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C. R. Vitasari

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Summary

Biomass is a potential source of renewable energy and chemicals. Biomass pyrolysis yields oil, gas, and char. Pyrolysis oil contains water and a considerable amount of bio-based platform chemicals, such as acetic acid, glycolaldehyde, acetol, levoglucosan, sugars, and phenolic compounds. Glycolaldehyde is one of the most abundant compounds in pyrolysis oil (5-13 wt%). It is a promising intermediate for producing bio-based ethylene glycol via fermentation. This research focuses on the isolation of glycolaldehyde from wood-derived pyrolysis oils, i.e. forest residue- and pine-derived pyrolysis oils.

Glycolaldehyde recovery is challenging since pyrolysis oil is a complex mixture of more than 300 oxygenated compounds with close boiling points. Furthermore, pyrolysis oil is chemically unstable, which makes distillation unfeasible. Therefore, extraction is expected to be a more promising separation method. To address these technical challenges, this research aims to develop an extraction-based separation process to isolate glycolaldehyde from wood-derived pyrolysis oils. In this thesis wood-derived pyrolysis oils are represented by forest residue- and pine-derived pyrolysis oils.

Direct glycolaldehyde extraction from pyrolysis oil with sodium bisulfite is not applicable due to the stable glycolaldehyde-bisulfite adduct. Therefore, water extraction of pyrolysis oil is employed as the initial step where glycolaldehyde and other polar compounds are isolated in the aqueous phase. The investigation was done at various stirring rates and water-to-oil ratios. The stirring rate does not affect either the equilibrium composition or the extraction performance. Van Krevelen diagrams show that the elemental distributions of pyrolysis oil between the two phases are independent of the water-to-oil ratio. These diagrams also indicate that water extraction is able to significantly decrease the hydrogen and oxygen contents of the forest residue- and pine-derived pyrolysis oils. The characteristics of pyrolysis oil feedstock determine the optimum water-to-oil ratio, which is in the range of 0.65-0.7 for forest residue-derived pyrolysis oil and 0.5 for pine-derived pyrolysis oil.

Water extraction is not selective but capable to extract 80-90% of the polar compounds present in the pyrolysis oil feedstocks in the aqueous extract phase. This aqueous mixture is the starting material for further treatment to isolate a particular bio-based chemical. On the other hand, the organic raffinate phase can be further extracted to recover phenolic fractions, which can be applied in the production of plywood and particle board.

The first alternative to extract glycolaldehyde from the pyrolysis oil-derived aqueous phase is reactive extraction with primary amines dissolved in organic diluents. Glycolaldehyde dissolves in the organic phase where it reacts with a primary amine extractant to

form a corresponding imine according to the Schiff-base mechanism. Several combinations of amine extractants and organic diluents have been investigated to select promising solvent candidates.

The ability of long chain alkane and alcohol diluents to dissolve glycolaldehyde reduces with the chain length in the following order: 1-octanol > 1-decanol > oleylalcohol > *n*-hexane > dodecane. The extraction capability of amine extractants declines as follows: octylamine > 4-ethylaniline > phenylethylamine >> Primene JM-T > 2-ethylaniline. Taking into consideration the reversibility of the Schiff-base formation, Primene JM-T and 2-ethylaniline are chosen as promising extractant candidates.

An excess amount of amine is necessary to significantly improve the distribution coefficient and achieve maximum single stage extraction yield. When a particular extractant is supplied in excess, for example at a concentration of 2 M Primene JM-T or 2-ethylaniline and a solvent-to-feed ratio of 2, the diluent has a minor influence on the extraction performance. Thus, in this case any organic diluents can be used as long as they are insoluble in water and able to dissolve the formed imine.

In addition, ^{1}H NMR spectra confirm that only Schiff-base formation takes place. *E/Z* isomerisation also occurs, but it does not form a new substance.

The Schiff-base formation is theoretically reversible and selective with a relatively high glycolaldehyde yield. However, the regeneration process is challenging, mostly due to imine stability and the nature of the organic phase. Thus, an antisolvent-induced regeneration method has been proposed. Imine solubility in the organic phase could be decreased by adding an antisolvent. The precipitated imine could be then stripped with a mixture of water and catalyst to enhance imine hydrolysis.

The second alternative is to extract the pyrolysis oil-derived aqueous phase with either 2-ethyl-1-hexanol or a solution of tri-*n*-octylamine (TOA) in 2-ethyl-1-hexanol. Both solvents are able to extract acetic acid and co-extract glycolaldehyde simultaneously. The effects of feed and TOA concentrations on the extraction performance have been investigated in a mixture of up to 12 wt% acetic acid and glycolaldehyde in water.

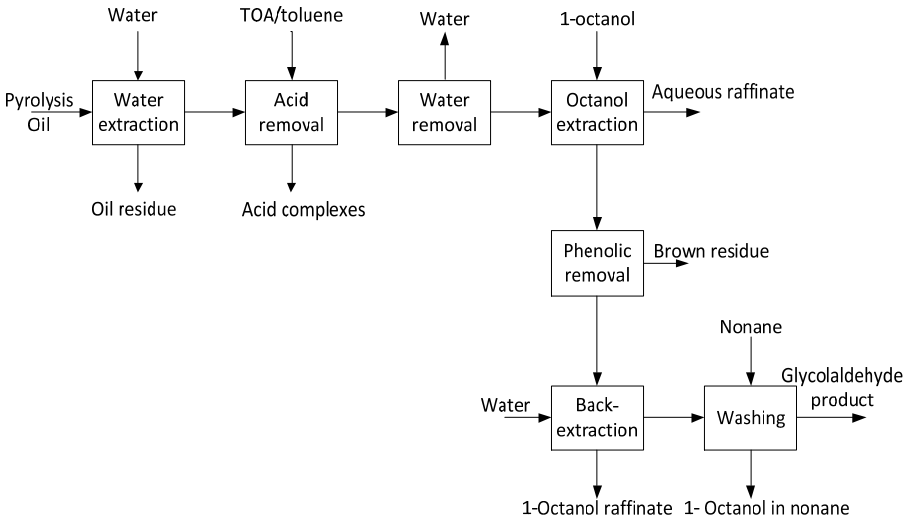
In the physical extraction with 2-ethyl-1-hexanol, acetic acid has about a fourfold higher distribution coefficient than glycolaldehyde within the studied concentration range. These distribution coefficients are only slightly affected by the feed composition. Furthermore, it has been proven that acetic acid and glycolaldehyde are extracted independently from each other. Besides acetic acid and glycolaldehyde also water is co-extracted into the organic phase with a concentration higher than its saturated concentration of 2.4 wt% at 20 °C.

In the reactive extraction with TOA/2-ethyl-1-hexanol, the performance of acetic acid extraction and glycolaldehyde co-extraction is nearly independent of the feed composition. The acetic acid distribution coefficient increases with the TOA concentration until it reaches a maximum at a concentration of 40 wt% TOA and then decreases. In contrast,

the glycolaldehyde distribution coefficient reduces proportionally with the TOA concentration. This proves that glycolaldehyde is only soluble in 2-ethyl-1-hexanol. Unlike in the physical extraction, water co-extraction in the organic phase is rather low.

In general, both physical and reactive extractions demonstrate that the isolation of acetic acid can be integrated with that of glycolaldehyde. For a combined one-step extraction, acetic acid and glycolaldehyde are extracted together with 2-ethyl-1-hexanol. The extraction and co-extraction yields are markedly improved by increasing the solvent-to-feed ratio in a multi-stage counter-current extraction column. For a two-step extraction, TOA/2-ethyl-1-hexanol at a concentration above 50 wt% is used to extract acetic acid prior to glycolaldehyde extraction with 2-ethyl-1-hexanol. Acetic acid is then recovered by distillation while glycolaldehyde is back-extracted with water.

Using the same principle as the proposed two-step extraction scenario, a batch laboratory-based process development has been executed. The process was designed to produce an aqueous glycolaldehyde solution as fermentation feedstock for producing bio-based ethylene glycol.



It starts with a single stage water extraction at a water-to-oil ratio of 1, which was able to isolate 63% of the glycolaldehyde available in the forest-residue pyrolysis oil feedstock in the aqueous phase together with acetic acid, acetol, and furfural.

This aqueous mixture was then extracted with TOA/toluene in three cross-current stages. In total, 81% of the acetic acid was removed with a very slight loss of glycolaldehyde.

The subsequent evaporation was included to remove about half the water from the acetic acid-lean aqueous mixture and thereby increased the glycolaldehyde concentration.

In the evaporation, there is a considerable loss of furfural (18-21%) and furanone (2-19%), which probably corresponds to their high volatility due to high activity coefficients.

The following glycolaldehyde extraction from the glycolaldehyde-enriched aqueous mixture with 1-octanol was conducted in four cross-current stages, which provided a total glycolaldehyde extraction yield of approximately 33%. The use of a more polar solvent than 1-octanol with a slight miscibility in water could further enhance the single stage extraction yield. In a continuous process, counter-current extraction will also improve the extraction yield and reduce the solvent requirement.

The presence of a small amount of phenolic substances imparts brown colour to the organic 1-octanol phase. Hence, these compounds need to be removed by evaporation. Up to 75% of glycolaldehyde was recovered in the colourless top product.

The next step was glycolaldehyde separation from 1-octanol by back-extraction with water. The total glycolaldehyde yield was 85.4% after two extraction stages. After washing with nonane, the final product fulfilling the product specification was obtained. It is octanol-free and comprises of 3.9 wt% glycolaldehyde, 0.3 wt% acetic acid, 0.3 wt% acetol, and 0.1 wt% furanone. The produced glycolaldehyde solution was then evaluated by Metabolic Explorer (France) in a continuous fermentation setup using a recombinant *Escherichia coli*. The results showed that it gave the same performance as pure glycolaldehyde with 98% bioconversion yield.

This batch process has a very low overall glycolaldehyde yield of only 17%, which makes it economically and environmentally unattractive. Nevertheless, it is able to demonstrate the integration of acetic acid and glycolaldehyde isolation processes in two-step extraction. Furthermore, the identified separation characteristics are beneficial to direct further process improvement in solvent selection and operating conditions.

Besides the batch laboratory development, the integrated concept of the combined one-step extraction of acetic acid and glycolaldehyde has been designed in Aspen Plus® for a continuous process using both forest residue- and pine-derived pyrolysis oils. The base capacity was 200 kton pyrolysis oil per year. The designed process includes extraction, distillation, and evaporation. Pyrolysis oil is firstly extracted with water to separate acetic acid, glycolaldehyde, and acetol in the aqueous phase. This aqueous mixture is then extracted with 2-ethyl-1-hexanol to separate acetic acid, glycolaldehyde, and acetol simultaneously. The 2-ethyl-1-hexanol phase is subsequently subjected to a distillation column to evaporate water and acetic acid while maintaining the less volatile components in the bottom product. Acetic acid is afterwards purified from water by state-of-the-art heterogeneous azeotropic distillation with isobutyl acetate entrainer.

The bottom fraction is back-extracted with water to recover glycolaldehyde and acetol from the 2-ethyl-1-hexanol phase, resulting in a very dilute aqueous extract comprising more than 95% water. Thus, a five-effect flash evaporation at reduced pressure is necessary prior to glycolaldehyde and acetol purification. In the final purification column, the

glycolaldehyde product is withdrawn from the bottom of the column while acetol is taken as a side stream. In addition to the aforementioned main steps, the process also incorporates solvent recycle and heat integration.

The forest residue- and pine-based designed recovery processes have very similar operating conditions, which give comparable product compositions and yields of acetic acid, glycolaldehyde, and acetol. About 70% of the total energy requirement is consumed in the distillation, whereas the other 30% is required in the evaporation. The pine based-process requires about 7% more energy, but consumes 28% less water and 22% less 2-ethyl-1-hexanol.

The economic evaluation in Aspen Process Economic Analyzer shows that the pine-based process has a slightly higher capital investment of 23 M€ than the forest residue-based process (21 M€) with a very similar working capital of 4 M€. Since the pine-derived pyrolysis oil has higher contents of the target platform chemicals (acetic acid, glycolaldehyde, and acetol), the pine-based process is more profitable than the forest residue-based process. It provides an about 30% higher annual revenue of 57 M€ which leads to an annual profit of 9 M€. On the other hand, the annual profit of the forest residue-based process is 44 M€, which is less than its total product cost of 48 M€.

The sensitivity analysis shows that the profit of the forest residue-based process is more sensitive to the changes in feedstock and product market prices. A 20% reduction in pyrolysis oil price improves the annual revenue by 34% and 11% for the forest residue- and pine-based process, respectively. Both processes have almost the same total capital investment and working capital, which increase with plant capacity. The pine-based process is significantly more profitable than the forest residue-based process. Above a capacity of 500 kton pyrolysis oil per year, the increase in the return on investment of both processes levels off. Since the economics of a pyrolysis oil-based process is determined by the feedstock composition, it is desirable to have a pyrolysis oil feedstock with higher contents of acetic acid, glycolaldehyde, and acetol.

To conclude, water extraction is important to reduce the complexity of pyrolysis oil before the recovery of bio-based chemicals. The reactive extraction of glycolaldehyde from a pyrolysis oil-derived aqueous phase with Primene JM-T or 2-ethylaniline provides high extraction performance and selectivity. Nevertheless, the glycolaldehyde hydrolysis from the corresponding imine remains challenging. Alternatively, 2-ethyl-1-hexanol is suitable to simultaneously extract acetic acid and glycolaldehyde. The economic feasibility of the isolation of glycolaldehyde and other bio-based chemicals depends on their concentrations in the pyrolysis oil. Thus, for bio-based glycolaldehyde pine-derived pyrolysis oil is a better feedstock than forest residue-derived pyrolysis oil. Comparing all investigated extraction methods, the combined one-step extraction process appears to be the most promising.

Contents

1 Introduction

Biomass is playing an important role in the future renewable energy supply and bio-based chemical production. In a pyrolysis-based biorefinery, biomass is converted into pyrolysis oil, which can potentially be used as a fuel and as starting material for producing liquid transportation fuels and platform chemicals. Some examples of potential platform chemicals are acetic acid, glycolaldehyde, and acetol. This chapter shows the technical challenges in recovering these platform chemicals and a proposed recovery scenario based on solvent extraction, which motivates the research discussed in this thesis.

1.1 Biomass as a source of renewable energy and chemicals

Biomass in general includes any hydrocarbon materials derived from living matter. It contains mainly carbon, hydrogen, oxygen, and nitrogen in the form of cellulose, hemicelluloses, and lignin. A small amount of sulfur compounds and inorganic minerals may also be found in biomass. Biomass sources vary greatly, from forest wood and crops to agricultural and municipal waste.

The interest in biomass as an alternative and renewable energy source has been increasing due to the depletion of fossil resources, climate changes, and global warming mitigation [1]. Furthermore, the transition to a bio-based economy makes biomass more attractive to produce not only heat and power but also biofuels, bio-based platform chemicals, and biomaterials.

Despite the potential to become renewable and sustainable, biomass-based processes face some challenges, which are related to feedstock characteristics and technology development.

Biomass varies widely with geographic location [2, 3]. In combination with its relatively high water content and low energy density, transportation costs contribute significantly to the feedstock price. Furthermore, the seasonal availability of biomass needs a proper production scheduling and pre-treatment to maintain a whole year plant operation [4].

The main challenge in the development of biomass-based technology is the competition with the well-established and economically viable petrochemical refinery. In order to address this challenge, efficient, low cost, and low energy consumption separation processes are required to reduce production cost. Furthermore, it is necessary to explore methods which can transform the multi-component mixtures of biomass into multiple products. It is also important that the developing technology is clean and green to ensure the sustainability [4].

1.2 Biorefinery concept

According to International Energy Agency (IEA) Bioenergy Task 42, biorefining is defined as the co-production of fuels, chemicals, power, and materials from biomass [5]. It is the key for the development of the bio-based economy, which includes bio-based products, bio-energy, and bio-fuels [6].

Considering the different types of biomass feedstock and processes, a biorefinery can be classified based on four main features: platforms, products, feedstock, and processes [7]. Among the different types of biorefineries, this thesis is discussing about a biorefinery which uses pyrolytic liquid (which is also known as pyrolysis oil) as a platform to produce conventional transportation fuels and bio-based chemicals from lignocellulosic forestry

feedstock via pyrolysis [8]. Thus, this type of biorefinery is later called a pyrolysis-based biorefinery.

A biorefinery is either erected in a new location or combined with an established process. A gasification-based biorefinery can be integrated with pulp mills to produce biofuels [9] or hydrogen [10]. Another example is the integration of a pyrolysis unit with a conventional petroleum refinery unit. This combined concept (Figure 1.1) has been investigated in the Biocoup project within the EU sixth framework programme for research and development. The combination facilitates the fast transition to bio-based economy without large capital investments [11].

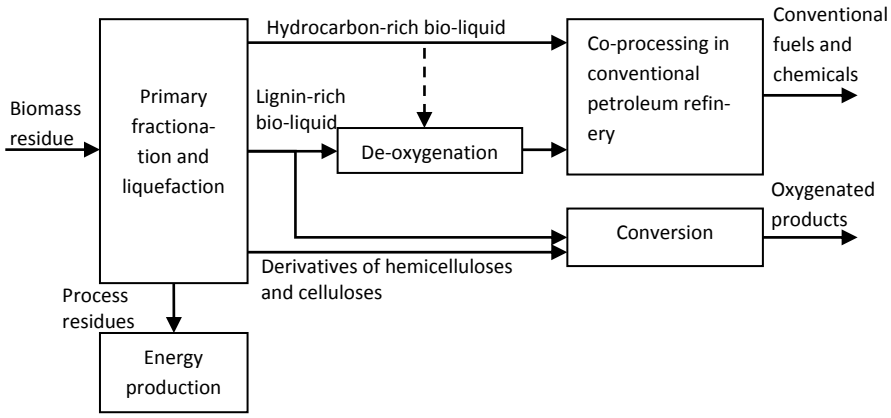


Figure 1.1: Biocoup integrated concept [12]

1.3 Pyrolysis oil

Biomass pyrolysis takes place at 300-500 °C in the absence of oxygen or another oxidizing agent to produce solid char, bio-liquid, and non-condensable gases. The yields of gas, liquid, and solid are mostly determined by the heating rate and the final temperature [13]. Slow pyrolysis at a low temperature produces charcoal, whereas fast pyrolysis with a residence time less than 2 s at a moderate temperature gives an optimum liquid yield. Wood fast pyrolysis typically yields 60-75% liquid, 15-25% char, and 10-20% gas [14, 15]. This liquid yield is larger compared to that of agricultural feedstock, such as sugarcane bagasse (12-18%) [16], straw, and hay (36-45%) [17].

Pyrolysis oil, which is also called pyrolysis liquid or bio-oil, is a free flowing liquid. Its colour can vary from black or dark brown to dark green, depending on its micro-carbon and elemental contents. The properties of pyrolysis oil depend on the type of pyrolysis and its operating conditions as well as the nature of biomass feedstock [18].

Table 1.1 shows that pyrolysis oil contains some amount of water, but it is still in a stable single phase. This water cannot be removed from pyrolysis oil by distillation. Pyrolysis oil comprises almost an equal amount of carbon and oxygen (Table 1.1) due the presence of more than 300 oxygenated compounds in the form of acids, alcohols, sugars, phenols, aldehydes, and ketones [19, 20]. These compounds are the degradation products of cellulose, hemicelluloses, and lignin [21]. The relatively high oxygen content results in a rather low energy density (16-18 MJ/kg) which is about half that of conventional fuels. In addition, the high oxygen content imparts polarity to pyrolysis oil and causes immiscibility with hydrocarbon liquids [22].

Volatile and non-volatile oxygenated compounds in pyrolysis oil contribute to the instability of pyrolysis oil, which depends on the biomass feedstock, pyrolysis conditions, solid and ash removal efficiency, and product collection [23]. Aldehydes react to form hydrates, hemiacetals, acetals, water, resins, and oligomers, while organic acids react into esters and water. Furthermore, air oxidation results in the formation of acids and peroxides which enhance the polymerisation of unsaturated compounds [24]. The presence of these high molecular weight substances increases the pyrolysis oil viscosity and water content, but decreases the volatility [19]. Moreover, phase separation also takes place due to the breaking down of the pyrolysis oil micro-emulsion [25]. As an example, the sediment of a heavy lignin-sugar complex could be observed after 6 month storage at room temperature of forest residue-derived pyrolysis oil [23].

Most of the wood-derived pyrolysis oils depicted in Table 1.1 have a hydrogen-to-carbon atomic ratio (H/C) around two, which is higher than that of heavy fuel oil (1.55) [22]. This H/C atomic ratio lies in the range of petroleum-derived feedstock, which is between slightly above one for highly aromatic residues and about two for highly paraffinic feedstock [26]. This indicates that pyrolysis oil is a potential starting material to produce liquid fuels. However, Table 1.1 also shows that the effective H/C (H/C_{eff}) ratio is an order of magnitude lower than the H/C ratio. This difference is caused by the almost equal amount of carbon and oxygen in the oils. Hence, catalytic upgrading is needed to reduce the oxygen content prior to co-feeding in a current refinery unit [27]. On the other hand, some oxygenated compounds are promising valuable platform chemicals [14, 22, 25].

Table 1.1: Properties of pyrolysis oil derived from different woody biomass

	Pine *P. Sylv.* [17]	Brown forest residue [17]	Green forest residue [17]	Eucalyp-tus *Crandis* [17]	Soft-wood bark [28]	Birch [29]	Poplar [29]	Pine saw-dust [30]	Mes-quite sawdust [30]	Various wood [29]
Water (wt%)	23.9	26.7	25.5	20.6	13.0	18.9	18.9	49.60	67.60	15 – 30
Ash (wt%)	0.03	0.3	0.1	0.03		0.004	0.01			0.004 – 0.3
Carbon (wt%)	40.6	41.4	41.2	42.3	54.20	44	46.5	45.8	59.4	32 – 49
Hydrogen (wt%)	7.6	7.4	8.0	7.5	6.09	6.9	7.2	8.7	5.8	6.9 – 8.6
Nitrogen (wt%)	< 0.1	0.3	0.3	0.1	0.96	< 0.1	0.15	< 0.1	< 0.1	0 – 0.2
Sulfur (wt%)	0.01	0.03	0.02	0.02	0.06	0	0.02			0 – 0.05
Chlorine (wt%)	0.006	0.002	0.004							
Oxygen (wt%)	51.7	50.9	50.5	50.1	25.23	49	46.1	45.3	34.5	44 – 60
H/C	2.25	2.14	2.33	2.13	1.35	1.88	1.86	2.28	1.17	2.11 – 2.59
H/C_{eff} [a]	0.33	0.28	0.47	0.34	0.60	0.20	0.36	0.79	0.30	0.26 – 0.52
Viscosity (cSt)	17 (40 °C)	17 (40 °C)	24 (40 °C)	23 (40 °C)	62 (50 °C)	28 (50 °C)	13.5 (50 °C)			13 – 80 (50 °C)
Density (kg/m^3)	1206 (15 °C)	1194 (15 °C)	1210 (15 °C)	1229 (15 °C)	1188 (15 °C)	1250	1200	1060	1060	1100 – 1300
HHV (MJ/kg)	16.9	16.9	16.7	17.3	24.27			10.03	7.72	
LHV (MJ/kg)	15.3	15.3	15.2	15.6		16.5	17.4			13 – 18
pH	2.7	3.2	-	2.2	3.0	2.5	2.8	3	3	2.0 – 3.7

[a] The effective hydrogen-to-carbon ratio (H/C_{eff}) is calculated using the following equation:

$H/C_{eff} = \frac{H-2O-3N-2S}{C}$, where H, C, O, N, and S are the moles of hydrogen, carbon, oxygen, nitrogen, and sulphur, respectively [26].

1.4 Chemicals from pyrolysis oil

Table 1.2: Potential oxygenated chemicals from pyrolysis oil

Compound	Minimum (wt%)	Maximum (wt%)	Reference
Sugars and dehydrosugars			
Levoglucosan	0.1	30.5	[18, 30]
Cellobiosan	0.4	3.3	[18]
1,6-Anhydroglucofuranose	0.7	3.2	[18]
Fructose	0.7	2.9	[18, 31]
Hydroxyaldehydes			
Glycolaldehyde	0.9	17.5	[18, 31]
Carboxylic acids			
Acetic acid	0.5	17.0	[18, 31]
Formic acid	0.3	9.1	[31]
Propionic acid	0.1	2.0	[18, 31]
Aldehydes			
Acetaldehyde	0.1	8.5	[18, 30]
Ethanedial	0.9	4.6	[31]
Methyl glyoxal	0.6	4.0	[18]
Formaldehyde	0.1	3.3	[31]
Furfural	1.5	3.0	[18]
Glyoxal	0.6	2.8	[18]
Alcohols			
Methanol	0.4	8.2	[30, 31]
Furfuryl alcohol	0.1	5.5	[18, 31]
Ethanol	0.5	3.5	[18]
Ethylene glycol	0.7	2.0	[31]
Hydroquinone	0.3	1.9	[18]
Hydroxyketones			
Acetol	0.2	7.4	[18, 31]
1-hydroxy-2-butanone	0.3	1.3	[18]
Phenolic compounds			
Isoeugenol	0.1	7.2	[31]
Catechol	0.5	5.0	[18]
Syringol	0.7	4.8	[31]
Phenol	0.1	3.8	[31]
Guaiacol	0.2	2.8	[18, 30]

Table 1.2: Potential oxygenated chemicals from pyrolysis oil (continued)

Compound	Minimum (wt%)	Maximum (wt%)	Reference
Cresol	1.03	2.5	[30]
4-methyl-2,6-dimethoxyphenol	0.5	2.3	[18]
Eugenol	0.1	2.3	[31]
Syringaldehyde	0.1	1.5	[18, 31]
3-ethylphenol	0.2	1.3	[18]
Ketones			
Acetone	0.4	2.8	[18, 31]
2-cyclopenten-1-one	0.3	1.5	[18]
2-furanone	0.1	1.1	[31]
Esters			
Methyl formate	0.2	1.9	[18]

Table 1.2 shows that sugars, (hydroxy)aldehydes, acids, alcohols, (hydroxy)ketones, and phenolics are the most abundant chemicals in pyrolysis oil. However, their presence in a particular pyrolysis oil depends on the nature of the feedstock and pyrolysis conditions. As an example, wood-derived pyrolysis oil generally comprises 3-12 wt% acetic acid [25, 32], 5-13 wt% glycolaldehyde, 0.7-7.4 wt% acetol, and 0.4-1.4 wt% levoglucosan [33].

Among those abundant chemicals, this thesis is mainly focusing on glycolaldehyde. Additionally, acetic acid and acetol will be included in the discussion since they are also potential bio-based platform chemicals and available in a considerable amount in wood-derived pyrolysis oil.

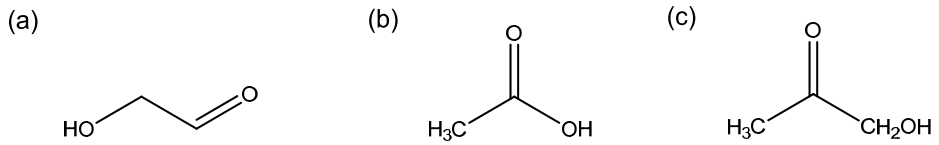


Figure 1.2: Molecular structure of glycolaldehyde (a), acetic acid (b), and acetol (c)

Acetic acid is a widely used solvent and raw material to produce vinyl acetate and cellulose-derived polymers [34, 35].

Acetol is the smallest hydroxyketone (Figure 1.2c). Beside used as a flavour additive for food and milk, acetol is an intermediate for producing renewable propylene glycol, acrolein, propionaldehyde, acetone, and furan derivatives [36].

1.5 Glycolaldehyde

Glycolaldehyde is the simplest sugar [37], which consists of both hydroxyl and carbonyl groups (Figure 1.2a). At room temperature it exists as a solid dimer (2-5-dihydroxy-1,4-dioxane) [38]. In a dilute solution or at elevated temperatures, it depolimerises into its monomer forms [37], which leads into a mixture of isomers of monomers and dimers [39]. For example, an aqueous glycolaldehyde solution at room temperature contains 9% dioxane dimer, 4% monomer, 70% hydrate, and 17% dioxolane dimer in equilibrium [39]. Only *cis* glycolaldehyde monomer is present in the vapour phase [40].

Glycolaldehyde is commonly used in food industries as a cross-linking agent for proteinaceous materials [41] and food browing agent. Moreover, glycolaldehyde can produce flavour by contacting it with amine or ammonia [42]. In bulk chemical production, glycolaldehyde is a potential intermediate to produce renewable ethylene glycol via hydrogenation [43] or fermentation [44].

It is known that glycolaldehyde can be synthesised from dihydroxymaleic acid. Chan [45] and Auvil and Mills [43] have converted carbon monoxide and hydrogen into glycolaldehyde via catalytic synthesis at high pressure. A few years later, Seto *et al.* [46] use vapour phase catalytic reaction to produce glycolaldehyde from ethylene glycol, whereas Ukeda *et al.* [47] converted ethylene glycol into glycolaldehyde with immobilised alcohol oxidase and catalase. These methods have been identified to have several disadvantages, such as low conversion and yield with relatively high concentrations of by products [48]. These may explain why there is no commercial scale production of glycolaldehyde at present.

