°C over night to produce the extract. The solution was used after filtration. The other compounds were tested as a solution of 0.25g compound in water and as 0.25g pure solid. Every sample of compound with 10mL of the metal containing solution was agitated for six days at room temperature before separating the solid from the liquid.

In contrast to the former results only the concentration of molybdenum ions was decreased. In the case of self-made extract of bark of chestnut the concentration of molybdenum ions was lowered a bit and in the cases of solubilized and of solid tannic acid the concentrations were decreased between 40 and 50%. The concentration of zirconium was too low to be analyzed significantly by the used method as the expected concentration was much higher than the real concentration. All the other elements, namely lanthanum, sodium, potassium, magnesium, calcium, aluminum, and iron, were not reduced to a significant extent. And therefore, also all the other samples were reducing none of the concentrations of the metal ions – even not for molybdenum. Finally, the former results seemed to have been calculated based on a wrong base of information. Therefore, those results will be mentioned no more. Own results based on measurements including blank values for comparison.

Thus, tannic acid proved to diminish the concentration of molybdenum ions for almost 50% in the case of adding 0.25g tannic acid for six days to 10mL of the solution. Other metal ions were not separated from the solution.

Existing results showed unselective precipitation of metal ions by organic compounds. These results could not be reproduced. Some results for molybdenum were promising.

5.2.4 Optimization

Basing on these literature reports, we attempted to separate molybdenum selectively from nitric acid solutions. It is worth noticing the transfer of results obtained in HCl to HNO_3 was not obvious, because tannins are known to be good reducing agents and HNO_3 is an oxidizing medium. Therefore, their combination and application for separating metal ions could not be foreseen.

Tests with a solution of Na_2MoO_4 verified that the separation of molybdenum can be carried out from a solution which does not contain other metal ions. Thus, the adsorption of molybdenum is not an expulsion by other ions. Remarkably, the same amount of tannic acid precipitated a higher percentage of molybdenum from a solution which had the 2.3-fold concentration of molybdenum ions.

After starting with results which could not reproduce the yet existing data, a screening was made without changing the solution. The composition of the solution is given by listing the metal containing compounds and their amounts. Succinic acid, tartaric acid, tannic acid, and hydroquinone were taken in higher amounts, notably twice, threefold and fourfold. According to the pretests, it was also stirred for six days at room temperature.

compound	amount of compound [g/l]
$La(NO_3)_3$	0.023
NaCl	0.028
NaF	1.555
$NaNO_3$	0.219
$MgSO_4$	2.737
$CaSO_4$	2.531
KNO_3	0.78
Al	1.659
ZrO_2	0.091
$Fe(NO_3)_3$	0.653
MoO_3	0.276
$Ca(NO_3)_2$	3.336

Table 5.6: Metal containing composition of the solution.

	Acide tannique 500 mg	Acide tannique 750 mg	Acide tannique 1000 mg
Mo	42.4%	36.0%	30.2%
Fe	98.6%	100.0%	102.1%
La	98.0%	99.7%	101.6%
K	91.5%	87.8%	86.4%
Mg	94.8%	93.6%	94.1%
Ca	97.3%	94.0%	95.7%
Al	98.4%	95.8%	98.1%
Na	97.2%	92.8%	93.1%

Table 5.7: Percentages of remained metal ions in the solution.

Tannic acid proved to precipitate more molybdenum the more tannic acid is employed. Additionally, potassium and magnesium were diminished slightly when higher amounts of organic acid were added. A correlation between the amount of added tannic acid and the remaining concentration of molybdenum ions in the solution is illustrated in Figure 5.13. A decrease of the Mo-ion concentration is evident as quadrupling the amount of tannic acid led to a decrease of the concentration from 53% to 30%. The decrease of concentrations of other metal ions is hardly significant. Only the concentration of potassium is slightly lowered.

