Exploratory studies on fast pyrolysis oil upgrading

Mahfud, Farchad Husein

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2007

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Mahfud, F. H. (2007). Exploratory studies on fast pyrolysis oil upgrading s.n.

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
CHAPTER 6


6.1 Introduction

Increased consumption of fossil fuels in the last century has created considerable environmental problems (i.e. green gas house emissions) and resulted in a significant increase in the price of crude oil. This has encouraged the exploration of renewable resources like biomass for energy generation. Flash pyrolysis oil, also known as bio-oil (BO), is a biomass-derived product. It is produced via flash pyrolysis technology yielding up to 70%-wt of BO. BO is a complicated mixture of a wide variety of organic compounds belonging to different compound classes (acids, ketones, aldehydes, phenolics). BO also contains significant amounts of water and values between 15-30 wt% have been reported. The possible applications of the BO are large, like the use as a bio-fuel for boilers, co-firing in power plants, as a green liquid transportation fuel or as a source for valuable chemicals [1].

Crude BO as such is not suitable as a fuel for stationary and non-stationary combustion engines and upgrading is required. The rather acidic nature of BO (pH ca. 2.5-3.0), caused by the presence of large amounts of organic acids (acetic acid, propionic acid), is considered a critical issue. Acetic acid levels up to 8-10%-wt have been reported [2], although the actual level depends on the feedstock and processing conditions. The acidity (pH ranges from 2 to 3) limits its application due to extensive corrosion a.o. of the Acetic acid is an important industrial commodity with a world wide production of over eight million tons per annum [4]. The demand for acetic acid has accelerated over the past few years [5, 6] due to increased demands for derivatives like vinyl acetate monomer (VAM). Currently, acetic acid is mainly produced from non-renewable feedstocks, e.g. by methanol carbonylation [6]. Market prices of acetic acid (1.2 $/kg, 2006 level) are considerably higher than price predictions for BO (0.05-0.15 $/kg). Therefore, extraction of acetic acid from the BO could, besides improving the product properties, also significantly boost the economic attractiveness of BO. In addition, such a process could be integrated with an upgrading process for fuel production. [1].
Various technologies have been reported for the separation of organic acids from complex mixtures. Examples are (catalytic) distillation [7], adsorption using ion-exchange resins [8], and micro emulsion liquid membrane separation [9]. However, none of these techniques seems to be applicable and/or compatible with a highly viscous, thermally not very stable, complex material like BO.

Reactive liquid-liquid extraction (RLLE) of carboxylic acids by suitable extractant could be a promising alternative [10-18]. Aliphatic tertiary amines in organic solvents are powerful extractants for carboxylic acids. Reactive-extraction using these tertiary aliphatic amines as extractants is commonly used for the recovery of carboxylic acids from aqueous mixtures such as fermentation broths and waste water streams. Examples are the extraction of citric and lactic acid from fermentation broths [10, 12]. For citric acid, the extraction was carried out with a long-chain tertiary amine in a hydrocarbon (kerosene, dodecane) solvent. After extraction, the acids are typically recovered by back extraction with hot water or distillation of the organic phase.

This study describes the recovery of acetic acid from BO by reactive-extraction using tertiary amines. To the best of our knowledge, this technique has not been applied to recover organic acids from BO. Factors affecting the extraction efficiency like the type and concentration of amines and co solvents were investigated. Two different BO sources were applied (i) crude BO derived directly from a flash pyrolysis process, and (ii) the aqueous layer of a thermally treated BO.

### 6.2 Experimental section

#### 6.2.1 Materials and analytical methods

**Materials.** Crude bio-oil and the aqueous fraction of a thermally treated water fraction of BO were kindly provided by the Biomass Technology Group, B.V. (BTG). The crude BO
was obtained by flash pyrolysis of beech wood in a rotating cone reactor [19]. The aqueous fraction of a thermally treated pyrolysis oil was obtained by treatment of BO at 300-340°C and 140 bar. The acetic acid level in the aqueous phase was 6.2 wt%. tri-n-Octylamine (TOA) and tri-dodecylamine (TDDA) were acquired from ACROS (98.0% purity). Tetrahydrofuran, hexane, octane and dodecane (all > 99.0% purity) and pet-ether were also purchased from Across Organics.

**Analysis.** Acetic acid and TOA concentrations in the various phases were quantified using GC-FID. An Hewlett Packard (5890 series II) gas chromatograph equipped with a fused silica column (CB–FFAP, 30 m x 0.32 m x 0.25 µm) and helium as carrier gas was applied. GC/FID conditions were as follows: oven temperature 250°C; heating rate 10°C/min, Injector temperature 300°C, 100:1 split ratio, Initial time 1 min.; final time 5 min. The acetic acid-tertiary amine complex was not detected in the GC-chromatograms due to reversible decomplexation in the GC at elevated temperatures and separate peaks for acetic acid and the tertiary amine were observed.