Another alternative in producing glycolaldehyde is via pyrolysis of ligno-cellulosic feedstock [49], starch [50], monosaccharides and oligosaccharides [48, 51-53]. Furthermore, Stradal and Underwood [42] have proposed a series of evaporation and distillation to concentrate glycolaldehyde and crystalisation for glycolaldehyde purification. The glycolaldehyde solution was used as food browning agent.

Considering the potential applications of bio-based glycolaldehyde and its abundance in wood-derived pyrolysis oils, a separation process needs to be developed to isolate glycolaldehyde. It is also important that the isolation process can be integrated with the separation of other bio-based platform chemicals, such as acetic acid and acetol.

1.6 Chemical recovery scenario

The isolation of a particular compound from pyrolysis oil is challenging due to the complexity of the multi-component mixture and close boiling point differences (Table 1.3).

Table 1.3: Physical properties of several common substances found in pyrolysis oil [54]

Compound	Molecular weight (g/mol)	Normal boiling point (°C)	Melting point (°C)	Density (g/cm^3)
Formic acid	46.03	101	8.3	1.22
Acetic acid	60.05	117.9	17	1.04
Acetol	74.08	145-146	-17	1.08
Glycolaldehyde	60.05	150[b]	97	1.37
Furfural	96.08	161.5	-38.3	1.16
Furanone	84.07	86-87	4 – 5	1.18
Guaiacol	124.14	204	28.3	1.13
Catechol	110.11	245.5	100 – 103	1.34
Syringol	154.16	261	50 – 57	n/a
Levoglucosan	162.14	285 [55]	182 – 184	1.60 [56]

[b] Aspen Plus® database PURE24

Furthermore, pyrolysis oil is a chemically unstable mixture whose activity increases with temperature. Above 100 °C, it reacts rapidly and nearly 50% of the total initial oil converts into char [57]. This in combination with the close boiling point difference makes pyrolysis oil distillation not promising.

Unlike distillation which employs heat and volatility difference, extraction is normally conducted at atmospheric pressure and ambient temperature. Hence, problems related to the reactivity of pyrolysis oil could be reduced. It is also expected that the energy consumption of extraction will be lower than that of distillation. Furthermore, extraction is widely applied in pyrolysis oil characterisation [23, 32, 55, 58, 59].

The extraction yield and selectivity of a particular solute are mainly solvent dependent. Moreover, several regeneration methods, such as back-extraction, temperature swing, pH swing, or evaporation, can be selected. Thus, extraction may be a good alternative to recover a targeted compound from pyrolysis oil.

Figure 1.3 illustrates a general proposed scenario to isolate different types of platform chemicals from pyrolysis oil based on physical and reactive extraction.

Aldehydes and ketones can be extracted directly from pyrolysis oil with an aqueous sodium bisulphite solution. They dissolve in the aqueous phase and subsequently react with the bisulphite to form the corresponding bisulphite adducts [60]. An aqueous solution of 3.3 M sodium bisulphite at a volumetric solvent-to-feed ratio of 1 could extract all glycolaldehyde together with 85% furfural and 99% acetol. About 65% of furfural and 10% of acetol could be recovered from their adducts by back-extraction with toluene and 1-octanol for furfural and acetol, respectively [61]. In contrast, back-extraction was not

able to recover glycolaldehyde most probably due to the stability of the glycolaldehyde-bisulphite adduct [60, 61].

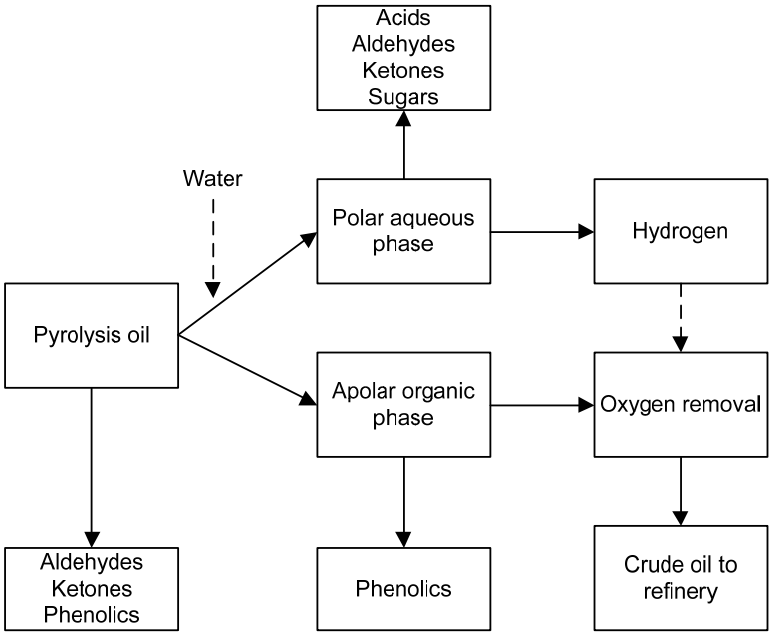


Figure 1.3: Chemical recovery scenario

Besides, phenolic compounds can also be extracted directly from pyrolysis oil with alkali solutions and organic solvents. Awang and Seng [62] used ethyl acetate and sodium bicarbonate to extract phenolics from oil palm shell-derived pyrolysis oil. In addition, it has been found that the addition of 0.1 M NaOH and methyl isobutyl ketone is effective to isolate 85% of phenolic compounds from forest-residue derived pyrolysis oil [63].

Water addition to pyrolysis oil can induce phase separation when the total water content exceeds its maximum limit, which is typically 30-45 wt% [64]. The aqueous phase contains mostly carbohydrate-derived compounds, whereas the organic phase comprises the lignin-derivatives [14]. Further separation of the aqueous phase can produce polar compounds, such as levoglucosan, acetic acid, glycolaldehyde, and acetol. On the other hand, the organic phase can be treated to isolate phenolic compounds, for example with methyl isobutyl ketone [63].

The levoglucosan containing aqueous phase can be readily hydrolysed to glucose, which is an intermediate to produce renewable ethanol [65, 66]. Acetic acid is isolated from the aqueous phase by reactive extraction with tri-*n*-octylamine (TOA) in organic diluents, such as toluene [67] or 2-ethyl-1-hexanol [68]. Glycolaldehyde isolation from the aqueous phase will be discussed in this thesis.

1.7 Liquid-liquid extraction

In liquid-liquid extraction, a particular solute moves to the solvent phase since the solvent has higher affinity for the solute than the carrier in the feed phase. There are two types of extraction which could be implemented for bio-based chemical isolation, i.e. physical extraction and reactive extraction. Physical extraction is limited by saturation. Although the extraction capacity corresponds to the amount of solvent, increasing solvent-to-feed ratio may lead to extract dilution.

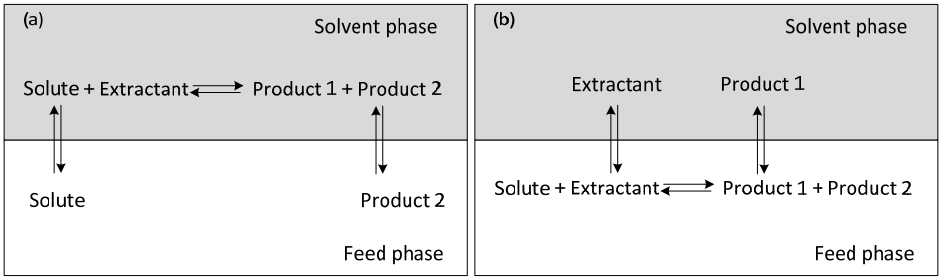


Figure 1.4: Reactive extraction mechanism in the solvent phase (a) and in the feed phase (b)

The extraction capacity and selectivity towards a particular solute in a multicomponent feed can be improved by reactive extraction. In reactive extraction the solvent is a mixture of an extractant and a diluent. Reactive extraction incorporates a chemical reaction between the solute and extract either in the solvent [60, 68, 69] or the feed phase [70], which is illustrated in Figure 1.4a and Figure 1.4b, respectively. The reaction products are generally water and a complex or adduct of the extractant and solute (Product 1), which is soluble in the solvent phase. To achieve a complete phase separation, the feed and solvent phase must be immiscible with each other. Depending on the types of extractant and solute, a catalyst may be required to enhance the complex or adduct formation reaction [70].

A good extractant is capable to combine high selectivity and capacity by reacting reversibly with the target solute to allow complete extractant regeneration. In general, both extractant and diluent need to have a sufficient density difference with the feed phase, low or moderate viscosity and favourable interfacial tension as well as reasonably fast reaction kinetics. Moreover, economics, safety, toxicity, and environmental impact need to be considered [71].

1.8 Objective and outline of the research

This research aims to develop an extraction-based separation process to isolate glycolaldehyde from wood-derived pyrolysis oil via water extraction. Glycolaldehyde is separated from a pyrolysis oil-derived aqueous phase either by physical or reactive extraction. Several extraction-based separation routes, including process integration with acetic acid recovery are investigated and evaluated (Figure 1.5).

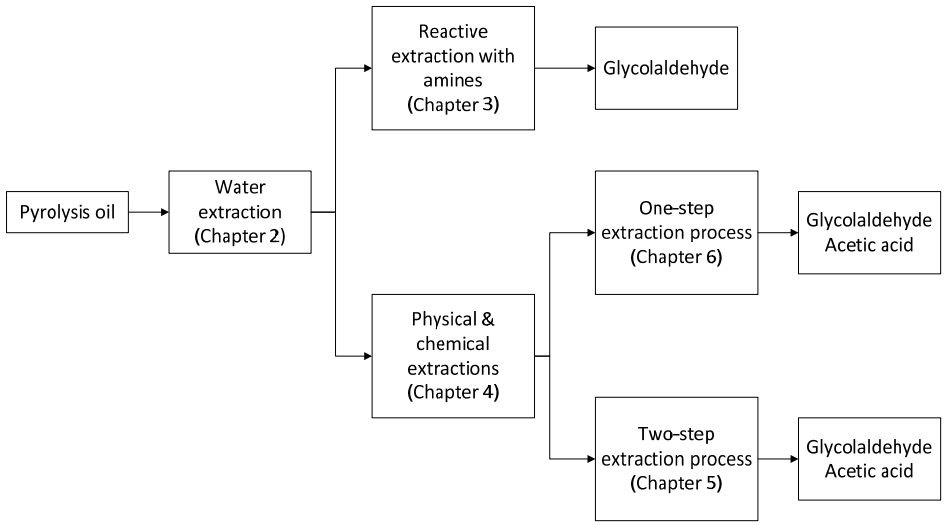


Figure 1.5: Schematic thesis outline

In Chapter 2 water extraction is studied at various stirring rates and water-to-oil ratios. The extraction performance is analysed based on the distribution coefficients and yields of several representative polar and non-polar compounds. In addition, the compositions of the aqueous and the organic phases are discussed.

Chapter 3 deals with the solvent screening for glycolaldehyde extraction from an aqueous solution. Several extractant/diluent combinations are evaluated based on the extraction performance, physical observation, and identified reaction mechanisms.

Chapter 4 investigates the co-extraction of glycolaldehyde from an aqueous mixture of acetic acid and glycolaldehyde in 2-ethyl-1-hexanol as well as in TOA/2-ethyl-1-hexanol. The distribution coefficients and yields of both solutes are investigated at various feed compositions and extractant concentrations. Two separation routes are proposed based on the experimental results.

Chapter 5 discusses the laboratory scale process development to produce an aqueous glycolaldehyde solution from forest residue-derived pyrolysis oil. This process also demonstrates that acetic acid recovery can be integrated with that of glycolaldehyde.

Chapter 6 presents the conceptual design of a glycolaldehyde production process from pyrolysis oil based on the recommendations in Chapter 4. The economic evaluation is based on cost, investment, and profit analysis as well as sensitivity analysis.

The last chapter (Chapter 7) summarises the important conclusions and recommendations for future research.

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2 Water extraction of pyrolysis oil

An important initial step in the chemicals recovery from biomass-derived pyrolysis oil is water extraction where most of the polar compounds are isolated in the aqueous phase. This chapter investigates the effects of the stirring rate and water-to-oil ratio on the extraction capability (denoted as distribution coefficient and yield), water content, and atomic composition of both aqueous and organic phases. The results show that the stirring rate does not determine the equilibrium composition. Increasing the water-to-oil ratio dilutes the aqueous phase without changing the atomic distribution. The results demonstrate that the optimum water-to-oil ratio is dependent on the nature of the pyrolysis oil feedstock.

2.1 Introduction

Pyrolysis liquid or pyrolysis oil contains a considerable amount of water, which is feedstock dependent: 15-30 wt% for wood [1,2], 39-51 wt% for straw and hay [3], and 28 wt% for rice husk [4]. Phase separation may take place when the addition of a certain amount of water directly to pyrolysis oil exceeds its maximum water content, which is typically in the range of 30-45 wt% [5]. The top aqueous phase is enriched in polar carbohydrate-derived compounds, while the bottom viscous oil phase is dominated by less polar lignin-derived chemicals [6].

It has been proven that the pyrolysis oil-derived aqueous phase is a good starting feed to isolate chemicals, such as levoglucosan, sugar compounds, and acetic acid.

Levoglucosan from pine-derived pyrolysis oil could be recovered in the aqueous phase prior to hydrolysis and fermentation to produce bio-ethanol [7,8]. Spruce-derived pyrolysis oil was extracted with water at 50 °C. Afterwards, sugar compounds were recovered from the aqueous phase by evaporation at 15 mmHg and 40 °C (Lindfors, Unpublished results).

Due to its high polarity, acetic acid can be collected in the aqueous phase, from which it is later extracted using tertiary amines. Water addition to forest residue-derived pyrolysis oil at a mass ratio of 1:1 and room temperature under vigorous stirring yielded an aqueous phase of 3.3 wt% acetic acid. The subsequent reactive extraction with 40 wt% tri-*n*-octylamine in 2-ethyl-1-hexanol could recover 86% acetic acid from the aqueous phase [9]. In comparison with direct extraction from pyrolysis oil with tri-*n*-octylamine, which yielded up to 92% acetic acid [10], the extraction of the aqueous phase is more beneficial due to negligible tri-*n*-octylamine loss to the aqueous raffinate [9].

Although water addition is commonly applied for pyrolysis oil characterisation [11-14] and is a potential initial step for producing renewable chemicals from biomass, there are so far only several rather broad researches done in this area. The optimisation of levoglucosan extraction with water was done by varying the total water content of Scots pine-derived pyrolysis oil and extraction temperatures. The optimum extraction yield (7.8 g levoglucosan/100 g pyrolysis oil) was obtained at 34 °C and a water-to-oil ratio of 0.5 [7]. The maximum levoglucosan concentration was about 5.1 wt%, which was also achieved in the later work [8]. Unfortunately, the levoglucosan content in pyrolysis oil feed was not analysed; thus, levoglucosan extraction performance cannot be determined. The focus in these works was on levoglucosan extraction; hence, information about other value-added chemicals was not available.

It is obvious that the co-extraction of other polar compounds takes place during water extraction. However, the distribution of polar and non-polar compounds has not yet been examined thoroughly. Therefore, the objective of this research is to investigate the effect of stirring rate and water-to-oil ratio on water content, the elemental composition of both

phases, and the water extraction performance of some components of interest: acetic acid, glycolaldehyde, acetol, furfural, furanone, levoglucosan, syringol, and guaiacol. Acetic acid, glycolaldehyde, and acetol are the most abundant valuable platform chemicals in wood-based pyrolysis oil with concentrations of 3-12 wt% [14,15], 5-13 wt%, and 1-7 wt% [16] on dry basis, respectively. Furfural, furanone, levoglucosan, syringol, and guaiacol were chosen to represent the other major functional groups in pyrolysis oil.

2.2 Methods

2.2.1 Materials

Forest residue- and pine-derived pyrolysis oils were kindly provided by VTT Technical Research Centre of Finland. These oils were produced by fast pyrolysis at 520 °C and a residence time of 1 s in the 20 kg/h VTT Process Development Unit. After delivery, both oils were stored in a freezer at -16 °C. Since the pyrolysis oil composition may change during storage, both pyrolysis oils were analysed for actual compositions before being used in the experiments. Acetone (≥ 99.5%), fluoranthene (98%), Hydranal Medium K, and Hydranal Composite 5K were purchased from Sigma-Aldrich. All chemicals were used as received. MiliQ water was used as solvent.

2.2.2 Experimental procedure

Extraction experiments were typically conducted in 50 mL erlenmeyer flasks for 24 h at 20 °C and 400 rpm, unless specified otherwise. Water-to-oil mass ratio was varied in the range of 0.3-0.8 and 0.4-0.9 for forest residue- and pine-derived pyrolysis oils, respectively. The minimum water-to-oil ratio was determined based on visual observation of phase separation. Subsequently, the mixture was allowed to settle for 2 h to ensure good phase separation. Both phases were then separated and weighed.

2.2.3 Analytical method

2.2.3.1 Water content determination using Karl-Fischer titration method

About 250 µL of an aqueous sample was diluted with 2.5 mL acetone. The analysis was done in Metrohm 795 KFT Titrino with Hydranal Composite 5K and Hydranal Medium K as reagent and solvent, respectively. The accuracy of the measurement was determined to be within 1%. A mass balance was used to calculate the water content of the respective organic phase.

2.2.3.2 Elemental analysis

The CHN analysis of the organic phase was performed using ThermoQuest EA 1112 elemental analyser. The O content was calculated by difference using an assumption that pyrolysis oil contains only C, H, O, and N. The CHON content of the corresponding aqueous phase was calculated using a simple mass balance.

2.2.3.3 GC analysis

About 48 mg of an organic sample was diluted in 1 mL internal standard solution of 200 µg/mL fluoranthene in acetone. The analysis was performed in a Varian CP 3900, equipped with an FID detector and a capillary column VF-1701ms (60 m × 0.25 mm; 0.25 µm). Helium flow was set to be 2 mL/min. The injector temperature was 250 °C with an injection volume of 1 µL [17]. The split ratio was 15. The detector operated at 280 °C while the initial oven temperature was maintained at 45 °C for 4 min and then ramped at 3 °C/min to 280 °C, which was held for 20 min. The measurement accuracy was determined to be within 3%. Aqueous phase compositions were calculated using a simple mass balance.

2.2.4 Definitions

Extraction capability is denoted as distribution coefficient and yield. The distribution coefficient of a particular component (D_i) is defined as the ratio of the equilibrium mass fraction of that component in the aqueous extract phase ($x_{i,aq}$) and its equilibrium mass fraction in the organic raffinate phase ($x_{i,org}$).

$$D_i = \frac{x_{i,aq}}{x_{i,org}} \tag{2.1}$$

The extraction yield of a certain compound (Y_i) is calculated by dividing the mass of that compound in the aqueous phase ($m_{i,aq}$) at equilibrium with its initial mass in the feed ($m_{i,f}$).

$$Y_i = \frac{m_{i,aq}}{m_{i,f}} \tag{2.2}$$

2.3 Results and discussion

2.3.1 Pyrolysis oil composition

In this research, forest residue- and pine-derived pyrolysis oils have approximately the same elemental compositions and water contents, as shown in Table 2.1

Table 2.1: Composition of forest residue- and pine-derived pyrolysis oils

	Forest residue-derived pyrolysis oil	Pine-derived pyrolysis oil
Elemental analysis		
Carbon (wt%)	40.6	41.3
Hydrogen (wt%)	7.7	7.6
Nitrogen (wt%)	0.4	0.2
Oxygen (wt%)	51.2	50.9
Composition		
Water (wt%)	25.6	24.9
Glycolaldehyde (wt%)	6.2	13.6
Acetic acid (wt%)	6.2	4.6
Acetol (wt%)	4.0	5.0
Furfural (wt%)	0.7	0.5
Furanone (wt%)	0.7	0.8
Levoglucosan (wt%)	1.7	1.6
Syringol (wt%)	0.3	0.1
Guaiacol (wt%)	0.2	0.6

The water content of pine-derived pyrolysis oil is slightly higher than that previously reported by VTT, which was 23.9 wt% [3]. In comparison with forest residue-derived pyrolysis oil, pine-derived pyrolysis oil contains more than twice as much glycolaldehyde with about 25% lower acetic acid content. Both oils contain approximately the same amount of levoglucosan. Regarding the phenolic compounds, forest residue-derived pyrolysis oil is enriched with syringol, whereas guaiacol concentration is higher in pine-derived pyrolysis oil.

The organic phase from both oils is very viscous, black, and nearly solid. The aqueous extract from forest residue-derived pyrolysis oil is dark brown, whereas that from pine-derived pyrolysis oil is light brown. The brown colour is caused by dissolved lignin-derivatives [18,19]. Since lignin-derivatives are not in the scope of the study, they are not further discussed. However, it is important to note that the presence of lignin-derivatives may influence subsequent separation processes as well as product composition.

2.3.2 Effect of stirring rate

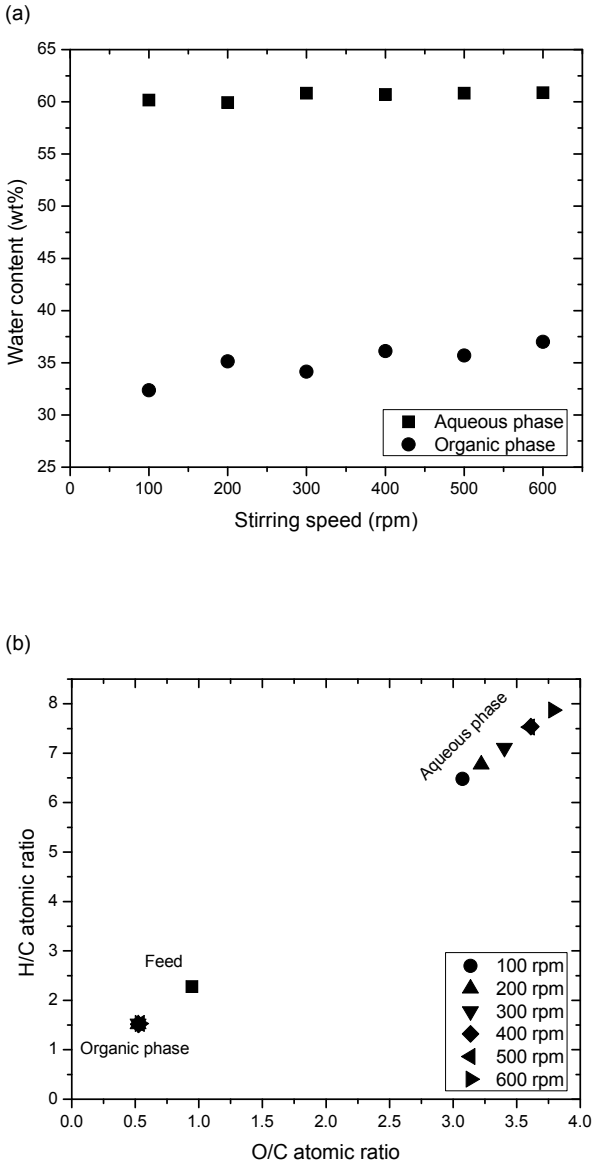

Figure 2.1: Water content of aqueous extract and organic raffinate (a) and two-dimensional van Krevelen diagram of the organic raffinate (b) at various stirring speed for forest residue-derived pyrolysis oil

In order to study the influence of stirring rate, experiments were done using forest residue-derived pyrolysis oil at a water-to-oil ratio of 0.65.

Figure 2.1a shows that water content in the aqueous phase is independent of the stirring speed, whereas that in the organic phases increases slightly with the stirring speed up to 300 rpm and afterwards tends to level off. This suggests that below 300 rpm the time needed to reach equilibrium is longer than 24 h, which was kept constant in the experiments. Apparently, the aqueous phase reaches saturation, which is revealed by the constant composition: 4.1 wt% glycolaldehyde, 4.1 wt% acetic acid, 2.7 wt% acetol, 0.3 wt% furfural, 0.4 wt% furanone, 1.2 wt% levoglucosan, 0.1 wt% syringol, and 0.1 wt% guaiacol. It is obvious from Figure 2.1b that the organic phase has lower oxygen and hydrogen contents than the feed due to the mass transfer. Both H/C and O/C atomic ratios of the organic phase hardly decrease with stirring rates, whereas those of the aqueous phase increase slightly up to a stirring speed of 300 rpm. This also indicates that below 300 rpm the equilibration time is longer than 24 h.

The stirring speed does not influence the order of the distribution coefficients: levoglucosan is the highest, followed by acetol, acetic acid, glycolaldehyde, furanone, furfural, syringol, and guaiacol (Figure 2.2a). The distribution coefficients of polar compounds (levoglucosan, acetol, acetic acid, and glycolaldehyde) decrease until 400 rpm before levelling off and always lay in the same range, which indicates poor extraction selectivity. The distribution coefficients of non-polar compounds increase slightly and become steady in the range of 300-400 rpm. The extraction yields of polar compounds decline with the stirring speed up to 400 rpm, whereas those of non-polar ones hardly change due to their low polarity (Figure 2.2b). Thus, extraction experiments should be performed at 400 rpm to ensure that equilibrium is reached within 24 h.

2.3.3 Effect of water-to-oil ratio

Upon water addition to pyrolysis oil, phase separation takes place as soon as the total water content reaches a maximum value, which depends on the nature of the pyrolysis oil. For example, the limit of some hardwood pyrolysis oils is above 30 wt%. Multi-phase formation may also occur at lower water contents due to imbalanced chemical substances, such as a lack of light water-soluble compounds and a concentrated lignin derivative fraction [2]. Due to polarity and solubility, polar compounds move to the aqueous phase while non-polar ones stay in the organic phase.