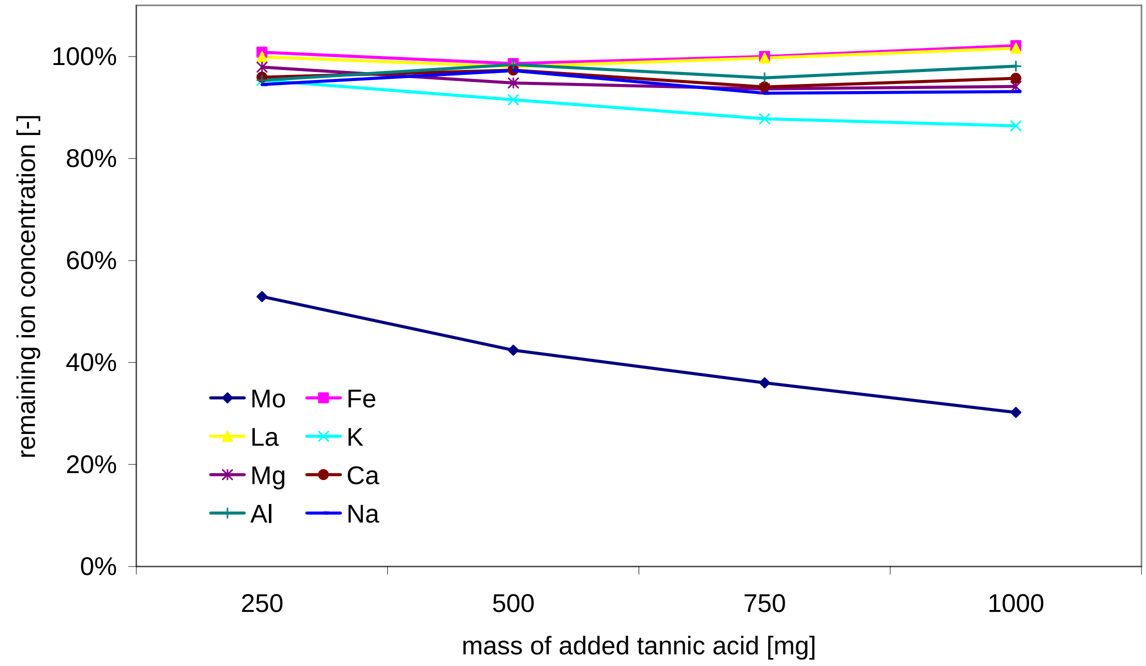

Figure 5.13: Remaining concentration of Mo-ions in the solution as a function of the amount of added tannic acid.

On the other hand, heating the metal ions containing samples with 0.50g tannic acid for 24h or 48h, respectively, without stirring has no effect on the concentration of the metal ions. In other words, the effect on molybdenum ions which is observed after stirring for six days at room temperature is not observed after 24h or 48h, respectively, at 50°C without stirring. This can be due to the temperature or it is caused by the lack of contact between the metal ions and the solid.

In the following, oxalic acid was studied. The new screening comprised 0.25g, 0.50g, 0.75g, and 1.00g oxalic acid as solid with 10mL of the model solution at 80°C. Each amount of oxalic acid was prepared five times – for five durations from 1 day, over 2 days, 6 days and 8 days until 10 days. If there was any effect, it was more intensive at short durations, but nonetheless not significant.

The next samples were prepared twice in order to determine any consequence of the used tubes as the tubes had been changed. So, if there was an effect of the tubes on the concentration of ones or others metal ions, it would have become evident here. Hexanoic acid and octanoic acid as well as two blank values were testes in each of the two types of tubes. The conditions were kept at room temperature for 6 days with agitating, but there was no effect at all. Nor the two carboxylic acids nor the tubes had any significant influence on any single concentration of metal ions. A precipitation could only be observed after increasing the pH up to 8. This corresponds to the solubility of non-dissociated oxalic acid and is not a proof for sparingly soluble oxalates of cations of the metals.

Also the kinetics of the separation of molybdenum is studied for a solution of Na_2MoO_4. Figure 5.14 presents the data in a visual form. According to the results, a short dwell time with tannic acid lowers the Mo-concentration more than long agitating with tannic acid. This might be caused by an overload of the tannic acid by molybdenum in the first moment and after a certain time equilibrium is formed.