**Quantification of acetic acid in the amine phase**

An internal standard solution for calibration (henceforth called THF-IS mixture) was prepared by dissolving hexadecane (internal standard, 160 mg) in THF (160 g). Subsequently, acetic acid calibration samples were prepared by the addition of the THF-IS mixture (0.72 g) into mixtures of BO (7.2 mg) and acetic acid (0.0 mg, 0.9 mg, 2.0 mg, 3.7 mg and 8.2 mg). The calibration samples were analysed using GC-FID (duplo run) to generate a calibration curve for acetic acid. To quantify the acetic acid in the amine phase, 0.72 g THF-IS was added to 7.2 mg of the amine phase. The acetic acid content was determined by comparing the area of the acetic acid signals of the samples with that of the calibration curve. All analysis were carried out in duplo.

**Quantification of TOA in BO phase**

The calibration curve for TOA in the BO-phase was prepared by GC-FID analysis of mixtures prepared from BO (1.0 mg), THF-IS (0.72 g), and TOA (0, 1.93 mg, 3.4 mg and 4.6 mg). All analyses were carried out in duplo. For TOA quantification in the BO phase after extraction, 1 mg of the BO phase was added to the 0.72 g of THF-IS mixture. The quantity of TOA was determined by comparing the area of the TOA signals with that of the calibration curve.
6.2.2 Typical experimental procedure for reactive-extraction of acetic acid from BO

The experiments were carried out in two experimental set-ups, differing in size and the method of stirring of the L-L system.

a. Reactions in a batch reactor with overhead stirring (Method A)

Typically, equal volumes of BO and a solution of TOA in an appropriate solvent (each 100 ml) were mixed in a 500-ml batch reactor using a Rushton turbine (1000 rpm) at atmospheric pressure and room temperature ($T = 293$ K). Samples of both layers were taken in time ($t = 10, 15, 30, 60$ and $120$ minutes and $3$ h). At the end of the extraction process, the two liquid phases allowed to settle and were separated using a separation funnel. Both liquid phases were analyzed and weighed to determine the mass balances for the various species.

b. Reactions in small glass vials using external stirring (Method B)

Typically, equal volumes BO (2.5 ml) in a co-solvent (2.5 ml) and a solution of TOA (2.5 ml) in a suitable organic solvent (2.5 ml) were added to a glass vial (20 mL). The vials were placed in a rotator device (Stuart scientific rotator, STR 4 series) and rotated at room temperature and maximum rotor speed (55 rpm). After $16$ hr, the two liquid layers were separated. Both liquid phases were analysed and weighted to determine the mass balances for the various species.

6.2.3 Terminology and theory

Organic acid extraction from aqueous mixtures using tertiary amines is a well established procedure. It is generally accepted that it involves transfer of the organic acid in its non-dissociated form from the aqueous phase to the organic phase and reaction in the organic phase with a dissolved tertiary amine that acts as extractant (Figure 6-2). Typically, a-polar organic solvents like hexane or kerosene are used for this purpose.
Acid-amine complexes are formed upon reaction [15,20]. This reaction is known to be reversible. Various types of acid-amine complexes may be formed differing in stoichiometry, i.e. (1,1) complexes with one amine and acid, (1,2) complexes and higher aggregates (1,3) and (2,3). Due to (rapid) complex formation, the rate of mass transfer of the organic acid is enhanced [21]. This leads to higher extraction efficiencies and $K_D$ values compared to physical extraction in the absence of an extractant. The locus of the reaction for such aqueous system is most likely the organic phase, because of the low solubility of TOA in water. This description of reactive extraction of acetic acid likely also holds for the extraction of acetic acid from the aqueous phase of a thermally treated BO. However, a different situation may occur when extracting organic acids from crude BO with TOA dissolved in an organic phase. BO contains hundreds of oxygenated compounds belonging to several organic compound classes (acids, aldehydes, ketones, phenolics, some hydrocarbons, water). As such, its composition and physical properties are considerably different from that of an aqueous phase.