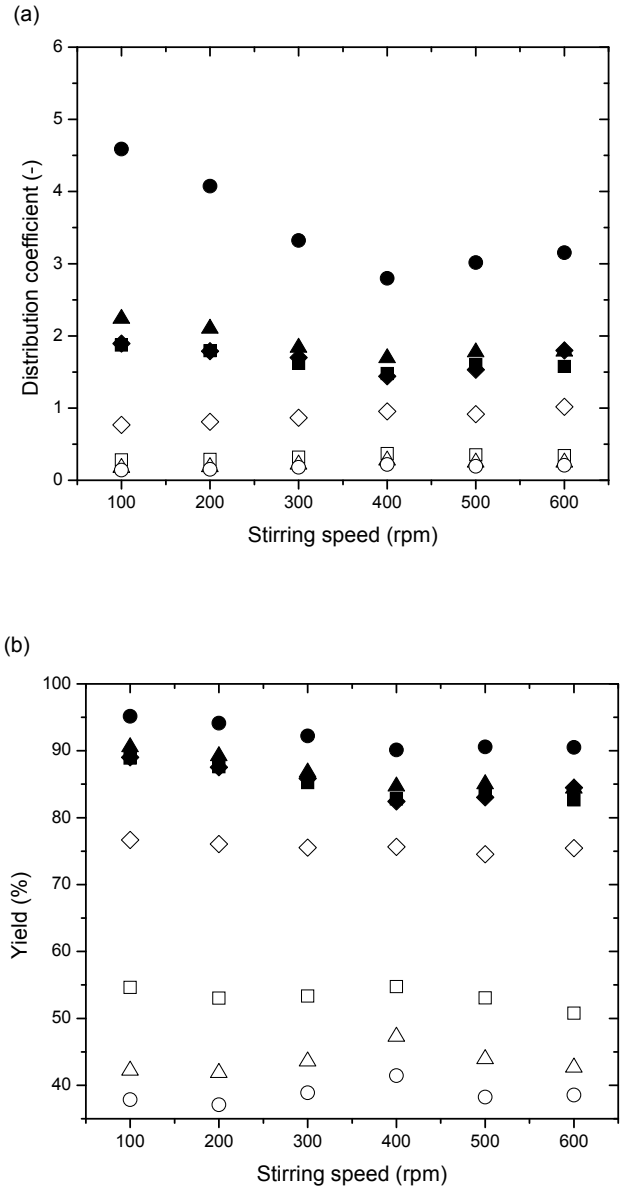

Figure 2.2: Effect of stirring rate on distribution coefficient (a) and extraction yield (b) of each component from forest residue-derived pyrolysis oil (♦: glycolaldehyde, ■: acetic acid, ▲: acetol, □: furfural, ◊: furanone, ●: levoglucosan, Δ: syringol, ○: guaiacol)

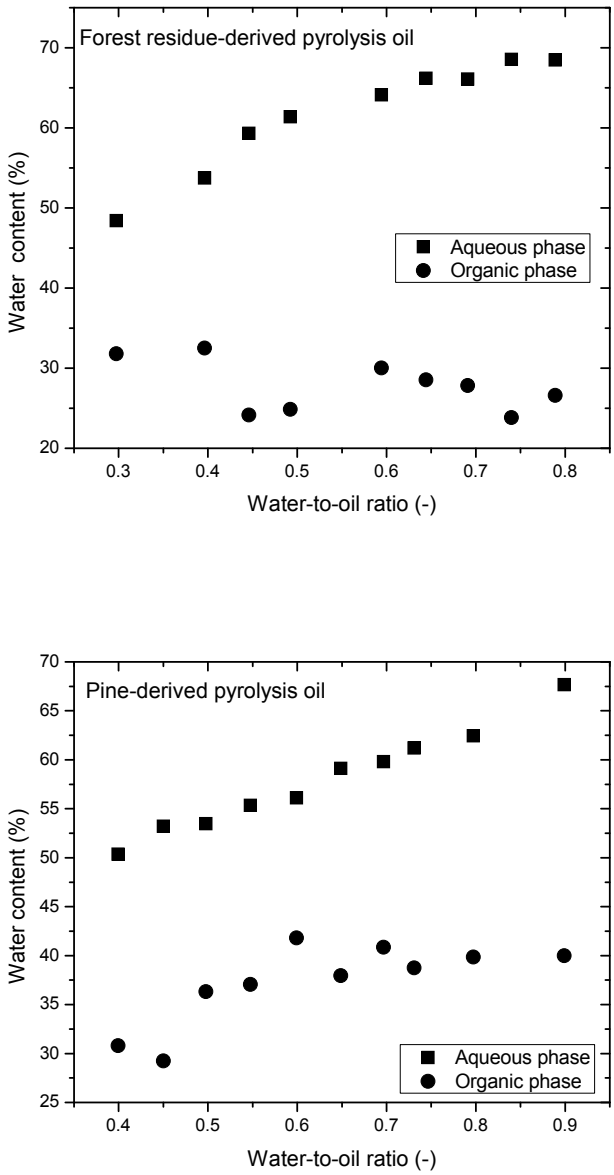

Figure 2.3: Water content of aqueous extract and organic raffinate from forest residue- and pine-derived pyrolysis oils

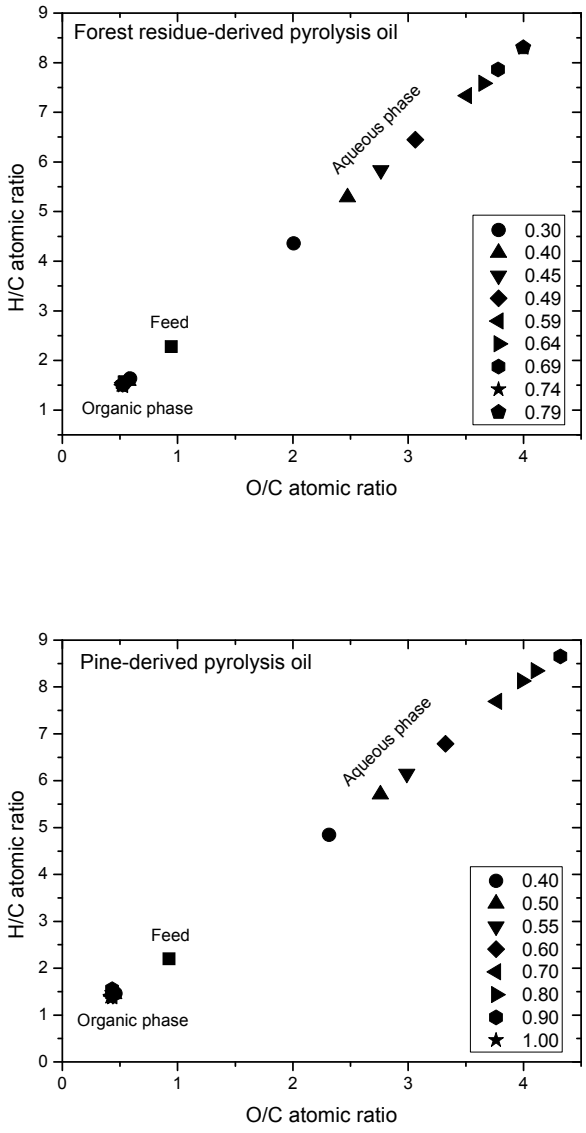

Figure 2.4: Two dimensional van Krevelen diagram of the organic phase from forest residue- and pine-derived pyrolysis oils at various stirring speed

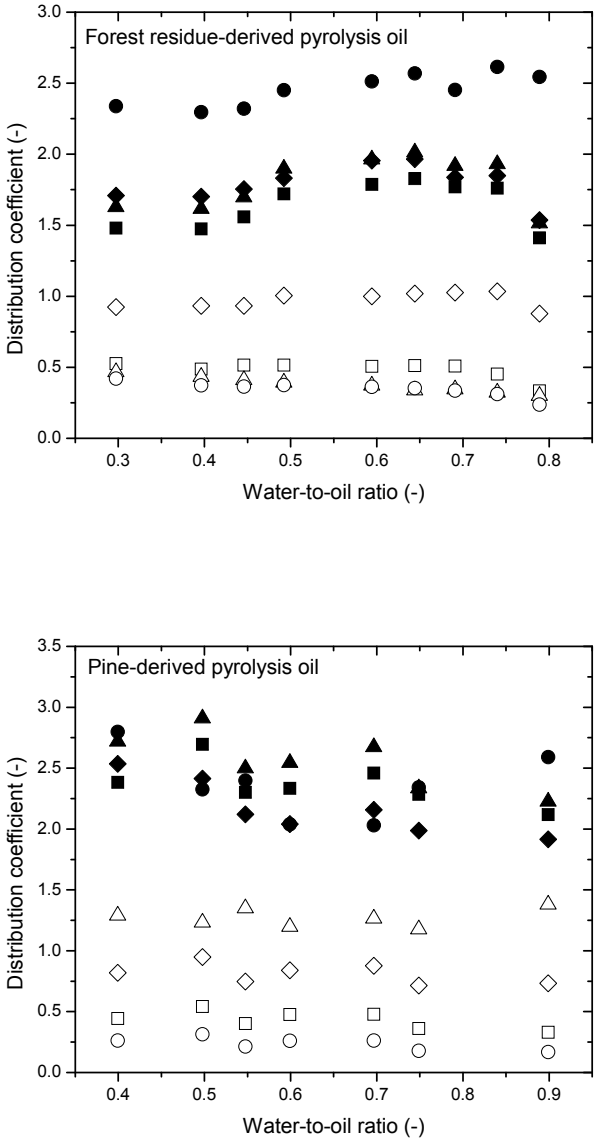

Figure 2.5: Effect of water-to-oil ratio on distribution coefficient of each component from forest residue- and pine-derived pyrolysis oils (♦: glycolaldehyde, ■: acetic acid, ▲: acetol, □: furfural, ◊: furanone, ●: levoglucosan, Δ: syringol, ○: guaiacol)

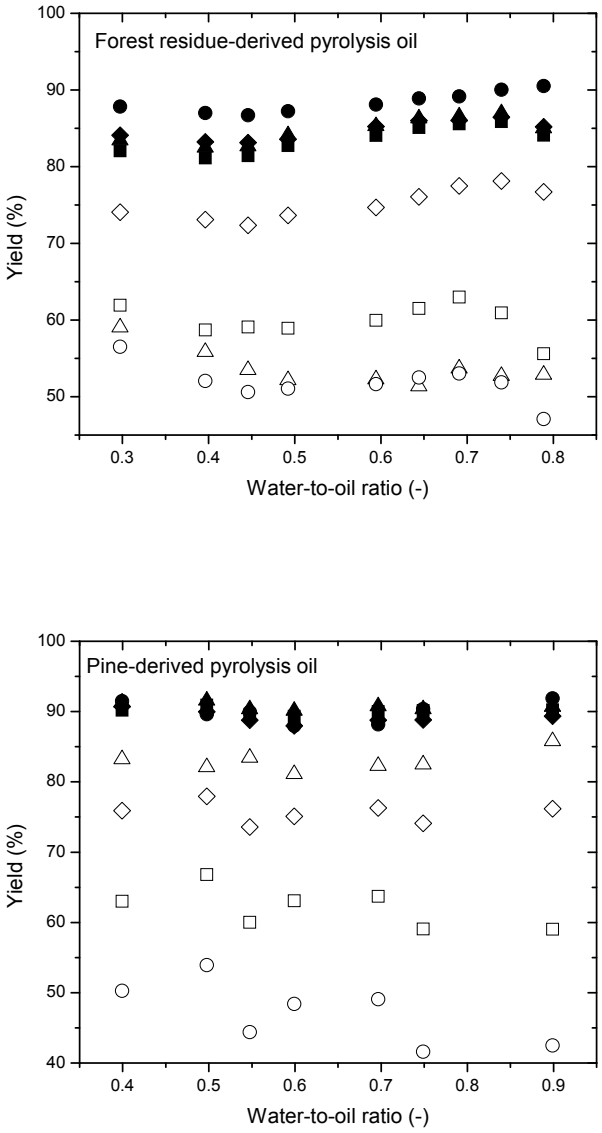

Figure 2.6: Effect of water-to-oil ratio on extraction yield of each component from forest residue- and pine-derived pyrolysis oils (♦: glycolaldehyde, ■: acetic acid, ▲: acetol, □: furfural, ◊: furanone, ●: levoglucosan, Δ: syringol, ○: guaiacol)

During extraction, some water moves along with the polar compounds to the aqueous phase. About 60% of the water in the forest residue-derived pyrolysis oil feed is extracted, independent of the water-to-oil ratio. Above a water-to-oil ratio of 0.5, the amount of organic phase hardly changes, leading to nearly constant water content in the organic phase and the dilution of the aqueous phase (Figure 2.3). For pine-derived pyrolysis oil, the amount of extracted water decreases with water-to-oil ratio from 70% to 40%. Aqueous phase dilution also occurs. However, the water content of the organic phase hardly changes above a water-to-oil ratio of 0.5. Hence, Figure 2.3 implies that there is a minimum water-to-oil ratio to achieve complete phase separation, which is 0.5 for both oils.

Water addition reduces considerably the hydrogen and oxygen content of both pyrolysis oil feeds. The H/C and O/C atomic ratios of the organic phase slightly decrease with water-to-oil ratio, whereas those of the aqueous phase increase proportionally due to water dilution (Figure 2.4). Therefore, the amount of added water hardly influences the elemental distribution of pyrolysis oil between the two phases.

For forest residue-derived pyrolysis oil, levoglucosan has the highest distribution coefficient, followed by acetol and glycolaldehyde with nearly equal distribution coefficients, acetic acid, furanone, and furfural. Syringol and guaiacol have approximately the same distribution coefficients, which are the lowest among the studied compounds (Figure 2.5). This distribution coefficient order can be explained using the Hansen solubility parameters given in Table 2.2.

Table 2.2: Hansen solubility parameters

Compound	Solubility parameter, δ ($MPa^{(1/2)}$)				Solubility parameter difference, $\Delta\delta$ ($MPa^{(1/2)}$)				Ra ($MPa^{(1/2)}$)
	δ_d	δ_p	δ_{hb}	δ_t	$\Delta\delta_d$	$\Delta\delta_p$	$\Delta\delta_{hb}$	$\Delta\delta_t$	
Water[a]	15.6	16.0	42.3	47.8	0.0	0.0	0.0	0.0	0.0
Glycolaldehyde[b]	16.5	11.7	14.9	25.1	0.9	4.3	27.4	22.7	27.8
Acetic acid[a]	14.5	8.0	13.5	21.4	1.1	8.0	28.8	26.5	30.0
Acetol[b]	16.6	10.5	13.4	23.8	1.0	5.5	28.8	24.0	29.4
Furfural[a]	18.6	14.9	5.1	24.4	37.7	3.0	1.1	37.2	37.7
Furanone[b]	17.1	8.5	9.1	21.1	1.5	7.5	33.2	26.7	34.1
Levoglucosan[b]	19.3	9.8	30.0	37.0	3.7	6.2	12.3	10.9	15.7
Syringol[b]	19.8	10.4	12.9	25.8	4.2	5.6	29.4	22.0	31.1
Guaiacol[b]	19.1	9.3	12.5	24.6	3.5	6.7	29.8	23.2	31.3

[a] Experimental data [20]

[b] Estimated using Stefanis and Panayiotou's group-contribution method [21]

The targeted compounds dissolve in water mostly because of dispersion (δ_d) and polarity (δ_p). Unlike the others, there is a weak hydrogen bond interaction between levoglucosan and water, which results in a higher aqueous concentration and higher distribution coefficient. Glycolaldehyde, acetic acid, and acetol, with similar molecular structures, diffuse almost equally in water. However, due to a smaller polarity difference with water ($\Delta\delta_p$), glycolaldehyde and acetol have higher distribution coefficients than acetic acid. Without considering the hydrogen bond contribution, the total solubility parameter (δ_t) of furanone is higher than that of furfural. It clarifies the higher distribution coefficient of furanone compared to furfural. Syringol and guaiacol, which have the least affinity to water, disperse slightly in the aqueous phase.

Raising the water-to-oil ratio from 0.3 to 0.4 hardly changes the distribution coefficients. In this region, complete phase separation cannot be achieved within 3 h. The aqueous extract is contaminated with small oil droplets. Above a water-to-oil ratio of 0.4, water dilution reduces the aqueous concentrations and increases the relative polarity of the aqueous phase. As a result, the aqueous phase affinity for non-polar compounds decreases and that for polar compounds increases. Thus, the distribution coefficients of the polar compounds increase. Nevertheless, when water dilution is dominating, the distribution coefficients decrease. Hence, there is an optimum distribution coefficient for each polar compound, as shown in Figure 2.5.

Unlike forest residue-derived pyrolysis oil, the water content of the organic phase of pine-derived pyrolysis oil increases with water-to-oil ratio (Figure 2.3), which raises the affinity for the polar components. This counteracts the dilution effect of the aqueous phase. Accordingly, the distribution coefficients of polar compounds tend to decrease with water-to-oil ratio (Figure 2.5).

Although syringol is less polar than furfural and furanone, it has higher a distribution coefficient due to its low initial concentration. Furthermore, comparing forest residue- and pine-derived pyrolysis oils in Figure 2.5, one can notice that the order of the distribution coefficients is not only dependent on the polarity and solubility in water, but also on the pyrolysis oil composition.

Figure 2.6 depicts the extraction yield profiles of forest residue-derived pyrolysis oil, which look similar to the distribution coefficient profiles illustrated in Figure 2.5. However, the maximum values are not achieved at the same water-to-oil ratio. For example, the maximum yields of glycolaldehyde, acetol, and acetic acid are obtained in the range of 0.7-0.75. For pine-derived pyrolysis oil, the extraction yields of levoglucosan, glycolaldehyde, acetic acid, and acetol are around 90% and nearly independent of the water-to-oil ratio (Figure 2.6). The extraction yield of syringol tends to increase with water-to-oil ratio, especially at a higher water-to-oil ratio. Water-to-oil ratio hardly influences furanone yield. In contrary with those of the other compounds, the extraction yields of furfural and guaiacol decline with the water-to-oil ratio.

Figure 2.5 and Figure 2.6 demonstrates that water extraction is a good method to recover 80-90% of the targeted polar compounds from pyrolysis oil. However, it is not selective due to the relatively pronounced co-extraction of non-polar compounds and the competition among polar compounds. In addition, water dilution reduces the aqueous concentrations. This phenomenon was also observed in levoglucosan extraction from Scots Pine-derived pyrolysis oil [22]. To get optimum separation of polar compounds from forest residue-derived pyrolysis oil, the extraction should be conducted at a water-to-oil ratio between 0.65-0.7. For pine-derived pyrolysis oil, it is advisable to use the lowest water-to-oil ratio where complete phase separation takes place, which is 0.5 in this case.

The aqueous phase obtained from water extraction of pyrolysis oil contains mostly polar compounds at relatively low concentrations (below 12%). This mixture can then be extracted with selective organic solvents to recover particular platform chemicals, such as acetic acid [9,10], furfuraldehyde, glycolaldehyde, and acetol [23]. The organic raffinate can further be extracted to recover phenolic compounds, which are later applied in plywood and particle board [23,24].

In general, the results give a clear picture about the distribution of polar and non-polar compounds in both phases. The distribution coefficient and yield profiles for each interested compounds provide useful data to design not only the water extraction process, but also subsequent extraction steps in a biorefinery system.

2.4 Conclusions

The stirring rate determines the time to reach equilibrium, but does not influence the equilibrium composition. The extent of water addition corresponds to water dilution. The elemental distributions of pyrolysis oil in both phases are independent of water-to-oil ratio. The distribution coefficient and extraction yield of a compound are determined by its polarity and solubility, water-to-oil ratio, and the nature of the pyrolysis oil. Water extraction is not a selective method, but very useful to recover 80-90% polar compounds and to reduce the complexity of pyrolysis oil prior to further isolation steps.

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3 Reactive extraction of glycolaldehyde from pyrolysis oil-derived aqueous phase

Glycolaldehyde can be separated from a pyrolysis oil-derived aqueous phase by reactive extraction employing primary amines dissolved in organic diluents. This chapter presents the solvent screening based on extraction performance, the occurrence of solid imine formation, and the competitive reactions in the organic extract phase. The results show that the extraction performance decreases in the following order: octylamine > 4-ethylaniline > phenylethylamine >> Primene JM-T > 2-ethylaniline. It is also demonstrated that no solid formation was observed for Primene JM-T/1-octanol, Primene JM-T/n-hexane, and 2-ethylaniline/1-octanol. ^{1}*H NMR spectra reveal that only Schiff-base formation takes place in the organic phase. Based on the investigation, an antisolvent-induced regeneration method is proposed.*

3.1 Introduction

Water extraction is the first step to isolate polar compounds from pyrolysis oil in an aqueous phase. It is capable to recover about 80% glycolaldehyde in the aqueous phase in a single stage at the optimum water-to-oil ratio, which depends on the nature of pyrolysis oil. Since water is not selective, the co-extraction of the other polar compounds also takes place, which leads to a multi-component aqueous mixture [1].

Reactive extraction has been identified as a promising technology to separate glycolaldehyde from the other polar compounds, considering the complexity of the aqueous mixture, a rather low glycolaldehyde concentration (4-6.2 wt%) [2,3], and small boiling point differences. It is also expected to be selective towards glycolaldehyde with a high extraction yield [4].

The reactive extraction of glycolaldehyde from an aqueous phase with primary amines refers to that of aldehydes [5-7]. Glycolaldehyde transfers from the aqueous phase to the organic phase where it reacts with primary amines to imine and water according to the Schiff-base formation depicted in Figure 3.1.

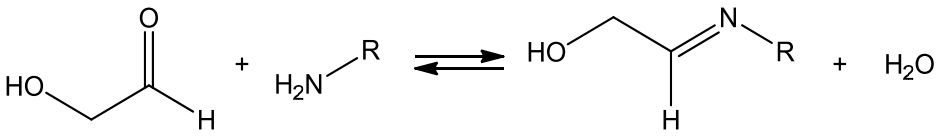

Figure 3.1: Reaction between glycolaldehyde and primary amines in the organic phase. R is either an alkyl or aryl group.

Like aldehydes, glycolaldehyde may subsequently be regenerated by hydrolysing the imine, exploiting the reversibility of the Schiff-base formation [8,9]. Thus, the objective of this study is to identify a suitable solvent to extract glycolaldehyde from an aqueous phase.

A primary amine extractant has to fulfil several requirements: adequate density difference, low viscosity, favourable interfacial tension, sufficiently fast complex formation kinetics, economically feasible, and environmentally benign [4]. In addition, it has to be non-polar to avoid extractant loss. Similar to primary amine extractants, a diluent has also to fulfil the above mentioned criteria. Furthermore, it should be able to dissolve the imine formed during the extraction.

Primene JM-T and octylamine (Figure 3.2) have been identified to be potential extractants for aldehydes. Primene JM-T could extract aliphatic and aromatic aldehydes [6], while octylamine was able to extract vanillin from an aqueous solution [7]. In addition, aniline derivatives (Figure 3.2) may be also applicable as extractant.

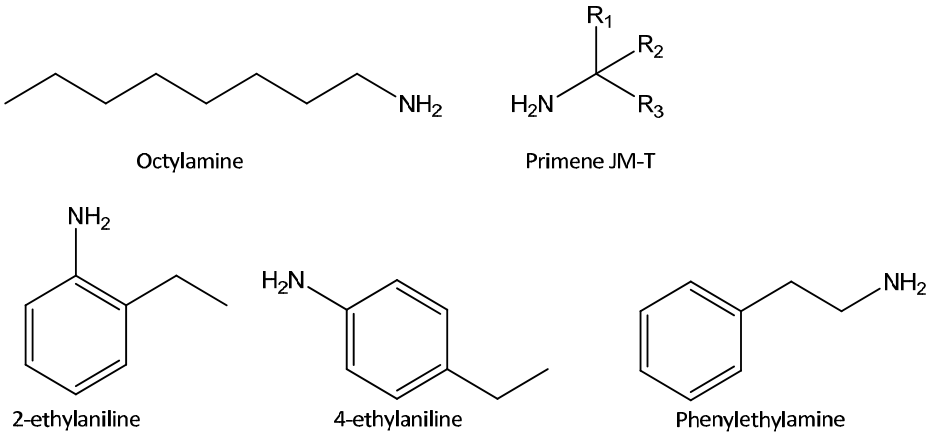

Figure 3.2: Molecular structure of several primary amine extractants. Primene JM-T is a commercial mixture of primary amines whose amino group is attached to a tertiary atom carbon. R_1, R_2, and R_3 are C16-22 highly branched alkyl groups.

This chapter presents the solvent screening for glycolaldehyde extraction from an aqueous phase. This screening involves several investigations:

- Diluent evaluation based on the extraction capability
- Comparison of the extraction performance of several primary amine/diluent mixtures
- Observation of solid imine formation, which commonly takes place in imine synthesis from pure primary amines and aldehydes [10-13]
- Identification of side reaction products based on ^{1}H NMR analysis

Like regular aldimines, glycolaldehyde-derived imines may undergo several reactions, such as *E/Z* isomerisation [14,15], imine-enamine tautomerisation [9,14], and oligomerisation [9,11,14-18], as illustrated in Figure 3.3. In addition, glycolaldehyde-derived imines could also form covalent cross-links with excess primary amines via Amadori rearrangement and aldoamine formation (Figure 3.4). The Amadori rearrangement occurs due to the presence of the α-hydroxyl group in the glycolaldehyde-derived imine [19,20]. These reactions may lead to the formation of new stable compounds, and as a consequence of this fact glycolaldehyde recuperation would be inhibited.

For the sake of comparison with regular aldehydes, possible reactions involved in the reactive extraction of benzaldehyde are also discussed.

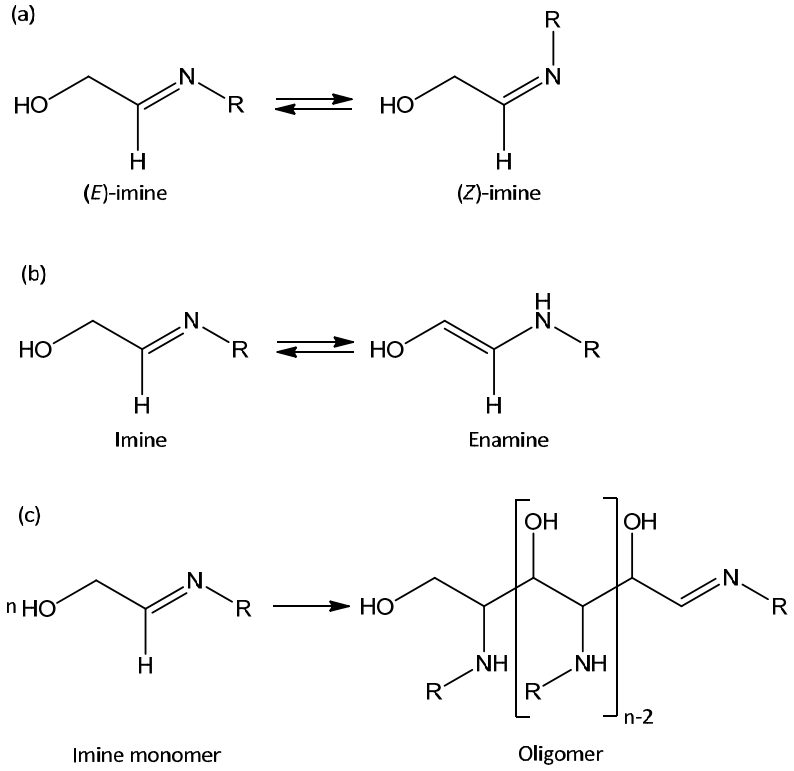

Figure 3.3: (*E/Z*) isomerisation (a), imine-enamine tautomerisation (b), aldol condensation to form oligomers (c) of glycolaldehyde-derived imines

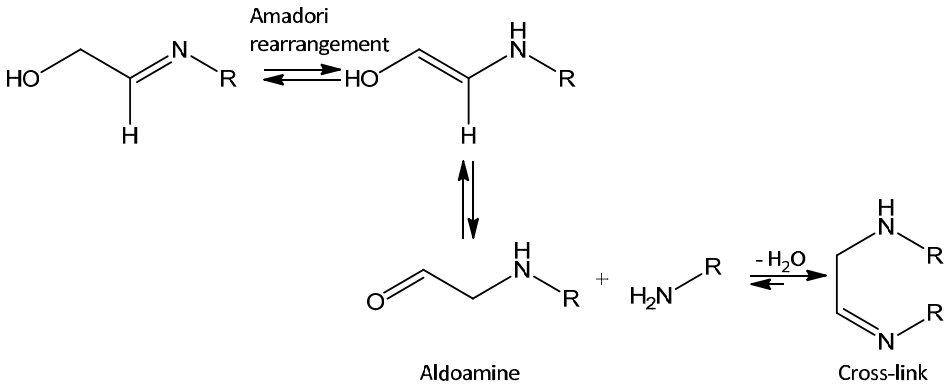

Figure 3.4: Cross-link formation from glycolaldehyde-derived imines via Amadori rearrangement

3.2 Experimental

3.2.1 Materials

Benzaldehyde (≥ 99%), glycolaldehyde (dimer, crystalline, a mixture of stereoisomers), *n*-hexane (≥ 99%), 1-octanol (> 99%), dodecane (≥ 98%), 1-decanol (≥ 98%), octylamine (99%), dibenzofuran (> 99%), and chloroform-d (100%, 99.96 atom% D) were purchased from Sigma-Aldrich. Phenylethylamine (99%), 2-ethylaniline (98%), and 4-ethylaniline (≥ 99%) were obtained from Acros Organic. Primene JM-T was kindly provided by Rohm and Haas, while ethanol (≥ 99.5%) was supplied by Merck Chemicals. All chemicals were used as received. MiliQ water was used to prepare aqueous mixtures.

3.2.2 Experimental procedure

Extraction experiments were conducted in 50 mL erlenmeyer flasks equipped with magnetic stirring bars at 20 °C and 200 rpm for 150 min for glycolaldehyde and 24 h for benzaldehyde [6], which were proven to be sufficient to reach equilibrium. The feed concentrations were 6.2 wt% and 0.5 wt% for glycolaldehyde and benzaldehyde, respectively. The extractant concentration was varied between 0.5-3.1 M [6]. The solvent-to-feed ratios were 2 for glycolaldehyde and 0.5 for benzaldehyde, unless specified otherwise. Subsequently, the mixtures were allowed to settle for at least 2 h to achieve a good phase separation.

3.2.3 Analysis

Aldehyde concentration in both phases was determined using gas chromatography (GC). In a GC vial, 350 µL sample was diluted with 1300 µL ethanol and 125 µL internal standard solution (0.025 M dibenzofuran in ethanol). The quantitative analysis was conducted in Varian CP 3900 equipped with an FID detector and a capillary column CP-Wax 52CB (50 m × 0.32 mm; 1.2 µm). The detector and injector temperatures were 280 °C and 250 °C, respectively. The oven temperature was kept at 30 °C for 30 s before ramped at 30 °C/min to 250 °C, which was maintained for 10 min. The helium flow rate was kept constant at 2 mL/min. The accuracy of the analysis was determined to be within 3%.

^{1}H NMR spectroscopy was used to identify reaction products in the organic phase. A few drops of the organic phase were diluted with about 700 µL chloroform-d and afterwards analysed in Varian Mercury 200 MHz NMR Spectrometer.

3.2.4 Definitions

Extraction performance is characterised by the distribution coefficient and extraction yield. The glycolaldehyde distribution coefficient (*D*) is defined as the ratio between the total mass fraction of glycolaldehyde in the organic phase and the mass fraction of glycolaldehyde in the aqueous phase (x_{aq}) at equilibrium. The total mass fraction of glycolaldehyde is the summation of the mass fraction of free glycolaldehyde (x_{org}) and the mass fraction of glycolaldehyde as imine (x_{imine}).

$$D = \frac{x_{org}+x_{imine}}{x_{aq}} \tag{3.1}$$

The glycolaldehyde extraction yield (*Y*) is the total mass of glycolaldehyde in the organic phase at equilibrium divided by the mass of glycolaldehyde in the feed (m_f). The total mass of glycolaldehyde is the total of mass of the free glycolaldehyde (m_{org}) and that of glycolaldehyde as imine (m_{imine}).

$$Y = \frac{m_{org}+m_{imine}}{m_f} \tag{3.2}$$

3.3 Results and discussion

Glycolaldehyde is the simplest α-hydroxyaldehyde, as well as the smallest aldose [21]. It dissolves in water as a mixture of monomers and dimers [22-25]. Thus, all forms of glycolaldehyde in an aqueous solution were considered as a single compound in this research.

3.3.1 Diluent screening

In addition to the previously mentioned criteria, a diluent has to be water insoluble with an ability to dissolve primary amines. It should also (slightly) dissolve glycolaldehyde to facilitate the Schiff base formation in the organic phase. Based on these requirements, several long chain alkanes and alcohols have been investigated.

Table 3.1 shows that alcohols extract more glycolaldehyde than alkanes. Although medium chain alcohols are relatively non-polar, their hydroxyl groups interact with glycolaldehyde through hydrogen bonds. This interaction enhances the solubility of glycolaldehyde in the organic phase. The extractability of long chain alkanes and alcohols decreases with the chain length, which corresponds to the decrease in polarity and mutual

solubility with water. Hence, medium chain alcohols are better diluent candidates compared to alkanes. However, the co-extraction of other polar chemicals may occur as well.