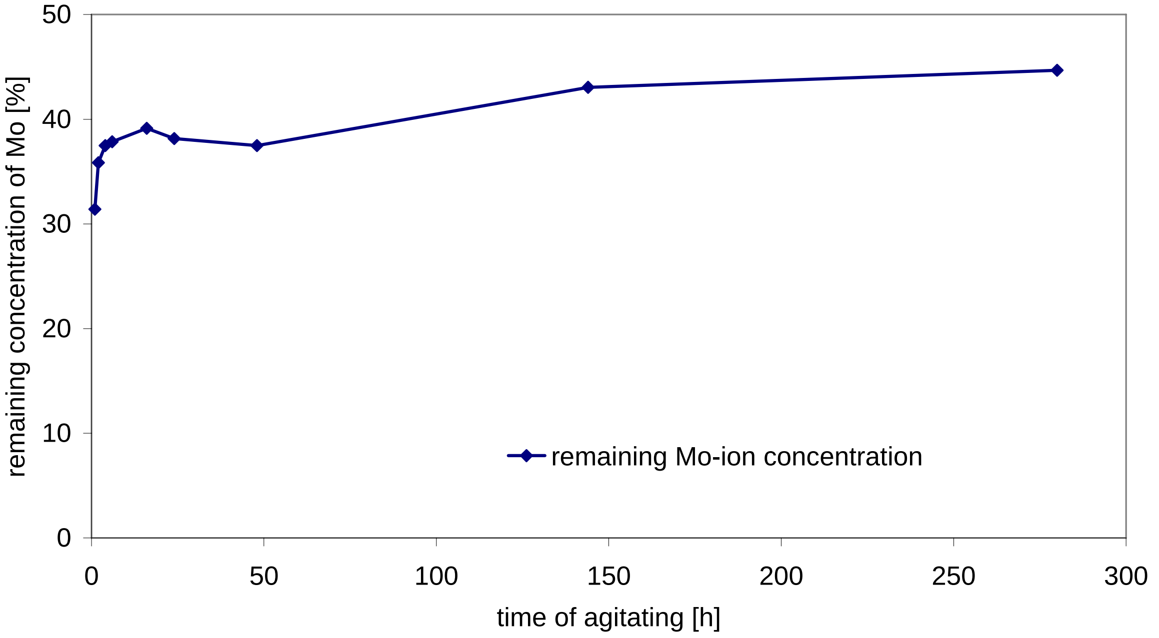

Figure 5.14: Time dependence for the remaining concentration of Mo-ions in the solution after stirring with added tannic acid.

Finally, a rough test on the separation time was made. Cotton was put into a syringe and after pressing the cotton to a crude filter, about 0.5g tannic acid were added as a solid. Afterward 10mL of the model solution were passed through the tannic acid within some seconds and the concentration on molybdenum yet fell significantly. Even if the decrease of 20% is much less than the diminution of 60% in the case of stirring with more tannic acid for several hours, the difference of the duration raises interest. Obviously, the tannic acid attracts the molybdenum ions to a high degree and very selectively. Thus, a column of tannic acid can be adequate in order to separate molybdenum ions as it was yet proposed in literature.

All in all, the aim to separate all the metal ions from the solution was not achieved, but the selective separation of molybdenum out of a mixture of several metal ions was carried out successfully.

Tannic acid separates molybdenum from a solution which contains several metal ions. More tannic acid separates more molybdenum. The separation is fast and highly selective.

5.2.5 Other systems

The selectivity of tannic acid for molybdenum was very high. In order to verify the selectivity, the system has been changed for two other solutions.

A solution with Ca^{2+}, MoO_4^{2-} and Fe^{3+} in 0.5mol/L H_2SO_4 was agitated with tannic acid for 24h. After separation of the tannic acid from the solution, the liquid was filtered and analyzed. The concentration of Ca^{2+} was not changed, less than 2% of Fe^{3+} were extracted and 68% of molybdenum were separated. This confirms the high selectivity as molybdate tends to react similar to sulfate ions.

In a second step, the solution known from chapter 5.1 was taken. Even if there were a lot of metal ions, not all of them were analyzed afterward. Only Mo, Fe, Nd, Ba, Al and Na were quantified. While 87% of Mo were separated, the amounts of the other metals decreased less than 1%, for Ba and Na less than 5%.

Thus, the very selective separation of molybdenum from complex metal solutions was applied successfully on other solutions. It was carried out in nitric acid as well as in sulfuric acid. As molybdenum was also separated from calcium and iron in sulfuric acid, the high selectivity was confirmed and the transferability to almost any other system in nuclear treatment was assured.