In this paper, the amount of acetic acid transferred from the BO layer to the amine layer during the extraction process is defined as the extraction efficiency ($\eta_E$) and follows from:

$$\eta_E = \frac{W_{\text{acid}}^{\text{org}}}{W_{\text{acid}}^{\text{aq}}} \times 100\%$$

(1)

$W_{\text{acid}}^{\text{org}} =$ weight (g) of acetic acid in the organic phase after extraction

$W_{\text{acid}}^{\text{aq}} =$ weight (g) of acetic acid in the original BO source before extraction
Another measure for extraction performance is the distribution coefficient ($K_D$), which is defined as:

$$K_D = \frac{C_{AA}^{\text{org}}}{C_{AA}^{\text{aq}}}$$  \hspace{1cm} (2)

Here $C_{AA}^{i}$ is the concentration of undissociated acetic acid (AA) in phase i. For reactive extraction systems, a high $K_D$ value is desirable.

During extraction, the extractant may be transferred from the organic phase to the BO phase. The amount of amine transferred from the organic phase to the BO phase during the extraction process is defined as:

$$\lambda_A = \frac{W_{\text{aq}}^{\text{TA}}}{W_{\text{org}}^{\text{TA}}} \times 100\%$$  \hspace{1cm} (3)

$W_{\text{aq}}^{\text{TA}}$ = amount of tertiary amine (g) in the BO layer after extraction

$W_{\text{org}}^{\text{TA}}$ = amount of tertiary amine (g) in the organic phase before extraction

In the experimental work, values for $\eta_E$ and $\lambda_A$ are determined for each experiment and compared: preferably, $\eta_E = 100$ and $\lambda_A = 0$.

### 6.3 Results and discussion

#### 6.3.1 Feedstock analysis

BO is a complex mixture containing a wide variety of organic molecules. The characteristics of the BO and the aqueous phase of a thermally treated BO used in this study are provided in Table 6-1. The latter was obtained by treatment of BO at 300-340°C and 140 bar.
Table 6-1. Properties of bio-oil and aqueous phase of thermally treated bio-oil

<table>
<thead>
<tr>
<th>Physical property</th>
<th>BIO-OIL</th>
<th>Aqueous phase of thermally treated BIO-OIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content (%-wt)</td>
<td>30</td>
<td>80</td>
</tr>
<tr>
<td>HHV (MJ/Kg)</td>
<td>20</td>
<td>1.5</td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>1.25</td>
<td>0.97</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
<td>2.3</td>
</tr>
<tr>
<td>Elemental analysis(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>50.9</td>
<td>13.0</td>
</tr>
<tr>
<td>H</td>
<td>7.7</td>
<td>7.8</td>
</tr>
<tr>
<td>N</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O(^a)</td>
<td>41.20</td>
<td>79.1</td>
</tr>
</tbody>
</table>

\(^a\) by difference \(^b\) %wt on wet basis

Various types of organic acids are present in both samples (formic acid, acetic acid, propionic acid, see Table 6-2).

Table 6-2. Analytical data for organic acids in BO and the aqueous phase of thermally treated BO\(^a\)

<table>
<thead>
<tr>
<th>Type of Acid</th>
<th>BO (wt%)</th>
<th>Aqueous phase of Stabilized BO (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>n.d.(^b)</td>
<td>n.d.(^b)</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>6.2</td>
<td>6.22</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>0.4</td>
<td>0.07</td>
</tr>
<tr>
<td>Butanoic acid</td>
<td>0.04</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Quantities based on GC analyses. \(^b\) not detectable

For comparison, the type and amounts of organic acids for a number of studies reported in the literature are given in Table 6-3.
Table 6-3. Amount of typical carboxylic acids in various pyrolysis oils from selected suppliers

<table>
<thead>
<tr>
<th>Acid</th>
<th>BTG (%wt)</th>
<th>Dynamotive (%wt)</th>
<th>Ensyn (%wt)</th>
<th>Pyrovac (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>3.18</td>
<td>2.45</td>
<td>4.73</td>
<td>2.24</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>0.28</td>
<td>0.32</td>
<td>0.65</td>
<td>0.29</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.19</td>
<td>0.12</td>
<td>0.12</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Evidently, acetic acid is the dominant organic acid in all samples, in line with our analysis. The actual amount varies considerable, likely the result of differences in biomass feedstock, reactor technology and processing conditions. In this study, we focused on the recovery of acetic acid as it by far the most abundant acid in BO.

6.3.2 Extraction studies with crude bio-oil

Acetic acid recovery using reactive amines has been studied both for crude BO and the aqueous phase of a thermally treated BO. The first part of this paper is dealing with crude BO. First, screening experiments with crude BO and TOA dissolved in a hydrocarbon solvent will be reported, followed by studies aimed to identify suitable co-solvents and diluents to enhance the acetic acids extraction efficiencies and to reduce TOA transfer from the TOA/solvent layer to the BO layer. Finally, optimization experiments with the preferred system are reported. All extractions were carried out at room temperature and atmospheric pressure.