Table 3.1: Distribution coefficient and extraction factor of glycolaldehyde in the organic phase

Diluent	Distribution coefficient (-)	Yield (%)
n-hexane	0.0041	3.9
Dodecane	0.0000	0.0
1-octanol	0.2341	31.5
1-decanol	0.0503	8.8
Oleyl alcohol	0.0403	7.9

3.3.2 Effect of solvent-to-feed ratio

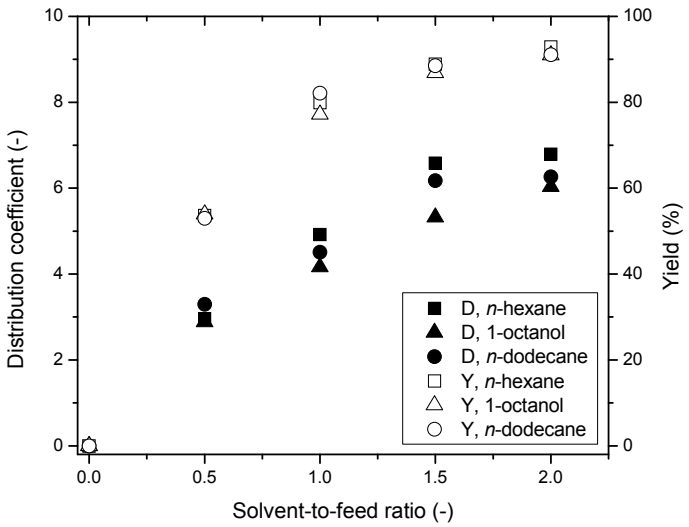

Figure 3.5: Distribution coefficient and yield of glycolaldehyde in 2 M Primene JM-T

Analogous to the diluent, a primary amine extractant has to be soluble in the diluent but insoluble in water. An extraction experiment using 2 M octylamine dissolved in *n*-hexane and dodecane demonstrates that all glycolaldehyde is extracted from the aqueous phase at solvent-to-feed ratios of 0.5-2. This leads to infinite distribution coefficients,

which indicate that the imine formation between glycolaldehyde and octylamine is practically irreversible.

Unlike linear aliphatic primary amines, branched fatty primary amines are more soluble in alkanes and alcohols and less reactive due to higher steric hindrance. Therefore, Primene JM-T was selected as an extractant to investigate the influence of the solvent-to-feed ratio on the reactive extraction capability.

Figure 3.5 depicts that all diluents give similar distribution coefficient profiles, implying that the reactive extraction is limited by extraction equilibrium. The distribution coefficient of glycolaldehyde increases with solvent-to-feed ratio, which indicates higher extraction capability. Above a solvent-to-feed ratio of 1.5 the distribution coefficient tends to level off. Although more glycolaldehyde is extracted, its mass fraction in the organic phase somewhat decreases due to the excess Primene JM-T. Figure 3.5 suggests that a solvent-to-feed ratio of 2 is sufficient to achieve a quite high distribution coefficient.

Similarly, the solvent-to-feed ratio has a positive influence on the extraction yield. Excess Primene JM-T is required to considerably enhance the glycolaldehyde extraction up to a solvent-to-feed ratio around one. Afterwards, the extraction yield increases to a less extent to about 90% at a solvent-to-feed ratio of two. This trend could also explain the levelling off tendency of the distribution coefficient.

Furthermore, Figure 3.5 depicts that the extraction yields are in the same order of magnitude for all Primene JM-T mixtures. Hence, the extraction ability of Primene JM-T in a diluent is somewhat independent of the type of diluent.

3.3.3 Effect of initial extractant concentration

Figure 3.6 depicts the dependency of glycolaldehyde distribution coefficient and yield on the initial amount of amine in the organic phase. From Figure 3.6a one can see that Primene JM-T/1-octanol provides higher glycolaldehyde distribution coefficients than Primene JM-T/*n*-hexane. This trend is in accordance with the fact that glycolaldehyde is more soluble in 1-octanol than in *n*-hexane (Table 3.1). When the initial Primene JM-T concentration exceeds 1.5 M (about 50-54 wt% amine, depending on the diluent), the glycolaldehyde distribution coefficients increase remarkably. This tendency indicates that excess amine is required to significantly improve the distribution coefficient. Increasing initial amine concentration at the same solvent-to-feed ratio shifts the equilibrium towards imine formation. In addition, the domination of amine in the organic phase enhances the solubility of glycolaldehyde since glycolaldehyde can form hydrogen bonds with the nitrogen atom of Primene JM-T. This solubility enhancement effect is particularly seen in case of Primene JM-T/*n*-hexane. As a result, the type of diluent has a minor influence on the glycolaldehyde distribution coefficient for Primene JM-T above 1.5 M.

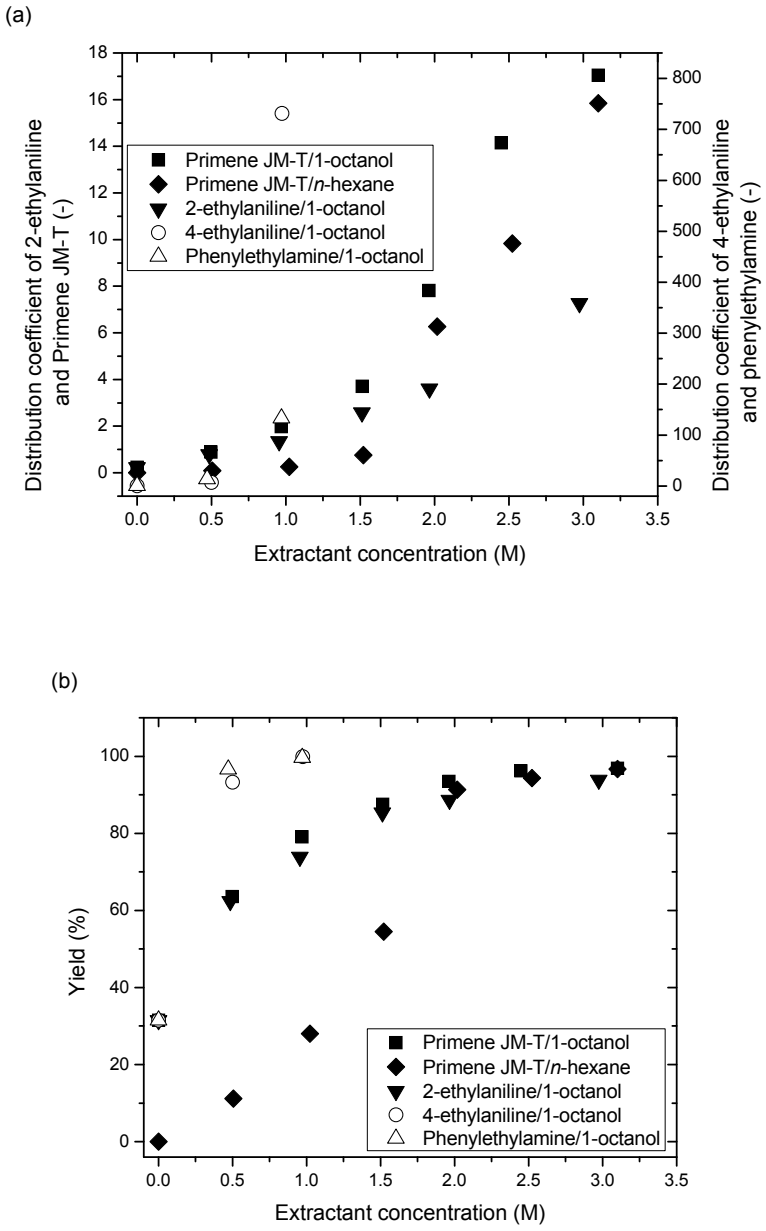

Figure 3.6: Distribution coefficient (a) and extraction yield (b) for glycolaldehyde extraction from the aqueous phase at various initial extractant concentrations

Figure 3.6a also depicts that Primene JM-T/1-octanol provides higher glycolaldehyde distribution coefficients than 2-ethylaniline/1-octanol. Glycolaldehyde has a higher affinity towards Primene JM-T since both can form hydrogen bond, in addition to the Schiff-base formation. These results are in agreement with those of Simion *et al.* [13] which reported that aliphatic amines have a higher capability in imine formation than aromatic amines. Figure 3.6b illustrates that the extraction yield also increases with the initial amine concentration, which is in accordance with the improvement in the distribution coefficient. Primene JM-T provides a higher yield compared to 2-ethylaniline in the same diluent as it is more reactive than 2-ethylaniline, which has a lack of hydrogen bond capability due to the conjugation of the amine group into the aromatic ring [26]. Below a concentration of 2 M, amine addition enhances the extraction capacity due to the Schiff base formation. Above 2 M both Schiff-base formation and solubility enhancement contribute to the reactive extraction. As a result, all extractant/diluent combinations give similar glycolaldehyde extraction yields. Increasing the initial amine concentration from 2 M to 3.1 M hardly changes the extraction yield since more than 93% of the glycolaldehyde is already extracted and the organic phase is somewhat saturated with the corresponding imine.

Unlike 2-ethylaniline, 4-ethylaniline and phenylethylamine extract more glycolaldehyde at the same amine concentration. In comparison with Primene JM-T at a concentration of 1 M, 4-ethylaniline and phenylethylamine give more than two orders of magnitude and 65 times higher distribution coefficients, respectively. Apparently the lack of hydrogen bonding capability is compensated by the linear structure of the amines, which means less steric hindrance. As a result, 2-ethylaniline provides more than two orders of magnitude lower distribution coefficient than its para isomer. With respect of the amine miscibility in 1-octanol, phenylethylamine has the lowest solubility of about 1 M, whereas the other amines can be dissolved up to 3 M in this study.

The high distribution coefficients denote that 4-ethylaniline and phenylethylamine are able to extract nearly all glycolaldehyde from the aqueous phase (Figure 3.6b). Similar to linear aliphatic amines, phenylalkylamines and para-alkylanilines are not recommended to be used as extractant because of the practically irreversible Schiff-base formation. Thus, only Primene JM-T and 2-ethylaniline are further studied. The fact that 2-ethylaniline gives lower distribution coefficients as well as extraction yields than Primene JM-T shows that hydrogen bond formation is more dominating than the steric hindrance effect.

3.3.4 Types of diluents and solid imine formation

Table 3.2 shows that the extractant/diluent combination determines whether solid imine is formed as the third phase at the interface between the aqueous raffinate and organic extract.

Table 3.2: Observed solid imine formation in the concentration range of 0.5-3.1 M extractant in a diluent

Extractant / diluent	dodecane	*n*-hexane	1-octanol
Primene JM-T	×	×	×
2-ethylaniline	✓	✓	×

The molecular structure of a glycolaldehyde-derived imine affects its solubility in a diluent. The presence of the hydroxyl group (Figure 3.7) enables the imines to dissolve in 1-octanol due to the hydrogen bond formation. (Primene JM-T)-2-hydroxyethanimine has highly branched hydrocarbon chains, which contribute to the non-polarity of the imine. As a result, it is soluble in *n*-hexane as well. On the other hand, (2-ethylphenyl)-2-hydroxyethanimine lacks long flexible hydrocarbon chains, which limits its solubility in alkanes.

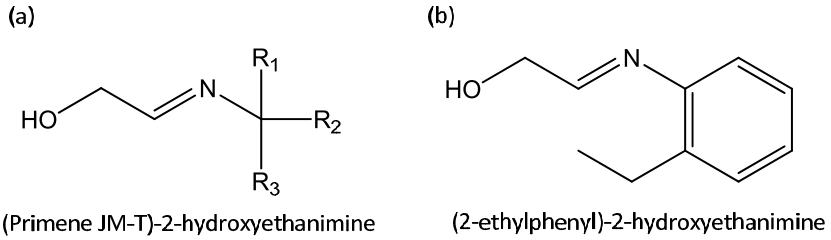

Figure 3.7: Imine structures formed from the reaction of glycolaldehyde with Primene JM-T (a) and 2-ethylaniline (b)

Therefore, to maintain the two-phase formation in glycolaldehyde extraction, 1-octanol is used as a diluent for both Primene JM-T and 2-ethylaniline while *n*-hexane and dodecane are only applied with Primene JM-T.

3.3.5 Competitive reactions in the organic phase

The reactive extraction of glycolaldehyde and benzaldehyde are compared in this section. The ^{1}H NMR spectra of the same extractant/diluent combination are identical within

the studied concentration range (0.5-3.1 M); hence, only representative spectra are shown. Most ^{1}H NMR signals have rather low intensity and resolution, except those of amines and diluents, due to their low concentrations. As a consequence, some signals appear as singlets, which made it difficult to determine the peak splits and integrate them accurately. Therefore, the spectra interpretation is mainly done based on the chemical shifts of a specific functional group.

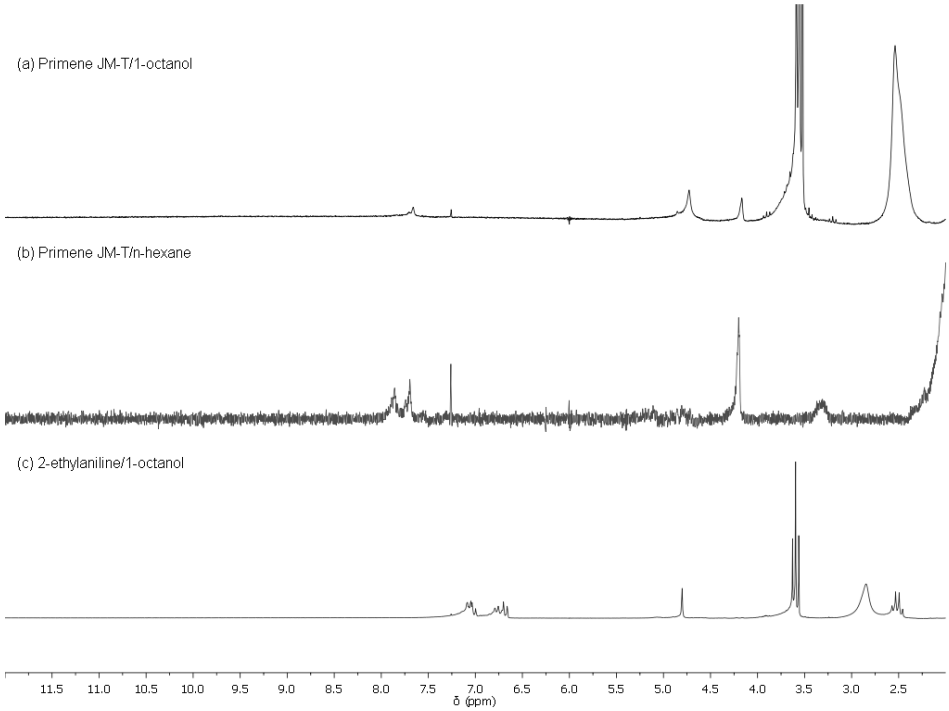

Figure 3.8: ^{1}H NMR spectra of the organic phase of glycolaldehyde extraction with various solvents

Figure 3.8 shows the absence of the aldehyde group (CHO) signal δ 10 in all solvents which confirms that all dissolved glycolaldehyde in the organic phase reacted completely with the amines into the corresponding imines.

The existence of imines is shown by the aldimine (CH=N) signals δ 7.7-7.9 for Primene JM-T (Figure 3.8a and b) and δ 6.95-7.2 for 2-ethylaniline (Figure 3.8c).

Furthermore, the enamine (Figure 3.3b) is not present in the organic phase, which is confirmed by the absence of the carbon-carbon double bond (C=C) signals δ 5.8-5.9. Although imine-enamine tautomerisation may happen in the presence of primary amines, the absence of the enamine signal is most probably caused by the low enamine concentration or the strong equilibrium shift to the imine [27].

The formation of oligomers (in this case dimer and trimer) does not take place in the organic phase, which is justified by the absence of the hydroxyl signal of the dimer δ 6.0 and multiple hydroxyl signals of the trimer δ 3.0-3.5. Apparently the high steric hindrance prevents aldol condensation to form oligomers [9].

The signals δ 4.2 (CH_2-OH) and δ 4.7 (H-CH_2) in Figure 3.8a reveal that both *E/Z* isomers (Figure 3.3a) of (Primene JM-T)-2-hydroxyethanimine could be present in the organic phase. In general, imines exist as (*E*) isomers, which are more stable than their corresponding (*Z*) isomers [28,29]. For Primene JM-T/*n*-hexane the other signal δ 4.7 (H-CH_2) is not visible (Figure 3.8b) due to the low imine concentration. The dominating isomer of (2-ethylphenyl)-2-hydroxyethanimine cannot be determined based on the ^{1}H NMR spectra given in Figure 3.8c since both (*E*) and (*Z*) isomers provide two signals with almost the same chemical shifts.

The glycolaldehyde-derived imines (Figure 3.7) do not undergo further Amadori rearrangement to form cross-links (Figure 3.4), confirmed by the missing signals δ 7.0 (CH_2-NH). The high excess of amine in the organic phase (see also Section 3.3.3) may cause the organic phase to be too basic for Amadori rearrangement, which usually takes place optimally in a near neutral medium [19,30]. Because of the absence of the Amadori rearrangement, the subsequent covalent cross-linking does not happen either.

These results confirm that in the organic phase glycolaldehyde and the studied primary amines react into imines, which do not react further to form oligomers and cross-links. (*E/Z*) isomerisation could occur, but it does not cause the formation of a new molecule.

Unlike glycolaldehyde, there remains some free benzaldehyde in the organic phase at equilibrium, which is confirmed by the signal δ 10 (CHO) (Figure 3.9). The Schiff-base formation is proven by the signals δ 8.17 (CH=N) and δ 8.24 (CH=N) for Primene JM-T/*n*-hexane and δ 8.4 (CH=N) for 2-ethylaniline/*n*-hexane. For Primene JM-T, the two signals denote that both (*E*) and (*Z*) isomers exist in the organic phase. For 2-ethylaniline, the single imine signal indicates that it is not possible to determine which *E/Z* isomer presents in the organic phase.

Furthermore, oligomerisation cannot occur in benzaldehyde-derived imines since they have no ethylene group attached to the carbon-nitrogen double bond (Figure 3.10). Enamine is not formed in the organic phase due to the lack of α-hydrogen atom [27]. Amadori rearrangement does not take place either because the benzaldehyde-derived imines contain no hydroxyl group [14].

The above results confirm that in the studied range, both free benzaldehyde and its corresponding imine exist in the organic phase.

Overall, it can be concluded that the ^{1}H NMR spectra verify that only Schiff-base formation takes place in the organic phase for both glycolaldehyde and benzaldehyde. Thus, the imine is the only reaction product and the aldehyde regeneration by hydrolysis can be expected to be possible.

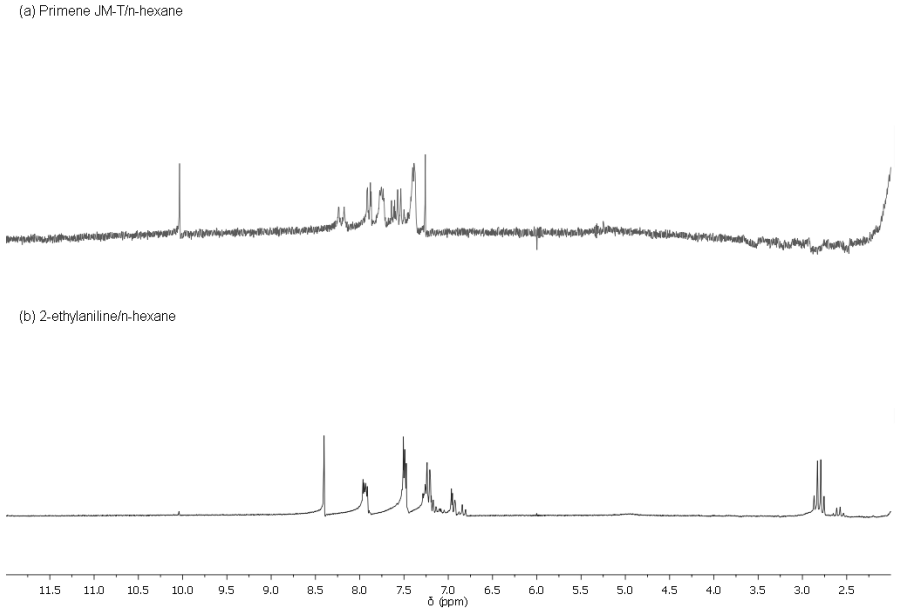

Figure 3.9: ^{1}H NMR spectra of the organic phase of benzaldehyde extraction with primary amines in *n*-hexane

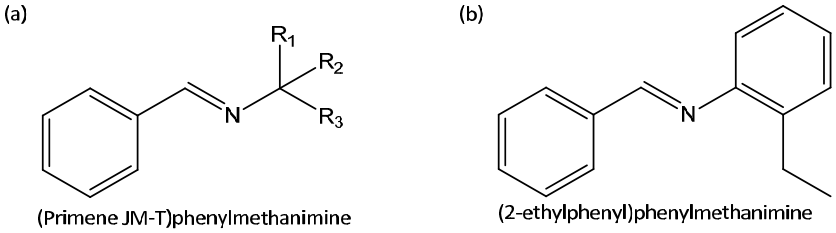

Figure 3.10: Benzaldehyde-derived imines from Primene JM-T (a) and 2-ethylaniline (b)

3.3.6 Glycolaldehyde regeneration from the imines

The discussed results confirm that Primene JM-T and 2-ethylaniline are promising candidates for isolating glycolaldehyde. The forward extraction is successful to provide high glycolaldehyde distribution coefficients and it extracts most of the glycolaldehyde from the aqueous phase (see also Figure 3.6).

It is expected that Primene JM-T and 2-ethylaniline in either 1-octanol or *n*-hexane have a similar performance in a real pyrolysis oil-derived aqueous mixture with high glycolaldehyde selectivity, especially towards acetol. From Figure 3.11 one can deduce that acetol is not extracted from a pyrolysis oil-derived aqueous phase with Primene JM-T, mostly because the Schiff-base formation from acetol requires a high temperature and a longer extraction time than glycolaldehyde [26].

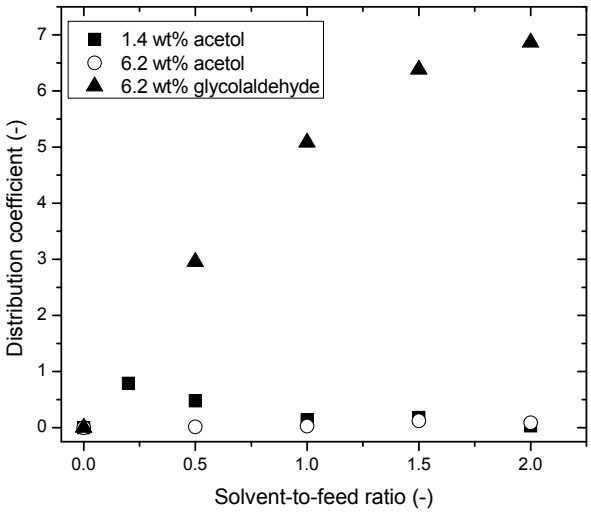

Figure 3.11: Distribution coefficients of glycolaldehyde and acetol in 2 M Primene JM-T/*n*-hexane at various feed concentrations

Imine hydrolysis should be possible considering the reversibility of imine formation. Furthermore, the presence of the hydroxyl group in the glycolaldehyde-derived imines (Figure 3.7) is expected to facilitate hydrolysis [26]. Nevertheless, the hydrolysis of glycolaldehyde-derived imines is challenging.

Figure 3.12 shows that the glycolaldehyde distribution coefficient in 2 M 2-ethylaniline/1-octanol is about doubled when the extraction temperature is increased from 20 °C to 75 °C. It can be expected that the trend will be similar for Primene JM-T as the temperature effect is solute dependent [6]. Hence, to apply temperature swing regeneration, the extraction needs to be performed at higher temperatures and the back-extraction has to be conducted at lower temperatures. To prove the temperature swing method, a 6.2 wt% glycolaldehyde model solution was extracted with 1 M 2-ethylaniline/1-octanol at 75 °C. Afterwards, the organic extract was back-extracted with

water at 20 °C and a solvent-to-feed ratio of 1 to 2. The obtainable aqueous solution contained 0.08-0.12 wt% glycolaldehyde with a glycolaldehyde regeneration yield of 4-6%. Thus, it appears that temperature swing alone is not a suitable method for glycolaldehyde regeneration.

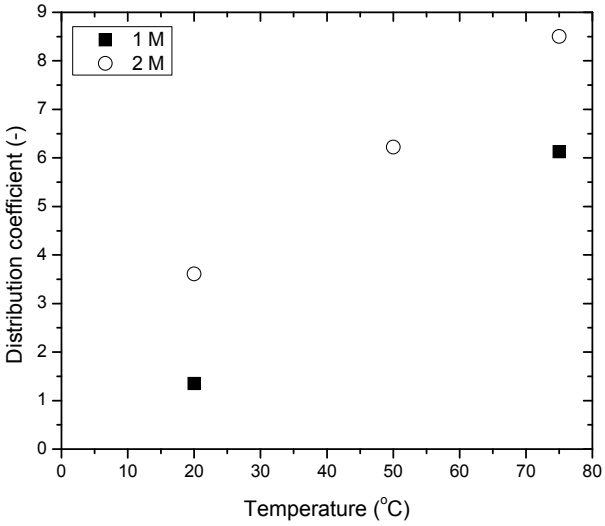

Figure 3.12: Temperature effect on the glycolaldehyde distribution coefficient for 1 M and 2 M 2-ethylaniline/1-octanol at a feed concentration of 6.2 wt% glycolaldehyde in water

Another investigated regeneration method was back-extraction with 10 mole% aqueous ethanol solution at 20 °C and a solvent-to-feed ratio of 1 to 2. This approach could regenerate about 9-14% glycolaldehyde from (Primene JM-T)-2-hydroxyethanimine and resulted in an aqueous concentration of 0.78-0.85 wt% glycolaldehyde. Although this method gives a better regeneration yield than the temperature swing, it is still rather low to make the process feasible.

The low back-extraction yield is most probably related to the stability of the glycolaldehyde-derived imines and the characteristics of the organic phase. The imines can be stable since the diluents have low dielectric constants [31], which are 10.30 and 1.87 for 1-octanol and *n*-hexane, respectively [27]. Thus, imine hydrolysis needs catalysts, such as acids (boric acid, diphenylborinic acid [32], and *p*-toluensulfonic acid [33]), metals (copper, nickel, zinc, and cobalt [34]), or a dual catalyst of thiourea dioxide and cobalt(II) phtalocyanine [35].

The organic extract phase has a high amine concentration and a low imine concentration due to the excess amine and high solvent-to-feed ratio. If imine hydrolysis takes place in the organic phase, this situation hinders the equilibrium shift towards glycolaldehyde formation. Moreover, water and catalyst have to transfer to the organic phase. Considering the polarity difference, the solubility of water and the catalyst may be limited.

Imine hydrolysis may also happen in the aqueous phase. The imine solubility in the organic phase has to be reduced by adding an antisolvent to facilitate imine precipitation. The imine is then stripped with a mixture of water and catalyst to allow imine hydrolysis into glycolaldehyde and the corresponding amine. Due to the solubility difference, the amine is not dissolved in water. The proposed extraction and antisolvent-induced regeneration scheme can be seen in Figure 3.13. This method refers to the gas antisolvent-induced regeneration of lactic acid from its complex in a mixture of Alamine 336, 1-octanol, and propane [36].

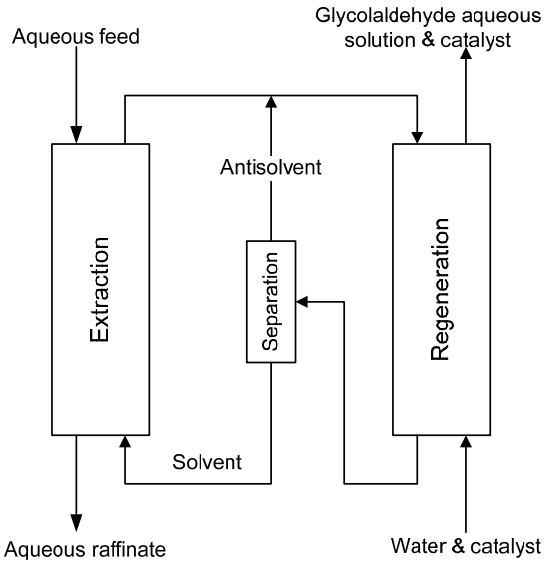

Figure 3.13: Proposed glycolaldehyde extraction and regeneration scheme

An imine hydrolysis catalyst has to be effective below 100 °C and must be easily separated from the glycolaldehyde aqueous solution. An antisolvent candidate should be less polar and more volatile than the diluent to initiate imine precipitation and enable flash separation, respectively. It is expected that the combination of a suitable catalyst and antisolvent will make the regeneration process more feasible.

3.4 Conclusions

The extraction capability of primary amines decreases in the following order: octylamine > 4-ethylaniline > phenyethylamine >> Primene JM-T > 2-ethylaniline. Considering the reversibility of the Schiff base formation, linear aliphatic primary amines, phenylalkylamines, and *para*-alkylanilines are not promising, whereas highly branched aliphatic primary amines and *ortho*-alkylanilines are selected for further investigation.