The selective separation by tannic acid was successfully transferred to other systems.

5.2.6 Conclusion and perspectives

To sum up, a very high selectivity of tannic acid for molybdenum was found. The more tannic acid was used the more molybdenum ions were extracted.

Elevations of the pH value up to 8 provoked a precipitation, but this is neither useful nor is it applicable as nitric acid should be purified and not decomposed. Kinetics show that the duration of stirring the solution with tannic acid as organic compound has not much influence. Yet very some seconds suffice in order to decrease the concentration of molybdenum ions in the solution.

Finally, the molybdenum selective process was successfully applied on other solutions. These confirmed that tannic acid was selective only for molybdenum, but it could be used under broadly different conditions.

In conclusion, it was shown that the non-ionselective precipitation of metal ions out of a model solution in order to recover the nitric acid does not work this way. The pH value cannot be increased to as elevated values as it would be necessary for a non-ionselective separation. Otherwise, the nitric acid would be destroyed. Anyhow, the ion-selective process for molybdenum is very convincing.

6. Conclusion and perspectives

Nowadays, most power plants have not very high efficiencies, because a lot of excess heat cannot be used. This thesis shows applications which can use excess heat for chemical reactions. These reactions could be used in order to generate potential biofuel out of glycerol, to carry out syntheses environmentally friendlier or to separate useful metals from waste.

Phenyl-ethanediol formed phenylnaphthalene in diluted acid under hydrothermal conditions. The mechanism was investigated and the two parts of this reaction, namely an aldol reaction and an intramolecular Friedel-Crafts type reaction, were the basis for two chapters of this thesis.

Aldol reactions were studied on the examples of ethanediol and 1,2-propanediol. The reactions of the diols under hydrothermal conditions showed dependencies. The temperature as well as the solvent had important influences on the progress of the reaction. Besides, the reaction conditions influenced the kind of main product as well as its amount. A trimerization followed by a cyclization and an aromatization was found. Ethanediol offered less reaction possibilities and a low conversion was found. 1,2-propanediol was studied in further detail and the aromatic trimer, mesitylene, was yielded as one of the main products. Anyhow, a cyclopent-2-enone derivative gave the highest yield. In this case, the reaction mixture can be used, especially after separation, as fuel or as chemical platform.

The intramolecular Friedel-Crafts type reaction was transferred to intermolecular ones. Thus, the original Friedel-Crafts reaction from 1877 was imitated under hydrothermal conditions. While the toxic chloroalkane was replaced by a much less harmful alcohol, the stoichiometric use of water sensitive $AlCl_3$ was substituted by 0.05mol/L HCl. By doing like that, also the excess of the aromatic compound was not required. Thus, the reaction was much greener and the corresponding products were the same. Therefore, hydrothermal conditions are useful in order to lower the toxicity of reactions significantly and to contribute to a greener chemistry. Nevertheless, the exact mechanism is not yet known.

A polymerization was found as side reaction and optimized. This polymerization was finally used in order to separate selectively metal ions out of a solution. The implementation of the principle from a simple model solution to a complex solution showed high selectivity between platinum group metal ions and other metal ions. Ion-specific selectivity for molybdenum was found for tannic acid at ambient temperature.

Taking everything into consideration, hydrothermal conditions offer many interesting and useful possibilities for organic reactions and simple biomass molecules. Even aromatic compounds can be synthesized from biomass, but also the Friedel-Crafts reaction under hydrothermal conditions possesses much lower toxicity. Thus, hydrothermal reactions contribute toward a greener chemistry and higher sustainability.

When the disadvantages of long reaction times and technical demands loose importance, excess heat can be used for chemical reactions. Additionally, the easy separation of hydrophobic products from the aqueous solvent at ambient temperature generates a further advantage.

Finally, the use of hydrothermal conditions raises benefits for the environment and novel reaction pathways for chemical reactions, especially with regard on decreasing amounts of fossil sources. Anyhow, further studies on higher selectivities, faster reactions and a better comprehension of side reactions are essential for an industrial implementation. The earlier the challenge is met, the earlier and easier it can be won.

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