Glycolaldehyde has more affinity towards Primene JM-T than 2-ethylaniline. The extraction performance corresponds to the initial extractant concentration. At amine concentrations above 2 M, the diluent has a minor effect on the glycolaldehyde extraction performance, but does play a role in dissolving the imine and maintaining two-phase formation. At an amine concentration of 3 M, the glycolaldehyde extraction yields are 97% for Primene JM-T/1-octanol and 94% for 2-ethylaniline/1-octanol.

Glycolaldehyde can be extracted from an aqueous phase with 2-ethylaniline in 1-octanol and Primene JM-T in either 1-octanol or *n*-hexane. In the organic phase, glycolaldehyde reacts with the amine into its corresponding imine, without forming side reaction products. The same mechanism also applies to benzaldehyde.

Glycolaldehyde regeneration from the corresponding imine may be done by antisolvent-induced regeneration with water in the presence of a suitable catalyst.

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4 Glycolaldehyde co-extraction with tri-*n*-octylamine/2-ethyl-1-hexanol

This chapter discusses the acetic acid extraction and glycolaldehyde co-extraction in two types of solvent: 2-ethyl-1-hexanol and tri-n-octylamine/2-ethyl-1-hexanol. In the physical and reactive extractions, glycolaldehyde and acetic acid are extracted independently from each other. In the physical extraction, the feed composition has a slight influence on the distribution coefficients and the yields of both acetic acid extraction and glycolaldehyde co-extraction. In the reactive extraction, the acetic acid extraction and glycolaldehyde co-extraction are relatively independent of the feed composition. For a combined one-step acetic acid and glycolaldehyde extraction pure 2-ethyl-1-hexanol solvent provides the highest yields. Although 40 wt% tri-n-octylamine provides the best acetic acid extraction performance, a solvent containing more than 50 wt% tri-n-octylamine in 2-ethyl-1-hexanol is preferred for a two-step scenario in which acetic acid is extracted prior to glycolaldehyde, due to the decrease of glycolaldehyde co-extraction with increasing tri-n-octylamine concentration.

4.1 Introduction

Glycolaldehyde and acetic acid can be isolated from a pyrolysis oil-derived aqueous mixture by either physical or reactive extraction [1-3].

Physical extraction of glycolaldehyde with medium polar organic solvents gives low yield and selectivity. Vitasari *et al.* [1] showed that 1-octanol could extract about 9% glycolaldehyde from a forest residue pyrolysis oil-derived aqueous mixture in a single stage extraction at a solvent-to-feed ratio of 0.5. Besides, 15% of acetic acid and 6% of acetol in the feed were co-extracted. Multistage cross-current back-extraction with water could recover up to 85% of the extracted glycolaldehyde [1]. Furthermore, water co-extraction to the organic phase may also take place, taking into account the considerable water solubility in fairly polar organic solvents. For example, the water solubility in 1-octanol and 2-ethyl-1-hexanol are 4.35 wt% at 19 °C and 2.40 wt% at 20 °C, respectively [4]. Nevertheless, physical extraction is rather straightforward and back-extraction can be done by simple water addition.

Reactive extraction of glycolaldehyde with primary amines is analogous to that of aldehydes [5]. It is promising in term of yield and selectivity [3], but more investigations need to be done regarding the glycolaldehyde regeneration from imines in the organic phase.

Physical extraction of carboxylic acids, in particular acetic acid, using organic solvents has been widely investigated [6-9]. In general, the distribution coefficient is remarkably low and nearly temperature independent [7,10-12]. Furthermore, when aliphatic alcohols are used as solvents, water co-extraction also takes place [7].

Since physical extraction is considered rather ineffective [13,14] due to the relatively low distribution coefficients, reactive extraction with tertiary amines has been widely used to recover acetic acid from dilute aqueous solutions, such as fermentation broth [14-16], waste water streams [17], and pyrolysis oil-derived aqueous mixtures [2,18].

Mahfud *et al.* [18] have shown that tri-*n*-octylamine (TOA) is a promising extractant to isolate acetic acid from a thermally treated pyrolysis oil-derived aqueous mixture containing 6.2 wt% acetic acid. The extraction yields were 71% and 75% for 50 vol% TOA in octane and toluene, respectively.

The extraction of a forest residue pyrolysis oil-derived aqueous mixture comprising 3.3 wt% acetic acid gave a maximum yield of 85% at about 50 wt% TOA/2-ethyl-1-hexanol for a solvent-to-feed ratio of 1 in a single equilibrium stage. It was also reported that phenolic compounds, such as guaiacol and syringol, and non-polar ketones were co-extracted to the organic phase with 80-90% yields at 40 wt% TOA. Moreover, about 40% of glycolaldehyde was also co-extracted [2].

In comparison with other active diluents such as chloroform, methyl isobutyl ketone [19,20], benzyl alcohol, and 1-octanol [20], 2-ethyl-1-hexanol is preferable considering its

low tendency to form esters [2], high boiling point (184.6 °C), and low water affinity. Furthermore, the glycolaldehyde co-extraction in 2-ethyl-1-hexanol creates an opportunity to combine glycolaldehyde and acetic acid extraction in a single step.

The objective of this chapter is to investigate the effects of the feed composition and TOA/2-ethyl-1-hexanol concentration on the acetic acid extraction and glycolaldehyde co-extraction performance. The results are useful to design suitable operating conditions of two separation scenarios for the process integration of acetic acid and glycolaldehyde recovery from pyrolysis oil. The first scenario is a one-step extraction in which acetic acid and glycolaldehyde are extracted simultaneously, whereas the second scenario is a two-step extraction where acetic acid is extracted prior to glycolaldehyde.

The studied feed compositions resemble the concentrations of acetic acid and glycolaldehyde in the aqueous phase typically obtained from water extraction of forest residue- and pine-derived pyrolysis oils [21]. For reasons of comparison, the physical extraction of acetic acid and glycolaldehyde was conducted prior to the reactive extraction.

4.2 Materials and methods

4.2.1 Materials

Glycolaldehyde (dimer, crystalline, a mixture of stereoisomers), acetic acid (≥ 99%), 2-ethyl-1-hexanol (≥ 99.6%), and dibenzofuran (> 99%) were supplied by Sigma-Aldrich. Tri-*n*-octylamine (≥ 93%) and ethanol (≥ 99.5%) were bought from Merck Chemicals. All chemicals were used as received. MiliQ water was used to prepare aqueous solutions.

4.2.2 Experimental

4.2.2.1 Physical extraction

For the physical extraction, 4 mL aqueous model solution containing glycolaldehyde and acetic acid was extracted with 4 mL 2-ethyl-1-hexanol in a 20 mL vial at 20 °C and 500 rpm for 22 h to ensure equilibrium. Afterwards, the mixture was settled for at least 2 h to allow complete phase separation. Both phases were then separated and analysed.

4.2.2.2 Reactive extraction

For the reactive extraction, 4 mL of aqueous model mixture was extracted with 4 mL organic solvent of TOA/2-ethyl-1-hexanol at 20 °C and 120 rpm for 24 h. The operating

conditions were adjusted in such a way to ensure equilibrium and avoid emulsification. The organic and aqueous phases were separated by centrifugation before analysis.

4.2.3 Analysis

The composition of the aqueous and organic phases was analysed using gas chromatography (GC). Rasrendra *et al.* [2] used the method developed by Windt *et al.* [22] for analysing lignin-derived pyrolysis oil using a medium polar fused-silica column of Varian f4 1701. However, this method was not reliable for this investigated system due to the high glycolaldehyde polarity. Thus, the following method has been developed.

The sample was prepared by adding 350 µL of solution, 125 µL of internal standard solution (0.025 M dibenzofuran in ethanol), and 1.3 mL ethanol into a GC vial. The sample was analysed in Varian CP3900 with an FID detector and a capillary column CP-Wax 52 CB (50 m × 0.32 mm; 1.2 µm). The injector temperature was 250 °C, while that of detector was 280 °C. Helium flow rate was 2 mL/min and the split ratio was 50. The initial oven temperature was 30 °C. It was ramped at 30 °C/min to 200 °C, which was kept constant for 5 min, afterwards followed by a ramp of 10 °C/min to 250 °C, which was maintained for 20 min. The analysis accuracy was determined to be within 3%. Water content in each phase was calculated using a mass balance.

4.2.4 Definitions

For physical and reactive extractions, the extraction capability of a solvent is designated as distribution coefficient and yield. The distribution coefficient of component *i* (D_i) is the ratio between the total mass fraction of component *i* in the organic extract and its corresponding mass fraction in the aqueous raffinate ($x_{i,aq}$) at equilibrium. The total mass fraction of component *i* is the sum of the mass fraction of component *i* in its free form ($x_{i,org}$) and that of component *i* in the complex ($x_{i,complex}$).

$$D_i = \frac{x_{i,org} + x_{i,complex}}{x_{i,aq}} \tag{4.1}$$

The extraction yield of component *i* (Y_i) is the total mass of component *i* in the organic phase at equilibrium divided by its mass in the feed ($m_{i,f}$). The total mass of component *i* in the organic phase is the total of mass of the component *i* in its free form ($m_{i,org}$) and its mass in the complex ($m_{i,complex}$).

$$Y_i = \frac{m_{i,org} + m_{i,complex}}{m_{i,f}} \tag{4.2}$$

It is important to note that the TOA-acetic acid complex cannot be quantified using GC since it undergoes reversible decomplexation at the GC operating temperature. As a result, separate peaks of acetic acid and TOA appear in the chromatogram [18]. Thus, we cannot differentiate $x_{i,complex}$ from $x_{i,org}$ and $m_{i,org}$ from $m_{i,complex}$ for reactive extraction. For physical extraction, there is no complexation; thus, $x_{i,complex}$ and $m_{i,complex}$ are equal to zero.

The selectivity of glycolaldehyde towards acetic acid ($S_{glycolaldehyde}$) is defined as the ratio of the glycolaldehyde distribution coefficient ($D_{glycolaldehyde}$) to the distribution coefficient of acetic acid ($D_{acetic\ acid}$).

$$S_{glycolaldehyde} = \frac{D_{glycolaldehyde}}{D_{acetic\ acid}} \tag{4.3}$$

4.3 Results and discussion

4.3.1 Physical extraction of aqueous glycolaldehyde and acetic acid in 2-ethyl-1-hexanol

The physical extraction performances shown in Figure 4.1 and Figure 4.3 are given as a function of glycolaldehyde-to-acetic acid (G/A) ratio, which is the ratio of the initial concentration of glycolaldehyde in the feed to the initial concentration of acetic acid in the feed.

Figure 4.1a shows that the distribution coefficients of acetic acid are about four times higher than those of glycolaldehyde. The distribution coefficients of acetic acid and glycolaldehyde are slightly influenced by the feed composition. This minor effect is further confirmed by the nearly linear equilibrium isotherms for both glycolaldehyde and acetic acid (Figure 4.2). The small change in acetic acid distribution coefficients was also observed for a dilute aqueous acetic acid solution extracted with 2-methyl-1-propanol and 1-pentanol [6]. Furthermore, the distribution coefficients of acetic acid are in the same order as those previously reported by Xu *et al.* [23] and Ghanadzadeh *et al.* [7]. This implies that both acetic acid and glycolaldehyde are extracted by 2-ethyl-1-hexanol independently from each other.

From Figure 4.1b, one can see that acetic acid has about three times higher extraction yield than glycolaldehyde. The extraction yields of acetic acid and glycolaldehyde are affected by the feed composition. The glycolaldehyde extraction yield increases by about 15% when the G/A ratio is decreased from 1 to 0.5.

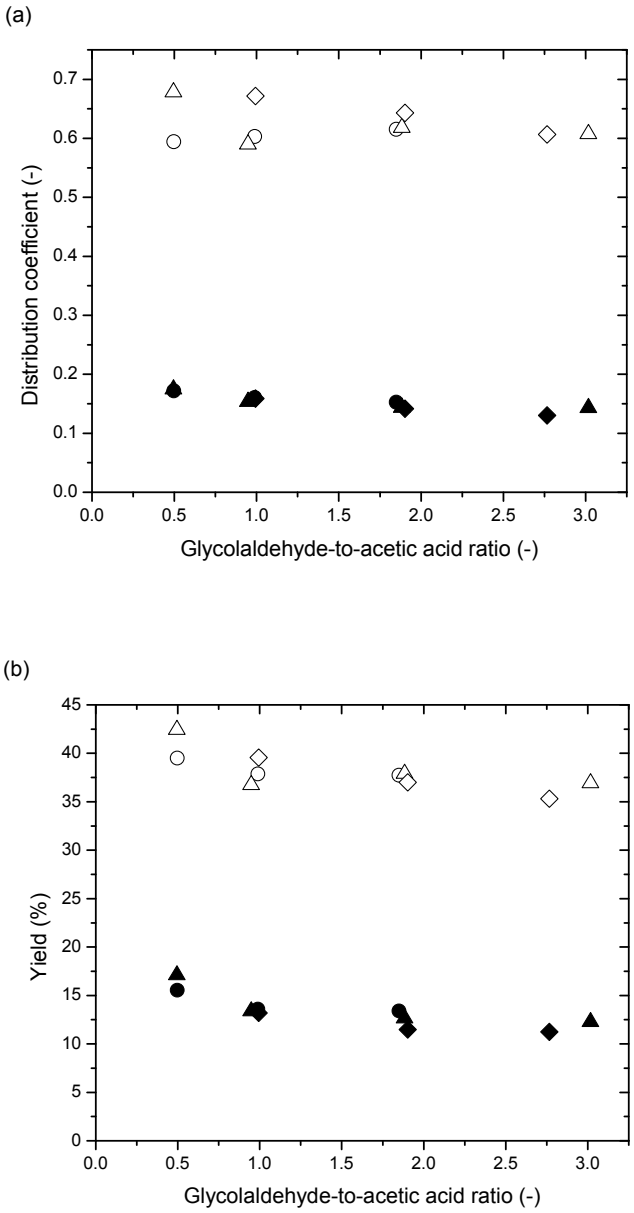

Figure 4.1: Distribution coefficients (a) and yields (b) of glycolaldehyde (full symbols) and acetic acid (open symbols) at various initial glycolaldehyde concentrations in the feed (○: 3 wt%, Δ: 6 wt%, and ◊: 12 wt%)

At a G/A ratio below 1, the acetic acid feed concentration is higher than that of glycolaldehyde. Since the acetic acid equilibrium concentration in both phases corresponds to its concentration in the feed, the polarity of the organic phase somewhat increases. As a result, more glycolaldehyde dissolves in the organic phase. This glycolaldehyde extraction enhancement due to polarity increase has less impact at higher G/A ratios where the glycolaldehyde concentration is higher than that of acetic acid, as shown in Figure 4.1b.

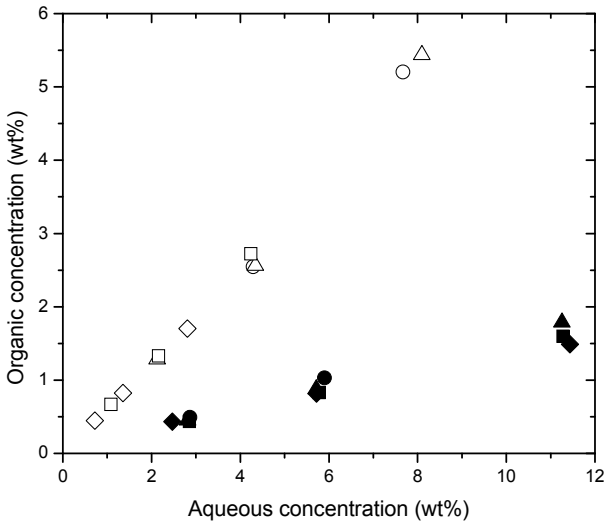

Figure 4.2: Equilibrium isotherms of glycolaldehyde (full symbols) and acetic acid (open symbols) in water and 2-ethyl-1-hexanol at 20 °C at various G/A ratios (○: 0.5, Δ: 1, □: 2, and ◊: 3)

2-Ethyl-1-hexanol is able to solvate acetic acid molecules [13,24] and form hydrogen bonds with the dissolved acetic acid [24,25]. Even though glycolaldehyde may form hydrogen bonds with 2-ethyl-1-hexanol, its dissolution in 2-ethyl-1-hexanol is hindered by its high polarity (shown by a dipole moment of 2.73 D [26]).

In a dilute aqueous solution, an acetic acid molecule forms hydrogen bonds with several water molecules [27]. On the other hand, the glycolaldehyde dimer dissociates in water into a mixture of several monomeric and dimeric isomers [28,29]. Most of these isomers have hydroxyl groups which can form hydrogen bonds with acetic acid and water [30]. The small change in the distribution coefficients of acetic acid and glycolaldehyde indicate that the hydrogen bond between glycolaldehyde and water and between acetic acid and water are more prominent than that between acetic acid and glycolaldehyde.

The lower glycolaldehyde co-extraction performance compared to that of acetic acid is related to the strength of the hydrogen bond. The higher glycolaldehyde affinity to water indicates that the hydrogen bond between glycolaldehyde and water is stronger than the hydrogen bond between acetic acid and water. As a result, the selectivity of glycolaldehyde is low, as depicted in Figure 4.3.

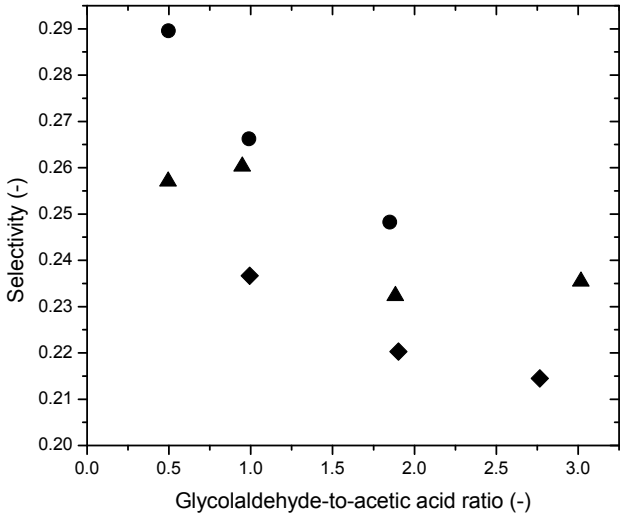

Figure 4.3: Selectivity of glycolaldehyde for various feed composition (●: 3 wt%, ▲: 6 wt%, and ♦: 12 wt% glycolaldehyde in the aqueous feed)

Figure 4.3 illustrates that the selectivity of glycolaldehyde reduces with the G/A ratio, which indicates that the feed composition has more influence to the glycolaldehyde co-extraction than acetic acid extraction.

Besides glycolaldehyde, some water is also co-extracted to the organic phase. Since the water content in the organic phase was calculated by using mass balance, its value is rather scattered around 3-4 wt%. The organic water content is higher than that of saturated 2-ethyl-1-hexanol (2.4 wt% at 20 °C [4]), meaning that the presence of acetic acid and glycolaldehyde increases the water co-extraction. Since the distribution coefficients of acetic acid and glycolaldehyde decline slightly with the G/A ratio, it is expected that the water co-extraction somewhat decreases. Unlike water, the solubility of 2-ethyl-1-hexanol in the aqueous phase is negligible, proven to be less than 0.1 wt%.

4.3.2 Reactive extraction

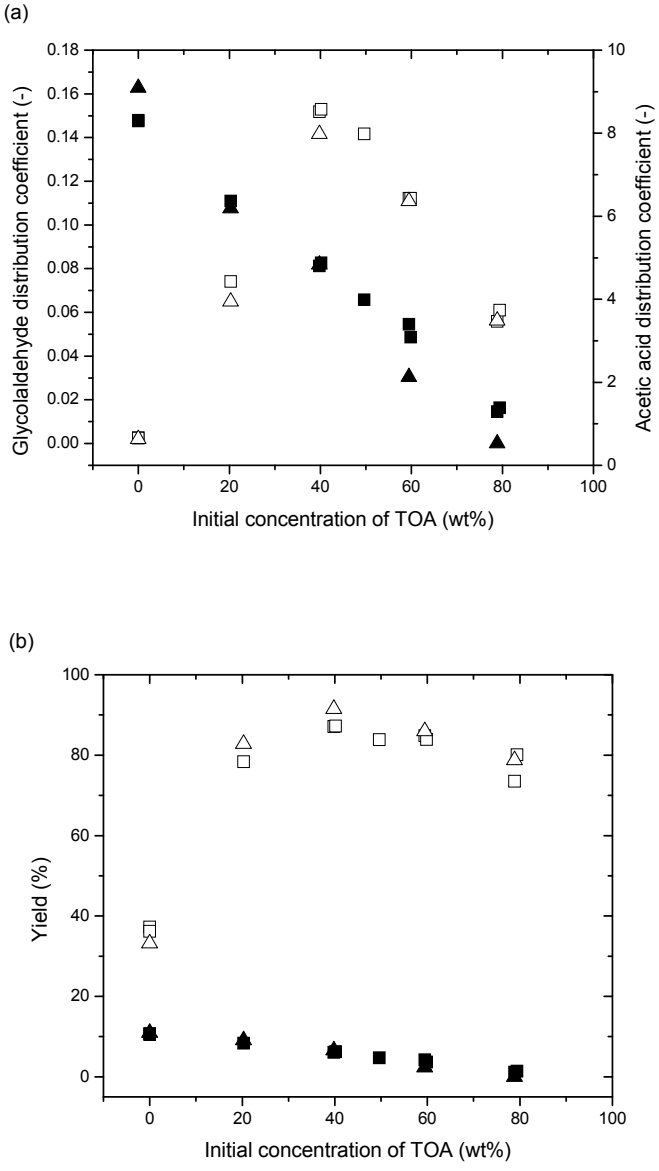

Figure 4.4: Effect of TOA concentration on the distribution coefficients (a) and extraction yields (b) of glycolaldehyde and acetic acid at various feed compositions

For the reactive extraction, two types of model feed have been investigated. The first model feed (Feed 1) represents the forest residue pyrolysis oil-derived aqueous phase, which contains 4.3 wt% glycolaldehyde and 4.3 wt% acetic acid [21]. The second model feed (Feed 2) corresponds to the pine pyrolysis oil-derived aqueous phase, which comprises 11.5 wt% glycolaldehyde and 3.8 wt% acetic acid [21].

Figure 4.4 depicts that the addition of TOA to 2-ethyl-1-hexanol improves the acetic acid extraction performance. The acetic acid distribution coefficient increases by a factor of 10 and reaches a maximum at around 40 wt% TOA (Figure 4.4a). Similarly, the maximum yield, which is three times higher than that with pure 2-ethyl-1-hexanol, is also achieved at the same TOA concentration (Figure 4.4b). At higher TOA concentrations, the acetic acid distribution coefficient and yield decline.

Below 40 wt% TOA, the amine-acid interaction increases with TOA concentration, while the excess amount of 2-ethyl-1-hexanol maintains the high polarity of the organic phase. In contrast, at higher concentrations of TOA the amine is dominating; thus, the organic phase becomes less polar [24]. As a result, less acetic acid dissolves in the organic phase, leading to lower distribution coefficient and extraction yield.

A very similar performance trend was also observed in the extraction of acetic acid, which reached the maximum yield at 50 vol% Alamine-336/2-ethyl-1-hexanol [24]. Rasrendra *et al.* [2] have used TOA/2-ethyl-1-hexanol to extract acetic acid from a pyrolysis oil-derived aqueous phase, which contained 3.3 wt% acetic acid, 0.6 wt% formic acid, and 0.2 wt% glycolic acid. They found that the maximum extraction yield was reached at 50 wt% TOA, whereas in this case it is shown to be at 40 wt% TOA (Figure 4.4). The difference in the optimum TOA concentration is caused by the co-extraction of formic and glycolic acids with TOA from the actual pyrolysis oil-derived aqueous phase.

Unlike acetic acid, the distribution coefficient and yield of glycolaldehyde decrease proportionally with the TOA concentration (Figure 4.4). This trend confirms that glycolaldehyde dissolves only in 2-ethyl-1-hexanol. Glycolaldehyde is not soluble in TOA due the difference in polarity and lack of hydrogen bond formation capability. Although it is possible to form hydrogen bond between the hydrogen of the hydroxyl group of glycolaldehyde and the nitrogen of TOA, the hydrogen bond is very weak due to the steric effect of the hydrocarbon tails of TOA [31]. Since the amount of 2-ethyl-1-hexanol in the organic phase decreases with TOA concentration, the distribution coefficient of glycolaldehyde decreases and accordingly the extraction yield reduces as well (Figure 4.4b).

From Figure 4.4a one can also see that in general the acetic acid distribution coefficients of both feeds are almost the same. The glycolaldehyde distribution coefficients are also relatively independent of the feed composition. Similarly, Figure 4.4b shows the same trends of acetic acid and glycolaldehyde yields. These profiles indicate the absence of the interaction between acetic acid and glycolaldehyde in the reactive extraction.

The effect of feed concentration is comparable with that previously published by Katikaneni and Cheryan [24], in which the acetic acid extraction performance improved by 5% when the acetic acid concentration was doubled from 5.2 wt% from 11.6 wt%. The slight effect of the feed composition implies that TOA and acetic acid can form strong complexes [24]. Besides, it is also related to the excess amount of TOA in the organic phase, which is mostly supplied more than its stoichiometric requirement. Assuming that only (1,1) acetic acid-TOA complex is formed in the organic phase, a stoichiometric ratio of 1 is obtained at a concentration of 29 wt% TOA for Feed 1 and 31 wt% for Feed 2. As a result, all dissolved acetic acid can form complexes with TOA. This also explains that the maximum yield is obtainable above 30 wt% TOA.

Water co-extraction in the organic phase is quite low, compared to that in the physical extraction. In the organic phase, TOA is dominating, which leads to a less polar organic phase compared to pure 2-ethyl-1-hexanol. As a result, the water content of the organic phase is in the range of 0.7-1 wt%, which is a little higher than the water solubility in TOA (0.7 wt% at 40 °C [32]).

Although the optimum TOA concentration provides the highest acetic acid yield, this work demonstrates that it is not preferable for glycolaldehyde co-extraction. At higher TOA concentrations the glycolaldehyde co-extraction in the organic phase is significantly reduced. Hence, almost all glycolaldehyde remains in the aqueous phase while the acetic acid yield is maintained around 80% in a single stage extraction. On the other hand, pure 2-ethyl-1-hexanol is needed to extract acetic acid and glycolaldehyde simultaneously. The limited single-stage acetic acid and glycolaldehyde yields (Figure 4.1) can be easily improved by increasing the solvent-to-feed ratio and operating multi-stage extraction counter-currently.

Thus, for the combined one-step extraction scenario acetic acid and glycolaldehyde are extracted using 2-ethyl-1-hexanol in a multistage counter-current column at a solvent-to-feed ratio higher than unity. Acetic acid is then recovered and purified by distillation while glycolaldehyde is subjected to back-extraction with water. For the two-step extraction scenario, acetic acid is firstly extracted using a solvent of TOA/2-ethyl-1-hexanol with a TOA concentration above 50 wt%, followed by glycolaldehyde extraction with 2-ethyl-1-hexanol from the raffinate phase of the previous acetic acid extraction. Acetic acid is regenerated from the TOA-acid complex by distillation, while glycolaldehyde can be separated from 2-ethyl-1-hexanol by back-extraction with water.

4.4 Conclusions

The extraction of acetic acid and co-extraction of glycolaldehyde with 2-ethyl-1-hexanol is slightly affected by the feed composition, whereas the extraction of

both components with TOA/2-ethyl-1-hexanol is almost independent of the feed composition in the investigated concentration range. For a one-step extraction process, pure 2-ethyl-1-hexanol provides the best acetic acid and glycolaldehyde yields. Although 40 wt% TOA provides the highest acetic acid extraction performance, a TOA concentration higher than 50 wt% is preferable for a two-step extraction scenario.

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5 Laboratory scale conceptual process development for glycolaldehyde isolation

A laboratory-based separation sequence has been developed to produce an aqueous glycolaldehyde solution as fermentation feedstock. It consists of water extraction of the pyrolysis oil feedstock, acid removal, water removal, octanol extraction, phenolic removal, back-extraction, and washing. The octanol-free aqueous glycolaldehyde solution meets the requirement of fermentation feedstock and contains 3.9 wt% glycolaldehyde, 0.3 wt% acetic acid, 0.3 wt% acetol, and 0.1 wt% furanone. A fermentation test showed that the mixture had the same performance as pure glycolaldehyde solution with a bioconversion yield of 98%. Although the total glycolaldehyde yield is rather low (17%), this process is a starting point for directing further process development and able to demonstrate the technical feasibility of a process integration with acetic acid recovery.

5.1 Introduction

Although glycolaldehyde is present in a substantial amount (5-13 wt%) in wood-derived pyrolysis oil [1,2], the nature of the pyrolysis oil gives a challenge in developing a process to isolate it.

Stradal and Underwood [3] have invented a separation process to isolate glycolaldehyde from pyrolysis oil. In principle, it consists of water extraction to separate water soluble compounds from water insoluble ones, evaporation or distillation to concentrate glycolaldehyde, and glycolaldehyde precipitation from methylene chloride to purify glycolaldehyde. In order to increase glycolaldehyde yield and minimise glycolaldehyde degradation, multiple evaporations or distillations are applied (Figure 5.1).

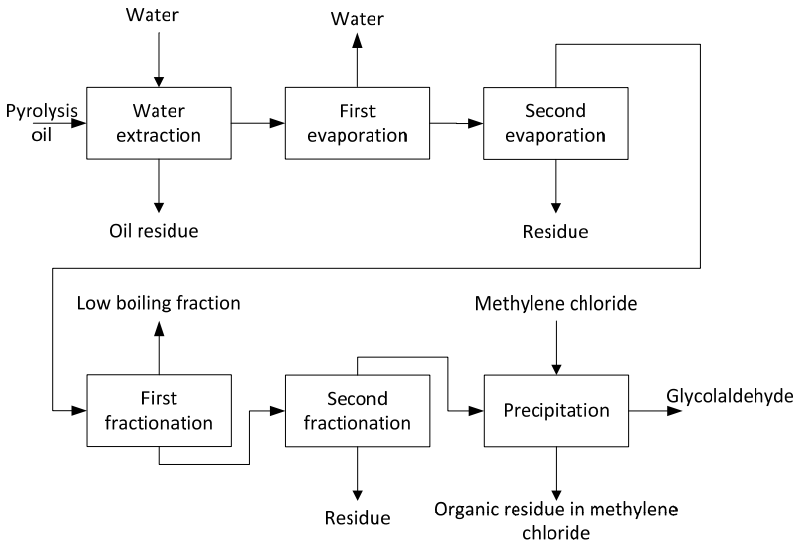

Figure 5.1: Stradal and Underwood's glycolaldehyde isolation process

All evaporation and distillation steps operate at vacuum to prevent the condensation reactions of glycolaldehyde, which can occur during heating, especially in basic solutions. Furthermore, the residence time at high temperature (above 100 °C) should be as short as possible to minimise glycolaldehyde loss. Although they claimed that the glycolaldehyde product was suitable for browning foodstuff [3], the type and concentration of impurities were not reported, neither the overall glycolaldehyde yield.

The objective of this study was to develop a separation sequence to recover glycolaldehyde from pyrolysis oil to be used as fermentation feedstock for renewable ethylene glycol synthesis. According to Metabolic Explorer (France), a company that develops fermentation-based industrial process technology, the aqueous feedstock has to contain

200-600 mM (1.2-3.6 wt%) glycolaldehyde, taking into consideration the toxicity of glycolaldehyde to the fermentation microorganism. Moreover, it must not contain any long chain alcohols, which are also poisonous.

5.2 Approach

In order to fulfil the above-mentioned requirements, a novel approach has been applied to develop a process to isolate glycolaldehyde from pyrolysis oil, which is a multi-component mixture. So far, apart from Stradal and Underwood's proposal, glycolaldehyde isolation has not been investigated. There is also a lack of literature on the physical and chemical properties of glycolaldehyde. Therefore, the conceptual process development was done by performing batch experiments in the laboratory.

A conventional separation method, such as distillation, produces fractions which are mixtures of several compounds, leading to low selectivities. For example, a vacuum distillation of wood-derived pyrolysis oil at 45-65 °C gave several aqueous fractions which contained glycolaldehyde, acetic acid, and acetol. The concentration of those compounds varied from 12-27 wt% [3].

Chromatography may be an alternative separation method. Gas and liquid chromatography have been widely applied for pyrolysis oil characterisation [4,5]. However, overlapping peaks in the chromatograms indicate low selectivity. Hence, this method needs a lot of investigation, especially to improve the selectivity, before it can be applied in a larger scale biomass separation.

Extraction has been applied as a fractionation step in the characterisation of pyrolysis oil prior to a chromatographic analysis [4,6]. In this way, the complexity of pyrolysis oil is reduced by concentrating compounds with similar properties in a certain solvent, for example: water soluble compounds are isolated in aqueous mixture by water extraction [4].

Like distillation and chromatography, solvent extraction may also give low selectivity of a particular compound due to co-extraction, which is solvent dependent. In bio-based chemical isolation from pyrolysis oil, the co-extraction of the other value-added chemicals may turn to be an opportunity to create a separation network for producing different types of chemicals.

Extraction is a conventional process. It is rather simple, easy to design, and shown to be able to reduce the complexity of pyrolysis oil [7]. Besides, it is usually performed at ambient temperature and atmospheric pressure. Thus, glycolaldehyde degradation and any side reactions which might occur at elevated temperatures can be avoided. Furthermore, by selecting an appropriate solvent, extraction can be selective towards a particular

compound. In addition, close boiling point components with different solubility in a solvent can also be separated using extraction.

A unit operation was selected based on the composition and properties of the pyrolysis oil raw material or the effluent of the preceding unit as well as the target of separation. The separation target could be either concentrating glycolaldehyde in a solvent or removing a particular compound/impurity from a glycolaldehyde containing mixture. In addition to extraction, distillation/evaporation was also considered, especially for concentrating a mixture. Furthermore, it is important to check if the isolation of the other value-added chemicals can be integrated in a certain step of the process. The operating conditions of every separation step were pre-determined by rough calculation and preliminary experiments.

Beside the feed and outlet compositions, the separation behaviour in a certain stage had to be observed. The formation of two or more phases as well as emulsification are important aspects to consider since the predetermined operating conditions may need some adjustments.

5.3 Methods

5.3.1 Material

The raw material was forest residue-derived pyrolysis oil obtained from VTT Finland. It was produced by fast pyrolysis at 520 °C and a residence time of 1 s. At the time of experiments, it contained 6.4 wt% glycolaldehyde, 5.2 wt% acetic acid, 1.4 wt% acetol, 0.2 wt% furfural, and 0.4 wt% furanone.

Tri-*n*-octylamine (≥ 98%), 1-octanol (≥ 99.5%), toluene (99.8%), nonane (≥ 95%), and dibenzofuran (≥ 99%) were purchased from Sigma-Aldrich. Ethanol (≥ 99.5%) was received from Merck Chemicals. MiliQ water was used as solvent. All chemicals were used without further purification.

5.3.2 Experimental procedure

The batch experiments were generated stepwise in the laboratory involving extraction and distillation. The experiment scheme is illustrated in Figure 5.2. Water and phenolic removal steps were distillation while the others were extraction.

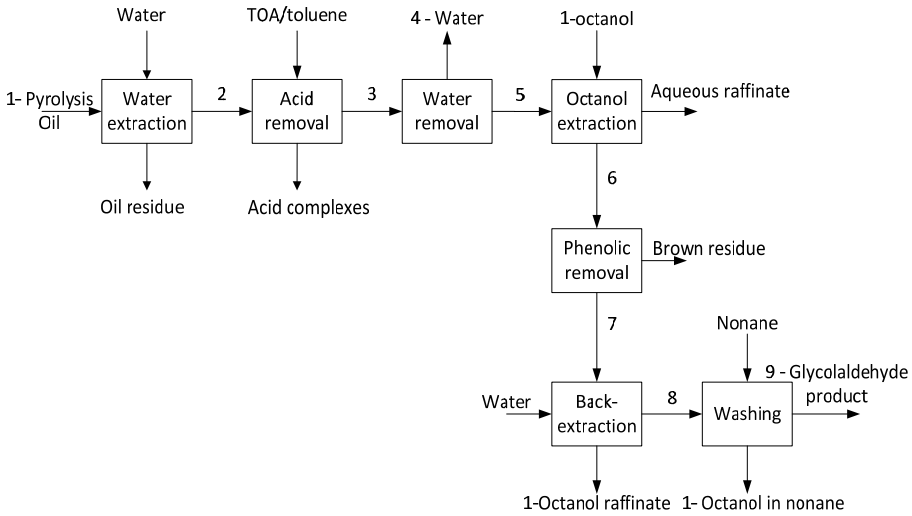

Figure 5.2: Process flow sheet of producing glycolaldehyde from pyrolysis oil

Table 5.1: Operating conditions of each extraction step

Extraction step	Extraction solvent	Stirring speed (rpm)	Extrac-tion time (h)	Solvent-to-feed ratio (-)	Number of stages (-)
Water extraction	Water	100	24	0.5	1
Acid removal	34 vol% TOA/toluene	300	20	1	1
	20 vol% TOA/toluene	100	20	0.5	2
Octanol extraction	1-octanol	200	6	0.5	4
Back-extraction	Water	400	2	0.2	2
	Water	400	2	0.1	1
Washing	Nonane	400	2.25	0.3	1
	Nonane	400	2	0.3	1

Table 5.2: Operating conditions of each distillation step

Step	Pressure (mbar)	Reflux (-)
Water removal	13-14	1
Phenolic removal	1.8-3.5	2

All extraction experiments were performed at 20 °C and 1 bar in 1 L erlenmeyer flasks equipped with magnetic stirring bars. Afterwards, the mixture was allowed to settle for at least 2 h to ensure complete phase separation. Multistage extraction was done cross-

currently by adding fresh solvent to each stage. Distillation experiments were carried out in a batch SPALTROHR® distillation column from Fischer with 90 theoretical stages. The operating conditions of each separation unit are listed in Table 5.1 and Table 5.2.

Extraction was treated as once-through process without solvent recovery. Rough calculations as well as preliminary experiments in 50 mL erlenmeyer flasks or a 50 mL round bottom flask using some part of each stream have also been done to predetermine the operating conditions of each separation step.

5.3.3 Analysis

The composition of each stream was determined by Gas Chromatography (GC). For GC analysis, 350 µL sample was mixed with 125 µL internal standard solution of 0.025 M dibenzofuran in ethanol and then diluted with 1300 µL ethanol. The quantitative analyses were performed in Varian CP 3900 equipped with an FID detector and a capillary column CP-Wax 52CB (30 m × 0.53 mm; 1 µm). Helium was used as carrier gas at a constant velocity of 2 mL/min. The split ratio was 50. The injector temperature was 250 °C, while that of detector was 280 °C. The initial oven temperature was 45 °C and then ramped at 10 °C/min to 60 °C, 3 °C/min to 160 °C, and 10 °C/min to 250 °C, which was maintained for 56 minutes. The accuracy of the analytical method was determined to be within 5%.

5.3.4 Definition

Distribution coefficient and yield are used to denote extraction performance. The distribution coefficient of component *i* (D_i) is calculated as the ratio of the mass fraction of component *i* in the extract phase ($x_{i,extract}$) to that in the raffinate phase ($x_{i,raffinate}$) at equilibrium.

$$D_i = \frac{x_{i,extract}}{x_{i,raffinate}} \tag{5.1}$$

The extraction yield of component *i* (Y_i) is the mass of component *i* in the extract phase ($m_{i,extract}$) divided by its initial mass in the extraction feed ($m_{i,feed}$) at equilibrium.

$$Y_i = \frac{m_{i,extract}}{m_{i,feed}} \tag{5.2}$$

5.4 Results and discussion

5.4.1 Conceptual process development

Since preliminary experiments were conducted using real mixtures and most of the separation steps were done in several batches, the actual mass balance is not presented. Furthermore, the composition of several important streams is given as an average, as listed in Table 5.3. The overall yield and loss were calculated theoretically without taking into account material loss.

Table 5.3: Composition of the streams denoted in Figure 5.2

Stream number	Concentration (wt%)								
	1	2	3	4	5	6	7	8	9
Glycolaldehyde	6.45	3.98	4.97	0.82	8.65	2.08	2.26	4.06	3.95
Acetic acid	5.17	4.45	0.81	0.23	1.34	0.44	0.26	0.24	0.28
Acetol	1.40	1.31	1.41	0.43	2.32	0.33	0.14	0.35	0.32
Furfural	0.24	0.17	0.03	0.02	0.04	0.03	0.02	0.00	0.00
Furanone	0.39	0.12	0.16	0.04	0.27	0.06	0.06	0.12	0.13

In the following section, each separation step shown in Figure 5.2 is briefly discussed.

5.4.1.1 Water extraction

The complexity of pyrolysis oil can be reduced by water addition, which leads to phase separation [8]. The amount of water required to achieve a complete phase separation depends on the nature of pyrolysis oil as well as the storage time and conditions. For example, oak wood-derived pyrolysis oil needs a minimum water-to-oil ratio of 0.25 [9]. In this case, a complete phase separation was initially observed at a water-to-oil ratio of 0.4. Upon water addition, more polar compounds transfer to the aqueous phase whereas less polar ones stay in the oil phase [10]. Hence, glycolaldehyde could be isolated in the aqueous phase together with other polar compounds.

The concentrations of all studied compounds in the extract are lower than those in the pyrolysis oil (Table 5.3), mostly due to water dilution [7]. In terms of distribution coefficient and extraction yield, acetol is the highest, followed by acetic acid, furfural, glycolaldehyde, and furanone (Table 5.4). This order of distribution coefficients is unexpected since glycolaldehyde is more polar than furfural due to its hydroxyl and carbonyl functional groups. The higher furfural distribution coefficient may be related to its considerable solubility in water, which is 7.94 wt% at 20 °C [11].

Table 5.4: Extraction performance of water extraction

Compound	Distribution coefficient (-)	Yield (%)
Glycolaldehyde	0.63	63
Acetic acid	2.67	88
Acetol	7.45	95
Furfural	1.06	74
Furanone	0.18	32

The aqueous extract composition (Stream 2 in Table 5.3) shows low selectivity towards glycolaldehyde, especially due to the co-extraction of acetic acid and acetol. This co-extraction cannot be avoided because the three compounds have comparable molecular structures and polarity.

Considering glycolaldehyde polarity, its distribution coefficient and yield could be improved by optimising the water-to-oil ratio to give the best compromise between aqueous glycolaldehyde concentration and yield. The optimum water-to-oil ratio is dependent on the nature of pyrolysis oil [7].

5.4.1.2 Acid removal

The aqueous extract from water extraction contains a considerable amount of acetic acid (4.4 wt%). Taking into account the toxicity of acetic acid to *Escherichia coli* [12-14], it has to be removed from the aqueous extract. It can then be further recovered and purified to produce bio-based acetic acid.

In general, acetic acid can be extracted from the aqueous phase by reactive extraction with tertiary amines [15-17]. A solution of tri-*n*-octylamine (TOA) in toluene has been proven to be a selective solvent to remove acetic acid and formic acid from a pyrolysis oil-derived aqueous fraction [18].

In the first extraction stage with a solvent-to-feed ratio of 1, emulsification occurred, most likely because of a rather high TOA concentration [19] (34 vol%) and vigorous agitation. As a result, the settling to obtain complete phase separation took 2 days instead of 2 h.

About two-thirds of acetic acid in the aqueous feed can be removed in one stage, without a considerable loss of glycolaldehyde, acetol, and furanone (Table 5.5). Since toluene is able to dissolve furfural [20], about 85% of furfural is also removed from the pyrolysis-derived aqueous stream.

In the following stages, emulsification was prevented by reducing the TOA concentration to 20 vol%, halving the solvent-to-feed ratio, and decreasing the stirring rate by a

factor of three (Table 5.1). No emulsification was observed and phase separation happened as soon as stirring was stopped.

Table 5.5: Extraction performance of the acid removal step

Compound	Stage 1		Stage 2		Stage 3	
	Distribution coefficient (-)	Yield (%)	Distribution coefficient (-)	Yield (%)	Distribution coefficient (-)	Yield (%)
Glycolaldehyde	0.02	0	0.01	0	0.04	1
Acetic acid	2.34	65	0.95	29	1.02	26
Acetol	0.00	0	0.00	0	0.05	2
Furfural	6.80	85	0.00	0	0.10	3
Furanone	0.00	0	0.04	2	0.49	17

The extent of the acid removal decreases by approximately 60% in the second and third stages (Table 5.5). Thus, it is in accordance with the decrease in amine concentration and solvent-to-feed ratio. This leads to a total acid removal of 75% for the second stage and 81% for the third one. Since the acetic acid yield changes slightly in the second and third stages, three cross-current stages are enough to achieve 82% lower acetic acid concentration in the aqueous raffinate.

Table 5.5 also implies that a minor loss of glycolaldehyde (1.3%) and acetol (1.8%) occurs in the third stage, which may be related to the slight increase in their concentration in the raffinate of the second stage. Furanone loss in the third stage is about 17%, which is 10 times higher than that in the previous stages. The explanation of this phenomenon is not known yet. Furfural loss in the second and third stages is relatively low compared to the first stage due to the major concentration decrease in the first stage.

In summary, the reactive extraction of acetic acid with TOA/toluene gives a rather high acetic acid yield (more than 80%) without a considerable glycolaldehyde loss. This means that acetic acid separation can be performed prior to glycolaldehyde isolation. The organic extract can be then further treated differently while the aqueous raffinate goes to the next separation step. Thus, this gives an opportunity of a process integration of acetic acid and glycolaldehyde production.

5.4.1.3 Water removal

The preliminary experiments indicated that the glycolaldehyde distribution coefficient in the subsequent octanol extraction is relatively independent of the glycolaldehyde concentration in the aqueous feed. Thus, to increase the glycolaldehyde concentration in

the extract phase, approximately half the water in the raffinate of the last stage acid removal (stream 3 in Figure 5.2) was removed by distillation.

Compared to the amount of aqueous raffinate from the preceding acid removal, the product loss with evaporated water is as follows: furfural 18-21%, acetol 8-15%, acetic acid 6-15%, furanone 2-19%, and glycolaldehyde 3-8%. The high furfural and furanone losses are unexpected since their boiling points are higher than that of acetol. These losses are caused by their high activity coefficients, which lead to remarkable vapour-liquid equilibrium constants. According to Aspen Plus® calculation using UNIFAC (Dortmund) property method, at 13 mbar the vapour-liquid equilibrium constants of acetol, furanone, and furfural are 0.6, 6.2, and 8.3 times higher than that of water, respectively.

5.4.1.4 Octanol extraction

Since there is no information about glycolaldehyde extraction from an aqueous phase, 1-octanol was chosen as solvent considering that it has a hydroxyl group which can form hydrogen bonds with glycolaldehyde. Furthermore, 1-octanol has a limited solubility in water (0.049 wt% at 20.9 °C) [21]. Unlike acid removal, there was no emulsification observed in any of the octanol extraction stages; therefore, phase separation started as soon as the agitation was stopped.

Table 5.6: Performance of octanol extraction

Compound	Stage 1		Stage 2		Stage 3		Stage 4	
	Distribution coefficient (-)	Yield (%)	Distribution coefficient (-)	Yield (%)	Distribution coefficient (-)	Yield (%)	Distribution coefficient (-)	Yield (%)
Glycolaldehyde	0.25	9	0.22	9	0.27	10	0.29	8
Acetic acid	0.51	15	0.56	20	0.46	19	0.44	13
Acetol	0.17	6	0.14	6	0.15	6	0.06	2
Furfural	1.44	45	1.44	45	1.9	51	2.89	62
Furanone	0.24	9	0.20	8	0.2	8	0.2	6

Table 5.6 indicates that the distribution coefficient of glycolaldehyde is almost constant and relatively independent of the feed concentration. The total glycolaldehyde recoveries are 17.8%, 26.3%, and 32.6% for two-, three-, and four-stage extractions, respectively. These yields are rather low. The extraction yield could be improved by choosing a better solvent, which is more polar than 1-octanol and slightly soluble in water. Furthermore, a higher glycolaldehyde yield will be obtained by counter-current

extraction in a continuous process and recycling the 1-octanol raffinate from the later back-extraction as extraction solvent.

5.4.1.5 Phenolic removal

The extract streams from the preceding unit operations are brown. This indicates the presence of a small amount of phenolic compounds in water as well as in 1-octanol. Even though their influence on fermentation is not known yet, they need to be removed from the organic extract prior to back-extraction to produce a colourless glycolaldehyde fraction.

Phenolic compounds in forest residue-derived pyrolysis oil can be categorised into lignin-derived phenols, guaiacol, and syringol derivatives. It is not yet known which chemicals impart the brown colour. However, the boiling points of phenolic compounds are commonly above 200 °C. Therefore, they can be separated from 1-octanol and other lighter components by evaporating 1-octanol.

Due to experimental set-up limitation, distillation was done in several batches. It was stopped when the liquid level was just below the temperature sensor inside the pot. As a result, some 1-octanol remained in the viscous, dark-brown bottom product, whereas the top liquid was colourless. On average, up to 75% of glycolaldehyde could be recovered in the condensate. The remaining glycolaldehyde was still distributed along the column when the distillation was stopped and eventually collected in the bottom residue.

5.4.1.6 Back-extraction

Table 5.7: Distribution coefficients and yields of the back-extraction

Compound	Stage 1		Stage 2		Stage 3	
	Distribution coefficient (-)	Yield (%)	Distribution coefficient (-)	Yield (%)	Distribution coefficient (-)	Yield (%)
Glycolaldehyde	4.49	54	4.04	54	3.79	31
Acetic acid	1.18	25	1.07	20	0.97	10
Acetol	10.25	95	11.46	76	8.88	56
Furfural[a]	n/d	n/d	n/d	n/d	n/d	n/d
Furanone	3.50	52	4.14	53	3.35	28

[a] Furfural was not quantified since its concentration was below the detection limit

Distillation is not a feasible method to separate glycolaldehyde from 1-octanol due to the diluteness of the glycolaldehyde solution. Instead, back-extraction with water was considered a better option since glycolaldehyde is soluble in water.

Similar to octanol extraction, the feed concentration in the back-extraction has a minor influence on the distribution coefficients of all components (Table 5.7), which are roughly the reciprocal of those of the octanol extraction, as shown in Table 5.6. More than 75% of glycolaldehyde can be recovered in two stages. The third extraction stage was added for further glycolaldehyde recovery. In this stage, the solvent-to-feed ratio was halved (see also Table 5.1) to prevent excessive water dilution. The total glycolaldehyde yield in the three extract streams is 85.4%. It is not feasible to add another extraction stage with a lower solvent-to-feed ratio since the increase in total glycolaldehyde yield cannot compensate the water dilution.

5.4.1.7 Washing

Despite its slight solubility in water (0.049 wt% at 20.9 °C) [21], some 1-octanol transfers to the aqueous extract during back-extraction. In order to meet the fermentation feedstock requirements, dissolved 1-octanol must be removed from the aqueous phase by washing with nonane.

Nonane is able to wash all 1-octanol out of the aqueous phase, which is confirmed by the disappearance of the 1-octanol peak in the GC chromatogram of the final aqueous product. It contains 3.95 wt% glycolaldehyde, 0.28 wt% acetic acid, 0.32 wt% acetol, and 0.13 wt% furanone. The GC chromatogram of the organic phase shows that neither acetic acid nor carbonyl compounds dissolve in nonane. The difference between the feed and extract concentrations is within the analytical error. Hence, the final aqueous solution meets the fermentation feedstock specification.

A continuous fermentation test has been performed at Metabolic Explorer using the aqueous glycolaldehyde product. The experiment was done at 37 °C with 10 g/L glucose and a recombinant *Escherichia coli* [22]. It gives 98% bioconversion yield, which is the same as that of pure commercial glycolaldehyde.

5.4.2 Overall yield and component distribution in the process

Table 5.8 shows the yield and loss of each investigated compound denoted as percentage of its amount in the initial pyrolysis oil feed. Unfortunately, the total glycolaldehyde yield cannot be compared with that of Stradal and Underwood's (Figure 5.1) due to lack of density data in the patent. However, one step fractionation distillation shows that the glycolaldehyde fraction which contains above 20 wt% glycolaldehyde is maximum 14% of the total distillate [3].

Table 5.8: Overall yield and major loss of each component in the separation steps

Compound	Overall yield (%)	Step with major loss	Loss (%)
Glycolaldehyde	17.2	Water extraction	36.9
		Octanol extraction	37.0
Acetic acid	1.8	Acid removal	71.5
Acetol	6.5	Octanol extraction	66.8
Furfural	0.2	Water extraction	25.8
		Acid removal	63.6
Furanone	6.0	Water extraction	67.4

Moreover, Table 5.8 suggests that a significant improvement is a must. The physical extraction steps (water and octanol extractions) need a considerable improvement to increase the total glycolaldehyde yield.

As previously discussed, the water-to-oil ratio can be optimised to isolate most of the polar compounds (in this case glycolaldehyde, acetic acid, and acetol) in the aqueous phase. Unlike water, 1-octanol is evidently not a good solvent for glycolaldehyde and acetol. Any organic solvent candidates have to be more polar than 1-octanol and immiscible with water. Furthermore, their boiling points are preferably below 200 °C to enable the separation of phenolic compounds by evaporation.

5.5 Conclusions and remarks

The proposed batch production scheme, which incorporates acid separation, can meet the required glycolaldehyde and 1-octanol concentrations as fermentation feedstock. It contains 3.9 wt% glycolaldehyde, 0.3 wt% acetic acid, 0.3 wt% acetol, and 0.1 wt% furanone.

However, at the moment the proposed batch process sequence is not yet economically feasible and environmentally benign, mainly due a low glycolaldehyde yield of 17%. Nevertheless, it is advantageous to provide an idea about the separation characteristics, which is a useful starting point to improve the overall process or to modify this process by combining the separation of one or more compounds into a single step by using an appropriate solvent. Furthermore, it also proves that the process integration with acetic acid recovery is possible.

At a larger scale, a continuous system seems to be more promising. Multistage counter-current extraction may be applied. If 1-octanol is used to extract glycolaldehyde, the organic raffinate stream from back-extraction can be recycled back to the octanol extractor.

Apart from technical aspects, a large variation of pyrolysis oil composition is also a challenge for further process development. Even though the process may remain the same, the operating conditions of a unit operation will need some adjustments to optimise the overall process.

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6 Conceptual process design and economic evaluation for integrated bio-based acetic acid, glycolaldehyde, and acetol production

This chapter discusses the conceptual process as designed for their integrated isolation and purification from forest residue- and pine-derived pyrolysis oils. The process simulation was performed in Aspen Plus®, while the equipment cost was estimated with Aspen Process Economic Analyzer. The process was designed for a capacity of 200 kton pyrolysis oil per year and involves extraction, distillation, and evaporation. Water and 2-ethyl-1-hexanol are used as extraction solvents. The designed process can isolate more than 99% of the glycolaldehyde and acetic acid and about two-thirds of the acetol present in the oils. In comparison with the forest residue-based process (21 M€), the pine-based process requires a higher capital investment of 23 M€ and a slightly higher production cost of 49 M€/a versus 48 M€/a, but is able to provide a higher revenue of 57 M€/a instead of 44 M€/a because pine-derived pyrolysis oil contains more acetic acid, glycolaldehyde, and acetol, which also makes it less sensitive to market price. The plant profitability increases considerably up to a capacity of 500 kton pyrolysis oil per year. Pine-derived pyrolysis oil is a preferable feedstock over forest residue-derived pyrolysis oil for an integrated chemical recovery process from pyrolysis oil.

6.1 Introduction

Acetic acid, glycolaldehyde, and acetol are three future bio-based platform chemicals which are available in a considerable amount in pyrolysis oil, for example wood-derived pyrolysis oil contains about 3-12 wt% acetic acid [1,2], 5-13 wt% glycolaldehyde, and 0.7-7.4 wt% acetol [3].

Acetic acid and glycolaldehyde can be extracted directly from pyrolysis oil by reactive extraction with tri-*n*-octylamine (TOA) [4] and sodium bisulfite [5], respectively. However, both methods are not promising due to considerable TOA losses [4] and the stability of glycolaldehyde-bisulfite adduct complicating product recovery [5].

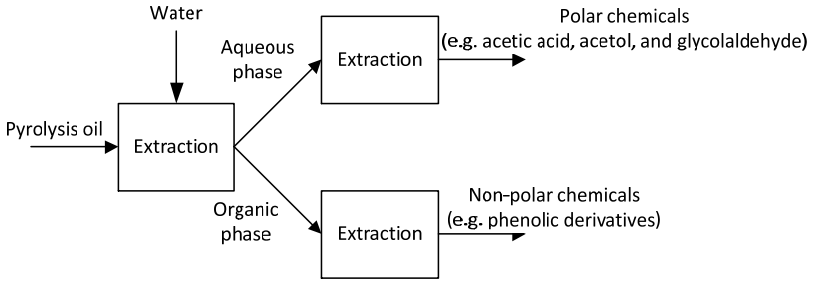

Figure 6.1: Indirect chemical isolation via water extraction

For these reasons, another approach has been proposed to separate the target bio-based chemicals from pyrolysis oil (Figure 6.1). Water addition to pyrolysis oil induces phase separation in which polar compounds are isolated in the aqueous phase, while non-polar ones remain in the organic phase. Hence, the complexity of pyrolysis oil is strongly reduced [6].

Based on literature data [8] and the preliminary water extraction experiments (Vitasari, Unpublished results), several integrated process configurations have been evaluated to isolate acetic acid and glycolaldehyde from pyrolysis oil via water extraction in Aspen Plus® using the UNIFAC (Dortmund) property method to predict all missing parameters [7]. It was also assumed that the TOA-acid complex could be regenerated in the distillation column.

Figure 6.2 illustrates the best configuration in which 40 wt% TOA/2-ethyl-1-hexanol is used to extract acetic acid and glycolaldehyde simultaneously. This scenario provides the overall acetic acid and glycolaldehyde yields of 89.4% and 99.8%, respectively and has 2.5 times lower energy consumption compared to separate acetic acid and glycolaldehyde isolation [7].

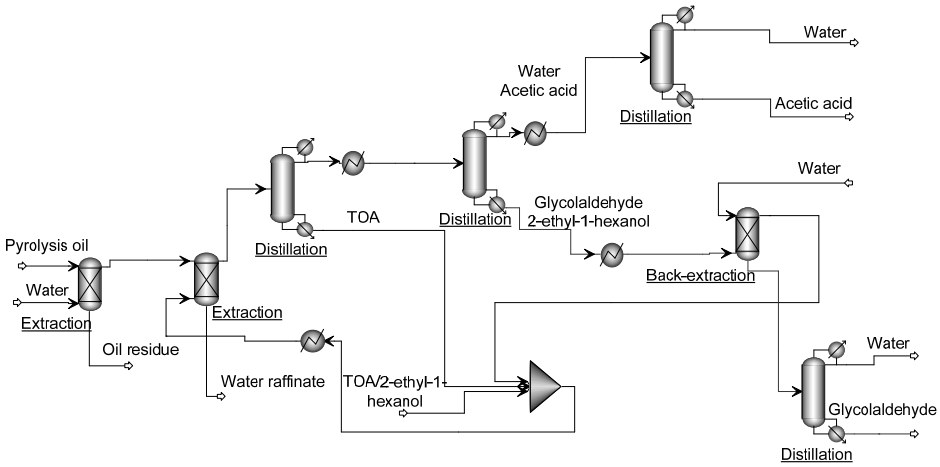

Figure 6.2: Integrated acetic acid and glycolaldehyde recovery from pyrolysis oil [7]

Considering the promising proposed production scenario, Vitasari *et al.* [9] extended the investigation on the simultaneous acetic acid and glycolaldehyde extraction [8] with a focus on the glycolaldehyde co-extraction. Two extraction schemes were recommended. The first one is the combined one-step extraction, where acetic acid and glycolaldehyde are simultaneously extracted with 2-ethyl-1-hexanol. The second method is the two-step extraction in which acetic acid is extracted with TOA/2-ethyl-1-hexanol at a concentration above 50 wt%, followed by the glycolaldehyde extraction with 2-ethyl-hexanol.

This chapter discusses the conceptual design and economic analysis of the combined one-step extraction process using 2-ethyl-1-hexanol as a solvent for forest residue- and pine-derived pyrolysis oils. The combined one-step extraction was selected over the two-step extraction since it does not employ TOA; hence, eliminates the complicated regeneration step by either temperature or diluent swings, which requires high temperature and energy consumption [10]. Unlike the previous conceptual design [7], this process simulation used more elaborate experimental data [6,9]. This process design aims to recover all acetic acid and glycolaldehyde with purity above 99%. Since some acetol may be co-extracted in the extraction, its recovery is also considered in the design. The subsequent economic analysis evaluates the economic potential of both feedstocks and the profit sensitivity to market price and plant capacity.

6.2 Process design

The conceptual process design was simulated in Aspen Plus® for a capacity of 200 kton pyrolysis oil per year, which is the same as that of the previous conceptual

design [7]. The operating time is 8000 hours per annum. The compositions of the forest residue- and pine-derived pyrolysis oils and their low heating values (LHV) are depicted in Table 6.1.

Table 6.1: Pyrolysis oil specifications [6]

	Forest residue-derived pyrolysis oil	Pine-derived pyrolysis oil
Elemental analysis:		
Carbon (wt%)	40.6	41.3
Hydrogen (wt%)	7.7	7.6
Nitrogen (wt%)	0.4	0.2
Oxygen (wt%)	51.2	50.9
Composition:		
Water (wt%)	25.6	24.9
Glycolaldehyde (wt%)	6.2	13.6
Acetic acid (wt%)	6.2	4.6
Acetol (wt%)	4.0	5.0
Furfural (wt%)	0.7	0.5
Furanone (wt%)	0.7	0.8
Levoglucosan (wt%)	1.7	1.6
Syringol (wt%)	0.3	0.1
Guaiacol (wt%)	0.2	0.6
LHV (MJ/kg)	15.3 [11]	15.3 [11]

Acetic acid and glycolaldehyde products were designed to have a purity higher than 99%. Since there is no information about the acetol purity requirement, the design aimed to achieve the highest possible acetol purity while maintaining more than 99% glycolaldehyde recovery in the glycolaldehyde purification step.

Figure 6.3 illustrates that the designed process involves three main separation methods: extraction, distillation, and evaporation, which were simulated using Extract, RadFrac, and Flash2 in Aspen Plus®, respectively. Heat integration is also incorporated for feed preheating prior to the fractionation, evaporation, and glycolaldehyde purification columns.

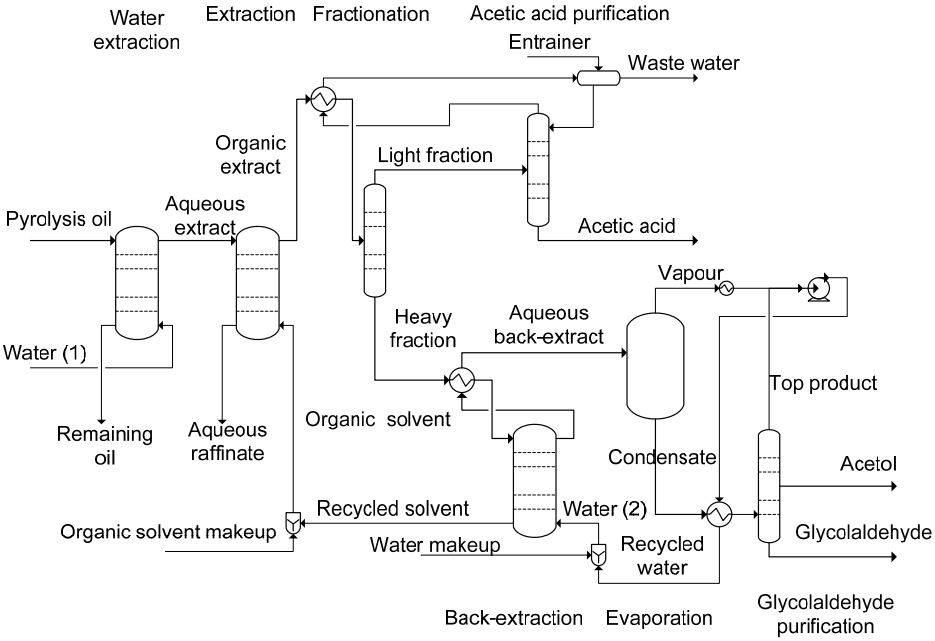

Figure 6.3: Process scheme of the integrated production of acetic acid, glycolaldehyde, and acetol

The temperature and pressure for each separation step are the same for both pyrolysis oils (Table 6.2). The extraction is conducted at atmospheric pressure, whereas distillation and evaporation are performed under vacuum to prevent glycolaldehyde degradation by keeping the operating temperature below 100 °C [12].

In the water extraction (Figure 6.3), forest residue-derived pyrolysis oil requires 50% more water compared to pine-derived pyrolysis oil to extract more than 99% acetic acid, glycolaldehyde, and acetol. This difference is mainly determined by the nature of pyrolysis oils. Forest residue-derived pyrolysis oil has an optimum water-to-oil ratio in the range of 0.65-0.7, while pine-derived pyrolysis oil should be extracted at the lowest feasible water-to-oil ratio (0.5) [6].

A solvent-to-feed ratio of 6 is needed to extract all acetic acid and glycolaldehyde from both pyrolysis oil-derived aqueous streams due to the slight independency of distribution coefficients on feed concentration [9]. Moreover, about two-thirds of the acetol is co-extracted. Hence, the aqueous raffinate of the extraction column contains a considerable amount of residual acetol and levoglucosan. This stream may be subsequently fermented to produce itaconic acid [13] or citric acid [14]. Levoglucosan may be also hydrolysed to glucose followed by fermentation to produce ethanol [15]. However, the

effect of acetol on the fermentation is still unknown. For this reason, the treatment of this aqueous raffinate stream is excluded in the process design and considered as waste.

Table 6.2: Temperature (T), pressure (P), and number of ideal stages (N) of the main separation steps

	Forest residue-derived pyrolysis oil				Pine-derived pyrolysis oil			
	T (°C)		P	N	T (°C)		P	N
	top	bottom	(mbar)	(-)	top	bottom	(mbar)	(-)
Water extraction	20		1000	55	20		1000	60
Extraction	20		1000	60	20		1000	60
Back-extraction	20		1000	3	20		1000	3
Fractionation	24.7	90.1	30	25	24.8	90.2	30	23
Acetic acid purification	87.4	117.5	1000	30	87.4	117.4	1000	45
1st effect evaporation	98.4		950		98.5		950	
2nd effect evaporation	82.9		521		82.6		518	
3rd effect evaporation	67.3		274		67.1		269	
4th effect evaporation	52.0		134		51.6		129	
5th effect evaporation	37		59		37		54	
Glycolaldehyde purification	17.5	79.6	20	20	17.5	80.1	20	20

Due to low extraction selectivity, the organic extract from the extraction column contains water, acetic acid, glycolaldehyde, and acetol in 2-ethyl-1-hexanol. In the fractionation column, only water and acetic acid are evaporated, while keeping the less volatile compounds in the bottom product. The pine-based process needs more than twice the reflux ratio compared to the forest residue-based process due to its higher acetol and glycolaldehyde contents.

Acetic acid is separated from water by heterogeneous azeotropic distillation with isobutyl acetate entrainer [16]. Pre-concentration is unnecessary prior to distillation although the distillation feed contains around 70% water [17]. Both reboiler duty and entrainer makeup flow rate were varied to achieve acetic acid purity above 99% and minimise the entrainer loss with the top water stream [16]. This water stream is saturated with 0.7 wt% isobutyl acetate. Since the effect of isobutyl acetate on the extraction and distillation is yet unknown, the water stream is considered as waste.

The bottom stream of the fractionation column is back-extracted with water to recover glycolaldehyde and acetol. The aqueous extract is very dilute, containing more

than 95% water. Thus, pre-concentration by water evaporation is needed prior to purification.

The five-effect flash evaporation is conducted at a reduced pressure (Table 6.2) to create vapour, which supplies heat to the subsequent effect. Hence, steam is only required to heat the first effect. The final concentrate comprises 79% and 63% water for forest residue- and pine-based processes, respectively.

The last separation step is glycolaldehyde purification, which is a ternary distillation with a side acetol product stream and glycolaldehyde bottom product.

Table 6.3: Comparison for forest residue- and pine-based processes at a capacity of 200 kton/a

	Forest residue-based process	Pine-based process
Glycolaldehyde:		
Yield (%)	99	99
Production rate (kton/a)	12.3	27.2
Composition (wt%)		
Glycolaldehyde	99.5	99.3
Water	0.2	0.2
Acetol	0.2	0.5
Acetic acid:		
Yield (%)	97	99
Production rate (kton/a)	12.1	9.2
Composition (wt%)		
Acetic acid	99.6	99.4
Water	0.4	0.4
Acetol		
Yield (%)	67	62
Production rate (kton/a)	5.5	6.3
Composition (wt%)		
Acetol	98.0	98.3
Water	2.0	1.7
Remaining oil (kton/a)	131.9	127.7
Aqueous residue (kton/a)	156.1	114.5
Water (kton/a)	118.7	85.4
2-ethyl-1-hexanol (ton/a)	112	88
Iso-butyl acetate (ton/a)	224	160
Total heating duty (MW)	60	64
Total cooling duty (MW)	60	65

The composition of each produced platform chemical is almost the same for both oils (Table 6.3). The glycolaldehyde from pine-derived pyrolysis oil has higher acetol content, which corresponds to the initial acetol concentration in the feedstock.

Table 6.3 also shows that the proposed process can isolate nearly all the glycolaldehyde from pyrolysis oil. In the forest residue-based process about 3% acetic acid is lost in the remaining oil and raffinate of the extraction column. Although the remaining acetic acid concentration in the bottom of the fractionation column is less than 0.1 wt%, its amount in the recycle stream somehow influences the separation degree in the extraction column.

In comparison with the previous design [7], this process gives about a 10% higher acetic acid yield, which is 97-99% versus 89% due to the use of isobutyl acetate as entrainer.

The amount of acetol loss in the extraction column corresponds to its distribution coefficient in 2-ethyl-1-hexanol, which is estimated to be two-thirds of that of glycolaldehyde, according to the Dortmund modified UNIFAC method in Aspen Plus®. However, the solvent-to-feed ratio is not increased further, considering the very dilute organic extract stream and reboiler duty of the subsequent fractionation column.

The pine-based process consumes about 7% more energy than the forest residue-based process (Table 6.3) mainly due to the higher reflux needed in the fractionation column. The distribution of the energy consumptions is illustrated in Figure 6.4.

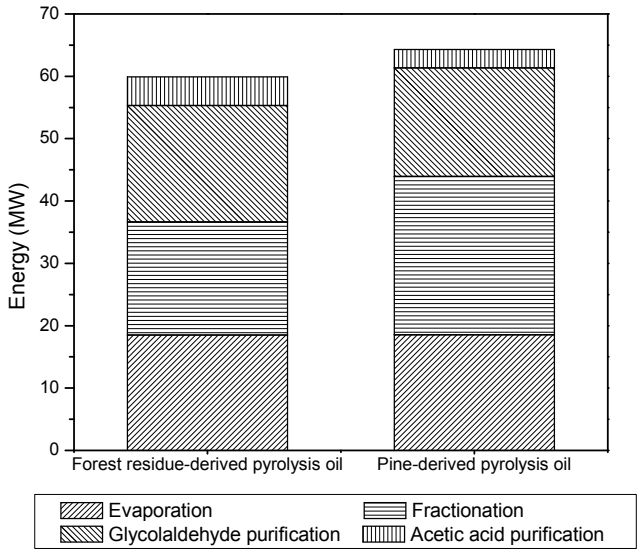

Figure 6.4: Energy requirements of the forest residue- and pine-based processes

Figure 6.4 depicts that both processes have nearly the same evaporation duty due to the same operating conditions (Table 6.2) and very dilute aqueous extract from the back-extraction. Furthermore, distillation contributes about 70% to the total energy consumption. It is also obvious that the 35% lower reboiler duty in the acetic acid purification of the pine-based process than that of forest residue-based process is caused by the lower feed flow rate at similar compositions.

6.3 Economic evaluation

Table 6.4: Important economic parameters

Parameters	Value
Operation time	8000 h/a
Capacity	25 ton pyrolysis oil per hour
Annual capacity	200 kton
Economic lifetime	10 years
Income tax rate	30 (%) [18]
Operating labour cost	96000 €/person/a
Material costs:	
Pyrolysis oil cost	30 €/MWh (LHV) [11]
Pyrolysis oil transportation cost with an average distance of 200 km	4 €/MWh (LHV)
2-ethyl-1-hexanol	1124 €/ton [19]
Isobutyl acetate	1800 €/ton [19]
Utility costs:	
Electricity	30 €/MWh
Low pressure steam	13 €/MWh transferred heat
Process water	0.6 €/m^3
Cooling water	0.0317 €/m^3
Waste water treatment	2 €/m^3
Product values:	
Glycolaldehyde	850 €/ton
Acetic acid	650 €/ton [19]
Acetol	636 €/ton
Remaining oil	30 €/MWh (LHV)

Aspen Process Economic Analyzer was used to calculate equipment dimensions and estimate the free-on-board (FOB) purchase equipment and direct costs based on the first

quarter 2009 pricing basis. Plant location was set to be adjacent to an established petroleum refinery.

The raw material, labour, and utility expenses were calculated from the generic data given in Table 6.4. The transportation cost from pyrolysis sites to the refinery was added to the pyrolysis oil price. The other capital expenditures and expenses were estimated using Peters and Timmerhaus investment factors, with a typical accuracy of ± 30% [20]. The glycolaldehyde and acetol prices were estimated to be 75% of the ethylene glycol and propylene glycol market prices, which were taken to be 1130 €/ton and 850 €/ton, respectively [19], considering that feedstock price may contribute up to 88% of the total cost of a biomass-based process [21].

This designed process will be a part of the whole pyrolysis oil-based biorefinery. The remaining oil after water extraction will be used for producing phenolic compounds or for catalytic upgrading. Thus, the remaining oil was designed to have a certain economic value.

Table 6.5: Composition of the remaining oils [6]

	Forest residue-derived pyrolysis oil	Pine-derived pyrolysis oil
Carbon (wt%)	54.61	58.88
Hydrogen (wt%)	6.96	6.95
Nitrogen (wt%)	0.40	0.22
Oxygen (wt%)	38.03	33.95
LHV (MJ/kg)	20.2	22.8

The elemental composition of the remaining oil was assumed to be the same as that of the organic raffinate phase given in the literature (Table 6.5). In comparison with the composition of pyrolysis oil feedstocks (Table 6.1), they have higher carbon content and significantly lower oxygen content, which are reflected in the increase of their heating values (Table 6.5). The higher heating value indicates that the remaining oil has better energy quality and is more suitable for catalytic conversion to conventional fuels.

Furthermore, it has been shown that the remaining oil had the same performance as the original forest residue-derived pyrolysis oil in the hydrodeoxygenation and fluid catalytic cracking processes [22]. Therefore, taking into account its higher heating LHV and performance, we assumed that the value of the remaining oil was the same as that of the pyrolysis oil feedstock (Table 6.4).

Table 6.6 shows that at the same plant capacity, the pine-based process needs higher capital investments than the forest residue-based process, which is related to its higher content of targeted bio-based chemicals leading to larger equipment.

Pyrolysis oil and steam prices have major contributions to the total product cost, which are 59-60% and 13-14%, respectively (Table 6.13). Since the pyrolysis oil price per MWh is the same for both oils and the difference in the total energy requirement is around 7% (Figure 6.4), both processes have almost the same working capital.

Table 6.6: Investments, costs, and profit for forest residue- and pine-based processes at a capacity of 200 kton pyrolysis oil per year

	Forest residue-based process	Pine-based process
Purchased equipment cost (M€)	10	10
Fixed capital investment (M€)	21	23
Working capital (M€)	48	49
Total production cost (M€/a)	44	57
Annual revenue (M€/a)	44	57
Annual revenue without the remaining oil (M€/a)	22	33
Gross profit (M€/a)	-4	9
$ROI_{before\ tax}$ (%)	-16	33
$ROI_{after\ tax}$ (%)	-	23

The larger amount of targeted compounds in pine-derived pyrolysis oil causes 30% higher annual revenue than forest residue-derived pyrolysis oil, as shown in Table 6.6. Even though the amount of the remaining oil in the pine-based process is less than that in the forest residue-based process, its LHV is higher due to the lower oxygen content (Table 6.5). In combination with the selling prices of the targeted chemicals, the value of the remaining oil brings 50% and 42% higher revenue to the forest residue- and pine-based processes, respectively.

The annual revenue of the forest residue-based process is less than the total product cost, which leads to 4 M€/a loss. In general, from Table 6.6 one can see that the economic feasibility of a pyrolysis oil-based process is determined by the composition of the pyrolysis oil feedstock.

6.4 Sensitivity analysis

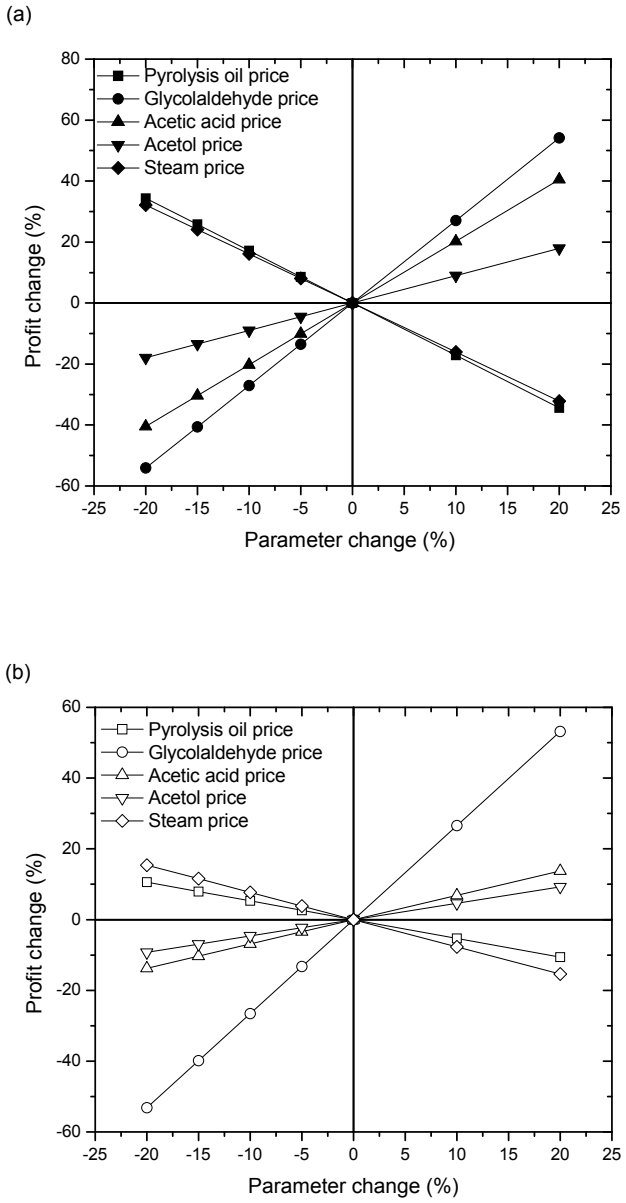

Figure 6.5: Effect of the change in feedstock, steam, and product prices for forest residue- (a) and pine-based processes (b)

The profit of the integrated bio-based chemical plant is predicted to be influenced by raw material price, energy price, product price, and plant capacity. Since these prices affect the expenditures, which are related to revenue and profit, their effects are shown in a spider diagram (Figure 6.5). Profit change is plotted against the change in price relative to the base value in Table 6.6 and Table 6.4 for profit and prices, respectively. The sensitivity to prices was assessed at a plant capacity of 200 kton/a.

Figure 6.5a illustrates that the profit of the forest residue-based process is the most sensitive to glycolaldehyde price. A 20% increase in glycolaldehyde price raises the revenue by 54%. Nevertheless, at this point the total product cost is higher than the revenue by 1.8 M€/a. In order to achieve the break-even point where the total revenue is equivalent to the total product cost, the market price of glycolaldehyde needs to increase by 37% to 1164 €/ton, assuming constant selling prices of acetic acid and acetol.

The profit is less sensitive to acetic acid and acetol prices due to their smaller contributions to the total revenue compared to that of glycolaldehyde. Increasing their selling prices by 20% improves the profit by 40% for acetic acid and 18% for acetol. The break-even point can be obtained by increasing acetic acid price by 49 % to 971 €/ton. Similarly, an acetol price of 1344 €/ton is required to cover the total product cost. In general, this sensitivity order corresponds to the price of each bio-based chemical (Table 6.4).

Pyrolysis oil and steam prices have almost the same influence on profit, which is less than glycolaldehyde and acetic acid prices (Figure 6.5a). The maximum price of forest residue-derived pyrolysis oil is 12.5 €/MWh to make the process profitable.

Figure 6.5b shows that the profit of the pine-based process is more sensitive to the glycolaldehyde price than the acetic acid price due to its larger contribution to the total annual revenue. A 20% raise in glycolaldehyde price increases the annual profit by 53% and $ROI_{before\ tax}$ to 50%. Oppositely, decreasing the glycolaldehyde price by 20% lowers the $ROI_{before\ tax}$ to 15%. Furthermore, the profit sensitivity to the steam price is slightly higher than to the pyrolysis oil price. A 20% higher steam price cuts the profit down by 15%, which gives 28% $ROI_{before\ tax}$. In contrast, a 20% lower steam price increases the $ROI_{before\ tax}$ to 38%. This more prominent steam price effect is caused by its higher energy consumption, compared to the forest residue-based process.

Figure 6.5 also depicts that the profit of the forest residue-based process is more sensitive to price change than that of the pine-based process. The total product cost of both processes is very similar; thus, the profit difference is highly determined by the revenue. Since the pine-derived pyrolysis oil contains a larger amount of glycolaldehyde, its revenue is less sensitive to the price of acetic acid and acetol.

Besides prices, plant capacity also influences the economic feasibility. The price only affects cost, revenue, and profit, whereas the change in capacity influences investments, cost, revenue, and profit.

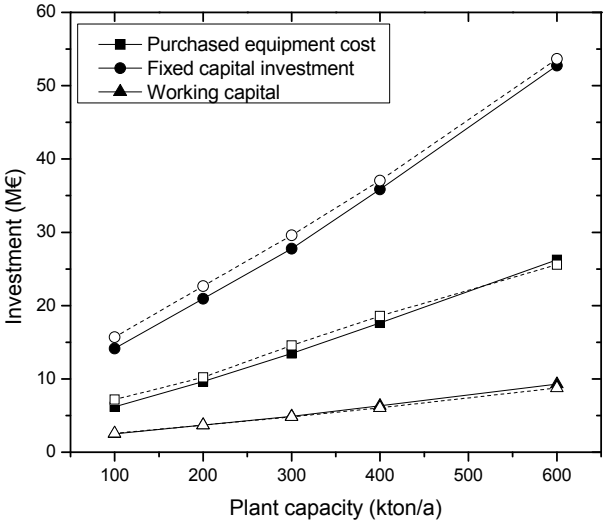

Figure 6.6: Investments for the forest residue- (closed symbols) and pine-derived pyrolysis oils (hollow symbols and dashed lines)

In agreement with Table 6.6, Figure 6.6 indicates that the pine-based process requires a slightly higher investment than the forest residue-based process. The working capital for both processes is almost the same, mainly due to the same feedstock price. The pine-based process has higher equipment cost, which corresponds to the higher separation load. However, the purchased equipment cost of both processes is very similar at the same plant capacity.

Figure 6.7 shows that the ratio between profit and investment (given as ROI) increases with plant capacity. Nevertheless, at a capacity higher than 500 kton/a the curve tends to level off, meaning that a stand-alone integrated chemical recovery process from forest-residue pyrolysis oil is not able to generate profit.

In contrast, the pine-based process is prominently more profitable than the forest residue-based process (Figure 6.7). At a plant capacity below 500 kton/a, the change in profit is more dominating than the total capital investment (TCI), leading to a considerable ROI improvement. However, above 500 kton/a the ROI levels off which indicates a relatively lower profit contribution.

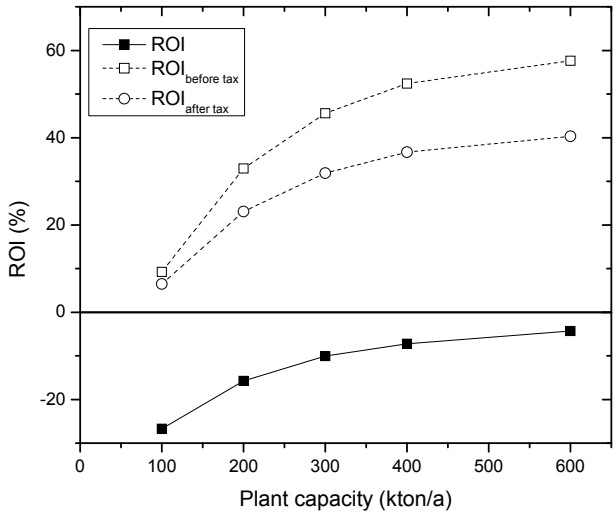

Figure 6.7: ROI as a function of plant capacity for the forest residue- (closed symbols) and pine-derived pyrolysis oils (open symbols and dashed lines)

In general, the sensitivity analysis demonstrates that pine-derived pyrolysis oil is a more feasible feedstock for chemical recovery due to the higher amount of targeted bio-based chemicals. In total, forest residue-derived pyrolysis oil contains 16.4% targeted compounds, while pine-derived pyrolysis oil comprises of 23.2% targeted chemicals (see also Table 6.1).

Since the investment does not vary remarkably with the type of pyrolysis oil as depicted in Figure 6.6, the chemical composition of the feedstock determines the process economics. Hence, it is preferable to have pyrolysis oil feedstock with high content of added value bio-based chemicals, for example glycolaldehyde, acetic acid, and acetol in this case. Furthermore, the profitability of a pyrolysis oil feedstock can be estimated by calculating its potential revenue.

6.5 Conclusions

The designed process includes three extraction, three distillation steps, and a five effect flash evaporation. It is able to produce acetic acid, glycolaldehyde, and acetol from forest residue- and pine-derived pyrolysis oils. The same operating temperature and

pressure are applicable for both processes with some design parameter adjustment to adapt with various feedstock compositions.

Both separation processes provide very similar product purities: ≥ 99.4 wt% acetic acid, ≥ 99.3 wt% glycolaldehyde, and ≥ 98 wt% acetol. The overall glycolaldehyde yield is 99%. The forest residue-based process yields 97% acetic acid and 67% acetol, whereas the pine-based process provides 99% acetic acid and 62% acetol yields. The pine-based process consumes 7% more energy than the forest residue-based process.

The forest residue-based process needs 21 M€ capital investment, while the pine-based process requires 23 M€ with an equivalent working capital of 4 M€. The remaining oil has significant contributions to the annual revenue of the design process, which are 50% and 42% for forest residue- and pine-derived pyrolysis oils, respectively. At a capacity range of 200-700 kton pyrolysis oil per year, pine-derived pyrolysis oil is more suitable feedstock that forest residue-derived pyrolysis oil. It gives positive ROI, which is in contrast with forest residue-derived pyrolysis oil with negative ROI.

The profitability of the forest residue-based process is more sensitive to feedstock and product prices compared to the pine-based process. Increasing the plant capacity above 500 kton pyrolysis oil per year only slightly improves the plant profitability further.

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Appendix 6.A: Process modelling in Aspen Plus®

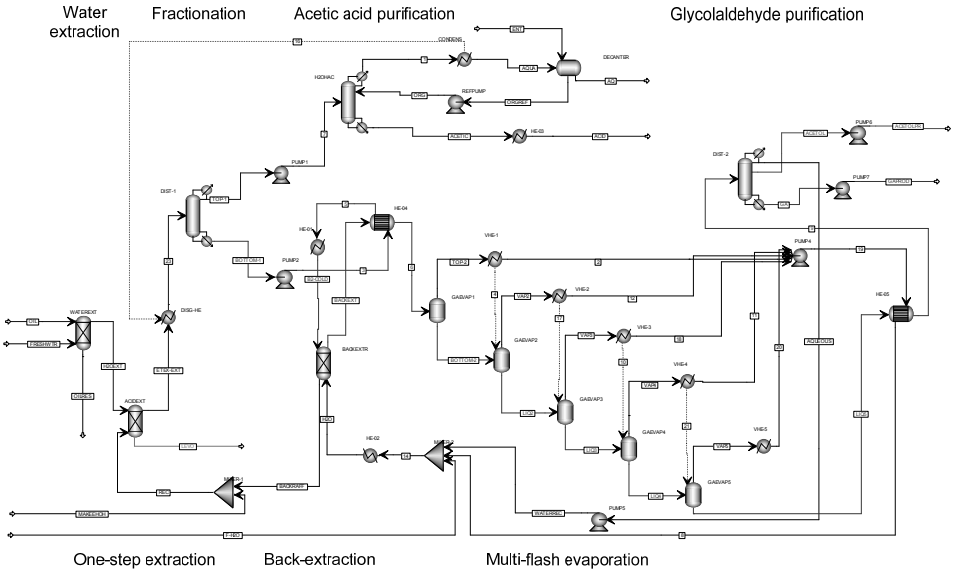

Figure 6.8: Process simulation in Aspen Plus®

The process design and simulation were performed in Aspen Plus® using Extract, RadFrac, and Flash2 blocks for extraction, distillation, and flash evaporation, respectively (Figure 6.8).

Table 6.7: Distribution coefficient data input for extraction simulation

	Water extraction		Extraction
	Forest residue-based process	Pine-based process	
Water	6.17	4.44	0.03
Furfural	0.48	0.44	0.66
Acetic acid	1.64	2.38	0.34
Guaiacol	0.35	0.26	1.59
Acetol	1.80	2.73	0.12
Glycolaldehyde	1.79	2.53	0.36
Syringol	0.37	0.78	0.20
Levoglucosan	2.46	2.8	0.04
Furanone	0.97	0.82	0.41

For the water extraction the distribution data of every investigated compound is available in the literature [6]. For the extraction step the acetic acid and glycolaldehyde distribution coefficients can be found in the literature [9], whereas those of the other compounds were estimated using the Dortmund modified UNIFAC (UNIF-DMD) property method in Aspen Plus® (Table 6.7). The distribution coefficients in the back-extraction were assumed to be the reciprocal of those in the forward extraction [23].

The non-random two-liquid (NRTL) property method was used for the vapour-liquid equilibrium calculation. The NRTL model modified with the Hayden-O'Connell equation (NRTL-HOC) was applied for acetic acid purification to incorporate acetic acid dimerisation in the vapour phase [16].

The Aspen Plus® built-in Antoine vapour pressure parameters were used in the simulation, except for syringol and glycolaldehyde. The syringol vapour pressure was predicted using the Riedel method. For glycolaldehyde, vapour pressure measurement of a mixture of glycolaldehyde and ethylene glycol in Fischer® VLE 602 equipment showed that the Wagner parameters in Aspen Plus® are reliable to estimate glycolaldehyde vapour pressure below its boiling point (Figure 6.9).

Pyrolysis oil was resembled in the simulation to consist of water, acetic acid, glycolaldehyde, acetol, furfural, furanone, guaiacol, syringol, and levoglucosan. The remaining components were represented by toluene, which was assumed to be non-extractable with water.

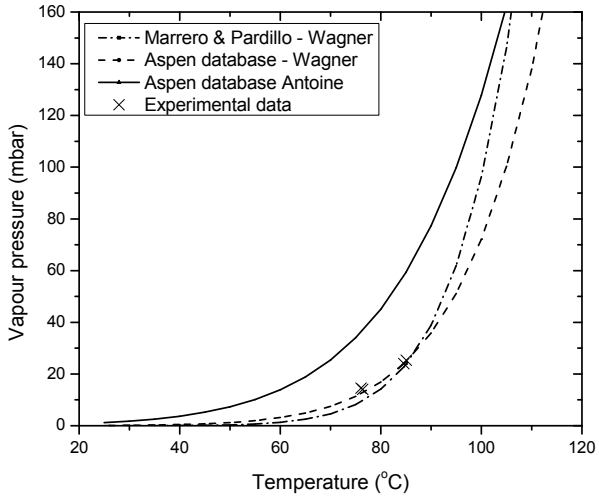

Figure 6.9: Comparison of experimental data and different estimation methods in Aspen Plus®

The high heating value (HHV) and low heating value (LHV) of the remaining oil are predicted using the following equations:

HHV (MJ/kg) [24]:

$$HHV = 0.335(\%C) + 1.423(\%H) - 0.154(\%O) - 0.145(\%N) \quad (6.1)$$

LHV (MJ/kg) [25]:

$$LHV = HHV - 0.21813(\%H) \quad (6.2)$$

The process simulation gives the operating conditions of each separation step as tabulated in Table 6.8. Furthermore, the flow rate and composition of several important streams are depicted in Table 6.9 and Table 6.10.

Table 6.8: Detail operating conditions of the main separation steps

	Forest residue-based process	Pine-based process
Water extraction		
Temperature (°C)	20	20
Pressure (bar)	1	1
Number of ideal stages	55	60
One-step extraction		
Temperature (°C)	20	20
Pressure (bar)	1	1
Number of ideal stages (-)	60	60
Fractionation		
Feed temperature (°C)	74.8	63.0
Top temperature (°C)	24.7	24.8
Bottom temperature (°C)	90.1	90.2
Pressure (mbar)	30	30
Number of ideal stages (-)	25	23
Reflux ratio (-)	5	11.7
Condenser duty (MW)	16.9	23.6
Reboiler duty (MW)	18.1	25.4
Acetic acid purification		
Feed temperature (°C)	24.9	24.9
Top temperature (°C)	87.4	87.4

Table 6.8: Detail operating conditions of the main separation steps (continued)

	Forest residue-based process	Pine-based process
Bottom temperature (°C)	117.5	117.4
Pressure (bar)	1	1
Number of ideal stages (-)	30	45
Reflux ratio (-)	3.96	3.97
Condenser duty (MW)	4.6	3.0
Reboiler duty (MW)	4.6	3.0
Back-extraction		
Temperature (°C)	20	20
Pressure (bar)	1	1
Number of ideal stages	3	3
Evaporation		
1st effect		
Temperature (°C)	98.4	98.5
Pressure (mbar)	950	950
Heat duty (MW)	18.5	18.6
2nd effect		
Temperature (°C)	82. 9	82.6
Pressure (mbar)	521.3	517.7
Heat duty (MW)	12.7	12.3
3rd effect		
Temperature (°C)	67.3	67.1
Pressure (mbar)	273.8	268.6
Heat duty (MW)	14.9	14.5
4th effect		
Temperature (°C)	52.0	51.6
Pressure (mbar)	134.0	128.8
Heat duty (MW)	16.5	16.1
5th effect		
Temperature (°C)	37.0	37.0
Pressure (mbar)	58.7	54.1
Heat duty (MW)	17.6	17.2
Glycolaldehyde purification		
Feed temperature (°C)	38.3	40.6
Top temperature (°C)	17.5	17.5
Side temperature (°C)	43.0	43.7
Bottom temperature (°C)	79.6	80.1

Table 6.8: Detail operating conditions of the main separation steps (continued)

	Forest residue-based process	Pine-based process
Pressure (mbar)	20	20
Number of ideal stages (-)	20	20
Reflux ratio (-)	2.8	3.2
Number of ideal stages (-)	30	45
Condenser duty (MW)	22.0	20.5
Reboiler duty (MW)	18.7	17.4

Table 6.9: Mass balance of the forest residue-based process (refer to Figure 6.3)

Stream	Mass flow (kg/h)	Composition (wt%)											
		Wa-ter	Fur-fural	Acetic acid	Guai acol	Ace-tol	Glycol-aldehyde	Syrin-gol	Levo-glucosan	Furan one	Organic fraction	2-ethyl-1-hexanol	Iso-butyl acetate
Pyrolysis oil	25000	25.6	0.7	6.2	0.2	4.0	6.2	0.3	1.7	0.7	54.4		
Water (1)	10100	100											
Aqueous extract	18608	74.4	0.4	8.3		5.4	8.3	0.1	2.3	0.7			
Remaining oil	16492	16.1	0.6		0.2			0.3		0.3	82.5		
Aqueous raffinate	15565	93.9	0.1			2.3			2.7	0.8			
Organic solvent makeup	14											100	
Organic extract	118048	3.3	0.1	1.3		0.6	1.3					93.2	
Organic solvent	115149	4.1	0.1									95.6	
Light fraction	5430	72.3		27.7									
Heavy fraction	112618		0.1			0.7	1.4					97.7	
Entrainer	28											100	
Waste water	3950	99.3											0.7
Water (2)	135719	99.3		0.1		0.5						0.1	
Aqueous back-extract	134214	97.6		0.1		1.0	1.2						
Condensate	10753	79.3		0.2		6.3	14.3						
Top product	8527	99.7		0.2									
Acetol product	684	2.0				98.0							
Glycolaldehyde product	1542	0.2				0.2	99.5						
Acetic acid product	1508	0.4		99.6									

Table 6.10: Mass balance of the pine-based process (refer to Figure 6.3)

Stream	Mass flow (kg/h)	Composition (wt%)											
		Wa-ter	Fur-fural	Acetic acid	Guai acol	Ace-tol	Glycol-aldehyde	Syrin-gol	Levo-glucosan	Fura none	Organic fraction	2-ethyl-1-hexanol	Iso-butyl acetate
Pyrolysis oil	25000	24.9	0.5	4.6	0.2	5.0	13.6	0.1	1.6	0.8	48.7		
Water (1)	6850	100											
Aqueous extract	15889	59.9	0.3	7.2		7.9	21.4		2.5	0.7			
Remaining oil	15961	22.3	0.5		0.2					0.6	76.3		
Aqueous raffinate	11739	91.5	0.1			3.8			3.4	0.9			
Organic solvent makeup	11											100	
Organic extract	96913	2.7		1.2		0.9	3.5					91.6	
Organic solvent	92856	4.1	0.1									95.6	
Light fraction	3703	69.1		30.9									
Heavy fraction	93210		0.1			0.9	3.6					95.2	
Entrainer	20												100
Waste water	2573	99.3											0.7
Water (2)	131170	99.0				0.7	0.2						0.1
Aqueous back-extract	131535	95.8				1.3	2.7						
Condensate	11370	63.2				7.1	29.7						
Top product	7186	99.7		0.1		0.2							
Acetol product	788	1.7				98.3							
Glycolaldehyde product	3396	0.2				0.5	99.3						
Acetic acid product	1150	0.4		99.4									

Appendix 6.B: Economics

Table 6.11: Equipment specification for forest residue- and pine-based processes at a capacity of 200 kton pyrolysis oil per year (see also Figure 6.8) and the Purchased Equipment Cost (PEC) and Direct Cost (DC)

		Forest residue-based process			Pine-based process		
Equipment	Code	Specification	PEC (k€)	DC (k€)	Specification	PEC (k€)	DC (k€)
Water extractor	WATEREXT	N:78, D: 1.44 m, H: 50.8 m	613.2	891.8	N: 79, D: 1.5 m, H: 51.4 m	654.7	959.1
Acid extractor	ACIDEXT	N: 86, D: 2.8 m, H: 43.6 m	800.3	1252.8	N: 86, D: 2.5 m, H: 55.6 m	757.9	1196
Back-extractor	BACKEXT	N: 5, D: 3.7 m, H: 6.4 m	140.8	474.3	N: 5, D: 3.5 m, H: 7.0 m	132.2	420.7
Distillation	DIST-1	N: 34, D: 9.8 m, H: 23.9 m	3080.0	4434.1	N: 31, D: 10.5 m, H: 22.1 m	3707.7	5237.2
Distillation	H2OHAC	N: 42, D: 2.3 m, H: 28.8 m	878.4	1549.1	N: 63, D: 1.8 m, H: 41.6 m	780.9	1341.5
Distillation	DIST-2	N: 26, D: 9.1 m, H: 19.5 m	2826.0	4177.6	N: 26, D: 10.2 m, H: 19.0 m	2950.6	5276.3
Evaporator 1	GAEVAP1	D: 2.0 m, H: 6.1 m	34.3	188.7	D: 2.0 m, H: 5.9 m	33.9	188.1
Evaporator 2	GAEVAP2	D: 2.0 m, H: 5.5 m	93.5	351.9	D: 2.0 m, H: 5.5 m	91.4	192.4
Evaporator 3	GAEVAP3	D: 2.4 m, H: 4.0 m	114.2	377.0	D: 2.3 m, H: 4.0 m	108.5	364.7
Evaporator 4	GAEVAP4	D: 3.0 m, H: 3.8 m	175.0	474.8	D: 3.0 m, H: 3.8 m	174.1	473.9
Evaporator 5	GAEVAP5	D: 4.4 m, H: 3.8 m	279.3	620.6	D: 4.4 m, H: 3.8 m	278.8	620.1
Heat exchanger 1	HE-01	23 m^2	13.9	70.0	19 m^2	12.5	68.5
Heat exchanger 2	HE-02	320 m^2	68.8	166.7	244 m^2	67.7	165.6
Heat exchanger 3	HE-03	4 m^2	1.8	71.5	3 m^2	1.6	71.1
Heat exchanger 4	HE-04	736 m^2	153.2	295.0	577 m^2	100.4	232.3
Heat exchanger 5	HE-05	300 m^2	65.9	170.0	296 m^2	65.6	169.7
Pump 1	PUMP1	1.7 L/s, 10 m, 0.6 kW	4.1	29.6	1.0 L/s, 10 m, 0.3 kW	4.0	29.5
Pump 2	PUMP2	43. 7 L/s, 13 m, 5.5 kW	11.8	61.5	32.2 L/s, 22 m, 6.4 kW	10.6	60.2
Pump 4	PUMP4	39.6 L/s, 10 m, 5.5 kW	11.2	60.8	35.0 L/s, 10 m, 4.6 kW	11.0	60.6
Pump 5	PUMP5	2.6 L/s, 10 m, 0.8 kW	4.3	28.6	2.0 L/s, 10 m, 0.5 kW	4.2	28.5
Pump 6	PUMP6	0.2 L/s, 0.5 m, 0.2 kW	3.8	24.5	0.2 L/s, 9.5 m, 0.1 kW	3.9	25.6
Pump 7	PUMP7	0.4 L/s, 7.5 m,0.2 kW	3.89	25.6	0.2 L/s, 0.5 m, 0.4 kW	4.0	29.5
Total			**9631.8**	**16206.5**		**10205.9**	**17616.3**

Table 6.12: Indirect cost of the Fixed Capital Investment (FCI)

Investment/cost items (M€)	Percentage [5]	Forest residue-derived pyrolysis oil	Pine-derived pyrolysis oil
Indirect cost			
Engineering and supervision	7% DC [6] or 5.4% FCI	1.13	1.23
Construction	10% PEC or 4.9% FCI	0.96	1.02
Legal	2% PEC or 1.1% FCI	0.22	0.23
Contractor's fee	5% PEC or 2.4% FCI	0.48	0.51
Contingency	18% PEC or 8.8% FCI	1.93	2.04
FCI		**20.93**	**22.66**

Table 6.13: Total product cost

Cost (M€/a)	Estimation [5]	Forest residue-derived pyrolysis oil		Pine-derived pyrolysis oil	
Raw materials:					
Pyrolysis oil		28.90		28.90	
Operating labour		1.54		1.54	
Operating supervision	15% operating labour	0.23		0.23	
Utilities:					
Electricity		0.12		0.18	
Steam		6.23		6.69	
Waste treatment and disposal		0.31		0.23	
Utility water		0.99		1.09	
Maintenance and repair	5% FCI	1.05		1.13	
Operating supplies	15% maintenance and repair	0.16		0.17	
Laboratory	15% operating labour	0.23		0.23	
Solvents:					
2-ethyl-1-hexanol		0.13		0.10	
Water		0.07		0.05	
Isobutylacetate		0.40		0.28	
Variable production cost			**40.36**		**40.82**
Depreciation	10% FCI	2.09		2.26	
Taxes	2% FCI	0.42		0.45	
Insurance	1% FCI	0.21		0.23	
Fixed charges			**2.72**		**2.94**
Plant overhead cost	50% (operating labour, supervision, and maintenance)		**1.41**		**1.45**
Manufacturing cost			***44.49***		***45.21***
Administration	15% operating labour	0.23		0.23	
Distribution and marketing	2% manufacturing cost	0.98		0.99	
Research and development	5% manufacturing cost	2.22		2.26	
General expenses			***3.43***		***3.48***
Total product cost			***47.92***		***48.70***

Profitability calculation

The annual gross profit/profit before tax (G_p) is defined as the difference between the annual revenue (*S*) and total production cost (*TPC*) [26].

$$G_p = S - TPC \tag{6.3}$$

The total annual revenue is the sum of the sales of acetic acid, glycolaldehyde, and acetol and the value of the remaining oil.

The annual net profit (N_p) is the amount of profit after income tax deduction. Therefore,

$$N_p = G_p - (1 - \emptyset) \tag{6.4}$$

In which Φ is the income tax rate [26].

Return on Investment (*ROI*) is used as the profitability criterion without taking into account the time value of money [27]. It is calculated based on both gross and net annual profit and total capital investment (*TCI*). Thus,

$$ROI_{before\ tax} = \frac{G_p}{TCI} \tag{6.5}$$

and

$$ROI_{after\ tax} = \frac{N_p}{TCI} \tag{6.6}$$

7 Conclusions and recommendations

This research aimed to develop a glycolaldehyde isolation process from wood-derived pyrolysis oils. Physical and reactive extraction routes have been investigated. The separation process based on the simultaneous extraction of acetic acid and glycolaldehyde with 2-ethyl-1-hexanol appears to be more promising than reactive extraction with amines and the two-step extraction process.

7.1 Conclusions

The objective of this research was to develop an extraction-based separation process to isolate bio-based glycolaldehyde from wood-derived pyrolysis oils. In order to achieve the objective, the following investigations have been done.

- Detailed study on water extraction
- Solvent screening
- Exploration of several routes based on physical and reactive extractions
- Conceptual process design and economic analysis

Water extraction of pyrolysis oil is proven to be an important initial separation step. It is not selective, but it is capable to decrease the oxygen content of the pyrolysis oil; hence, it reduces considerably the complexity of the pyrolysis oil. Water extraction suffers from water dilution and therefore, the extraction needs to be done at the optimum water-to-oil ratio which provides the highest distribution coefficient of the targeted polar compounds (in this case glycolaldehyde and acetic acid). This optimum ratio is feedstock dependent.

It has been demonstrated that glycolaldehyde can be extracted selectively from a pyrolysis oil-derived aqueous phase by reactive extraction with 2-ethylaniline in 1-octanol, Primene JM-T in *n*-hexane, or Primene JM-T in 1-octanol. Glycolaldehyde dissolves in the organic phase and subsequently reacts with an amine extractant in the organic phase according to the Schiff-base formation. Although a single stage forward extraction is capable to provide more than 90% glycolaldehyde yield, imine stability and the characteristics of the organic phase hinder glycolaldehyde regeneration by hydrolysing the imine into glycolaldehyde and the corresponding amine.

Since a glycolaldehyde regeneration method is not yet established, the physical extraction of glycolaldehyde with an organic solvent was selected as an alternative. It appears that 2-ethyl-1-hexanol can simultaneously extract acetic acid and glycolaldehyde with a slight effect of the feed composition. The addition of tri-*n*-octylamine to 2-ethyl-1-hexanol improves the acetic acid extraction, but reduces the glycolaldehyde co-extraction. Based on this knowledge, two integrated process scenarios have been proposed. For a combined one-step extraction process acetic acid and glycolaldehyde are extracted together with pure 2-ethyl-1-hexanol. For a two-step extraction process acetic acid is firstly extracted with an organic solution containing more than 50 wt% tri-*n*-octylamine in 2-ethyl-1-hexanol, followed by glycolaldehyde extraction in pure 2-ethyl-1-hexanol.

The principle of the two-step acetic acid and glycolaldehyde recovery has been proven in a batch laboratory scale process developed to produce an aqueous glycolalde-

hyde solution as fermentation feedstock. This process includes acetic acid removal from a pyrolysis oil-derived aqueous mixture with tri-*n*-octylamine/toluene, glycolaldehyde extraction from the acetic acid-lean aqueous mixture with 1-octanol, and back-extraction with water. The aqueous product fulfils the product specifications and contains 3.9 wt% glycolaldehyde, 0.3 wt% acetic acid, and 0.3 wt% acetol. A fermentation test at Metabolic Explorer (France) showed that it provides the same performance as pure glycolaldehyde feedstock with a bioconversion yield of 98%.

Furthermore, a conceptual process design has been developed for a continuous industrial scale process based on the one-step simultaneous extraction principle. The design incorporates experimental data, solvent recycle, and heat integration. The simulation shows that the separation sequence and operating temperatures and pressures are independent of the nature of pyrolysis oil. The designed process is proven to provide similar product compositions: ≥ 99.4 wt% acetic acid, ≥ 99.3 wt% glycolaldehyde, and ≥ 98 wt% acetol. Pine-derived pyrolysis oil is more profitable than forest residue-pyrolysis oil, which is in accordance with their acetic acid, glycolaldehyde, and acetol contents.

In conclusion, water extraction is a very useful initial step to reduce the complexity of pyrolysis oil. Although reactive extraction with Primene JM-T or 2-ethylaniline is promising to be selective with high performance, glycolaldehyde regeneration by hydrolysis from the corresponding imine is currently still a challenge. As an alternative, physical extraction with 2-ethyl-1-hexanol is capable to extract acetic acid and glycolaldehyde from a pyrolysis-derived aqueous mixture. The economy of the isolation of glycolaldehyde and other bio-based chemicals is determined by their concentrations in the pyrolysis oil. In this case, pine-derived pyrolysis oil is preferable over forest residue-derived pyrolysis oil. The combined one-step extraction process is more promising than the other discussed extraction technologies.

7.2 Recommendations for future research

This study on wood-derived pyrolysis oils can also be done for agricultural- and waste-derived pyrolysis oils. Compared to wood-derived pyrolysis oils, agricultural- and waste-derived pyrolysis oils have in general higher nitrogen contents (Table 7.1). Thus, besides oxygenated compounds these pyrolysis oils may also contain nitrogenated components in the form of indoles, nitriles, pyrroles, amides [1,2], indan, and pyrazines [1].

The investigation on water extraction can be expanded to various wood- and non-wood-derived pyrolysis oils. It will be useful to study whether there is a general trend of the influence of pyrolysis oil composition on the optimum water-to-oil ratio. Furthermore, it is also necessary to verify whether the process conditions described in Chapter 6 are also applicable for non-wood-derived pyrolysis oils.

Table 7.1: Elemental compositions of non-wood-derived pyrolysis oils

Elements	Switch-grass [4]	Alfalfa [4]	Waste sludge [5]	Corn-cob [6]	Orega-num stalk [6]	Straw [6]	Micro-algae [7]
C (wt%)	47.47	53.88	70.9	45.01	53.70	48.34	61.52
H (wt%)	6.96	8.47	10.3	8.48	5.78	6.16	8.5
O (wt%)	45.19	32.37	11.1	45.26	37.57	43.99	20.19
N (wt%)	0.36	4.59	7.5	1.10	2.64	1.25	9.79
S (wt%)		0.05	0.2	0.15	0.44	0.27	
Cl (wt%)		249					
Ash (wt%)	0.01	0.28					
H/C	1.76	1.89	1.74	2.26	1.29	1.53	1.66

It has been shown in Chapter 3 that antisolvent-induced regeneration can hydrolyse imines and recover glycolaldehyde in an aqueous mixture. However, an investigation needs to be done to select a suitable antisolvent as well as a high performance catalyst, which works effectively below 100 °C and is easily separated from the glycolaldehyde aqueous product solution. Antisolvent candidates could be either inert liquids or gases. A gaseous antisolvent may have more potential than a liquid one since it can be easily removed by flash distillation, resulting in a considerable lower energy consumption [3].

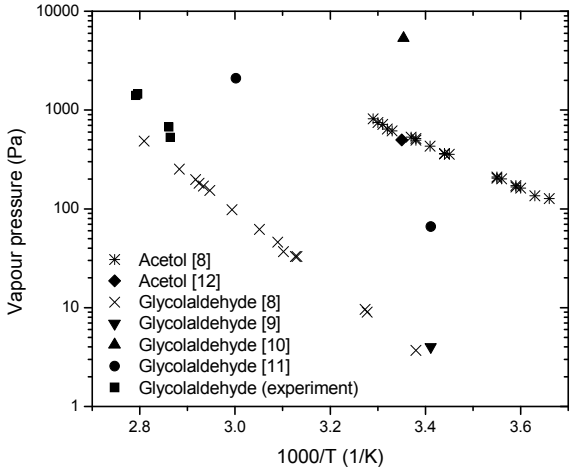

Figure 7.1: Literature and experimental data of the vapour pressure of glycolaldehyde and acetol

The conceptual process design in Chapter 6 involves multi-component distillation of glycolaldehyde and acetol for product purification. This distillation needs experimental verification taking into account a large difference of some reported data of the vapour pressure of glycolaldehyde [8-11] and acetol [8,12], as indicated in Figure 7.1.

The data discrepancies may be related to the complex behaviour of glycolaldehyde in different phases. At ambient temperature glycolaldehyde exists as a solid dimer (2,5-dihydroxy-1,4-dioxane) in a mixture of α and β phase [13] with a melting point of 80-90 °C, while the melting point of glycolaldehyde monomer is 97 °C [14]. As a melt, as a super cooled liquid at 30 °C, or in a mixture with water or polar organic solvents, glycolaldehyde is present as an equilibrium between monomers and dimers [15]. This equilibrium depends on the type of solvent and the temperature [16,17]. In the vapour phase, it exists as (*Z*)-monomers [16]. The measurement of glycolaldehyde vapour pressure from different mixtures will be useful to correlate the dimer-monomer equilibrium and glycolaldehyde vapour pressure. This correlation might be also useful to explain the discrepancies shown in Figure 7.1.

Chapter 6 shows that the extraction of acetic acid and glycolaldehyde requires a rather large amount of 2-ethyl-1-hexanol due to the fairly low distribution coefficient of glycolaldehyde in 2-ethyl-1-hexanol. As an alternative, 1-heptanol may be also used as a solvent. Experimental data show that the distribution coefficient of acetic acid in 1-heptanol [18,19] is higher than that in 2-ethyl-1-hexanol [20,21]. Since 1-heptanol is more polar than 2-ethyl-1-hexanol and 1-octanol, it is expected to be capable to provide a higher glycolaldehyde distribution and yield.

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List of Publications

Journals

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C.R. Vitasari, M. Jurascik, K.J. Ptasinski (2011) *Exergy analysis of biomass-to-synthetic natural gas (SNG) process via indirect gasification of various biomass feedstock,* Energy, 36(6), 3825-3837.

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C.R. Vitasari, G.W. Meindersma, A.B. de Haan, Production of renewable glycolaldehyde from pyrolysis oil for fermentation feedstock. Biocoup Book (in preparation).

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C.R. Vitasari, G.W. Meindersma, A.B. de Haan (2011) *Renewable glycolaldehyde isolation from pyrolysis oil by reactive extraction with primary amines*, Proceeding of the 19th International Solvent Extraction Conference (ISEC 2011), Santiago de Chile, Chile, 3 – 7 October 2011, L. Fernando Valenzuela, B. A. Moyer (Eds.), 142.

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Conference presentations

Oral presentations

Techno-economic evaluation of integrated renewable acetic acid, glycolaldehyde, and acetol production from biomass-derived pyrolysis oil, 2012 AIChE Annual Meeting, Pittsburgh, USA, 28 October – 2 November 2012.

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Curriculum Vitae

Caecilia Vitasari was born on 7 March 1980 in Tanjung Karang, Indonesia. After finishing Bachelor of Engineering in Chemical Engineering in 2003 at Gadjah Mada University in Yogyakarta, Indonesia, she worked for three years as a Chemical Engineering lecturer at Lampung University, Indonesia. In 2006 she was granted a scholarship from the TU/e Scholarship Foundation to pursue a master study in Process Engineering at Eindhoven University of Technology, the Netherlands. In May 2008 she graduated within the Chemical Reactor Engineering group on Exergy analysis of biomass-to-synthetic natural gas conversion via indirect gasification. From 1 May 2008 she started a PhD project at Eindhoven University of Technology. The topic of the research was Renewable chemicals from biomass, which was a part of the Biocoup project from the European Commission. During her PhD she completed the education program within the Netherlands Research School in Process Technology (OSPT) and obtained the OSPT certificate in October 2011. On 1 May 2012, she joined Institute of Sustainable Process Technology (ISPT) as a post-doctoral researcher, working on the new selector/ligand families for recovery intensification by affinity separations.