6.3.2.1 Screening studies using crude BO

Initial screening experiments were carried out in a batch set-up (Method A, see experimental section) with crude, undiluted BO using TOA dissolved in an a-polar solvent (pet-ether or dodecane) as the extractant phase. The extractions were performed at 20°C and atmospheric pressure for 12 hours. For these experiments, a 1 to 1 phase ratio was applied. After extraction, the organic acid in the amine phase and TOA content in the BO phase were determined and the results are summarized in Table 6-4.
Table 6-4. Experimental overview for screening experiments using crude BO

<table>
<thead>
<tr>
<th>Entry</th>
<th>TOA solvent</th>
<th>$C_{\text{AA}}/C_{\text{TOA}}$</th>
<th>$\eta_E$</th>
<th>$\lambda_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[M/M]</td>
<td>(wt%)</td>
<td>(wt%)</td>
</tr>
<tr>
<td>1</td>
<td>Dodecane</td>
<td>1.1</td>
<td>4</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>Pet ether</td>
<td>1.1</td>
<td>4</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>Dodecane</td>
<td>2.7</td>
<td>2.5</td>
<td>73</td>
</tr>
</tbody>
</table>

*a. Experimental procedure A was applied, see experimental section for details. b. Based on intakes.*

It is evident that only a very limited amount of acetic acid is extracted from the BO to the organic phase. Due to the prolonged reaction time (12 h), it is highly likely that the system has reached equilibrium and that the low extraction efficiency is an intrinsic thermodynamic feature of the systems. To exclude kinetic effects, the concentration of acetic acid in the organic phase was followed in time for an experiment (entry 2 in Table 6-4). The results are represented in Figure 6-3.

![Figure 6-3](image-url)  

*Figure 6-3. Acid extraction efficiency as a function of time (entry 3 in Table 6-4). Line for illustrative purposes only*
Clearly, equilibrium is reached within less than 1000 s, implying that the results provided in Table 6-4 are not biased by kinetics and are an intrinsic thermodynamic feature of the system.

Another striking feature is the large amount of TOA present in the BO layer after the extraction process. This is highly undesirable, TOA is a relatively expensive chemical and the presence of bound organic nitrogen reduces the attractiveness of the remaining BO layer for energy generation. To reduce the amount of TOA transferred to the BO layer, the solubility of TOA in the BO phase should be minimized. A variety of experiments were performed with co-solvents to modify the polarity of the BO phase and thus affinity of TOA for this phase. These are described in the following paragraph.

### 6.3.2.2 Effects of co-solvent addition to the BO phase on the extraction process

The addition of several co-solvents to the BO phase (THF, ethanol, 2-ethyl-1-buthanol and dichloromethane) was investigated to modify the polarity of the BO layer with the objective to reduce the TOA solubility in the BO phase and to improve acetic acid extraction. The experiments were carried out in batch mode (method B, see experimental section) at room temperature with BO dissolved in a co-solvent (50 vol%) and TOA dissolved in pet-ether (20 vol%). An overview of the experiments is given in Table 6-5.

<table>
<thead>
<tr>
<th>BO co-solvent</th>
<th>Phase behavior</th>
<th>$\eta_c$ (%)</th>
<th>$\lambda_A$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No solvent, (pure BO)</td>
<td>L-L</td>
<td>4</td>
<td>78</td>
</tr>
<tr>
<td>THF</td>
<td>L-L</td>
<td>60</td>
<td>39</td>
</tr>
<tr>
<td>Ethanol</td>
<td>L-L</td>
<td>29</td>
<td>60</td>
</tr>
<tr>
<td>2-ethyl-1-buthanol</td>
<td>Miscible</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>Miscible</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a. BO-co-solvent: 50-50 %vol, 20 %- vol. TOA in pet ether.
b. Number of phases formed after mixing both liquids.
c. Extraction with TOA in dodecane instead of pet-ether

Employment of 2-ethyl-1-buthanol and dichloromethane produced single phase systems when contacting the BO phase with the TOA/pet-ether phase and are therefore not suitable for this application. For ethanol and THF immiscible two-phase liquid-liquid systems were formed upon contacting. The extraction efficiency for acetic acid was 60% for THF, which is considerably higher than for ethanol (29%). The amount of TOA ending up in the BO layer are also lowered considerably when using THF (39% versus 78% for the base case,
however, is still far from acceptable. These numbers are significantly better than for the base case (no co-solvent, see Table 6-5) and clearly shows the benefits of the use of a co-solvent for the BO phase. The exact role of co-solvent addition to the BO phase is not clear at this stage. The co-solvent distributes between the BO layer and the TOA-pet-ether layer and affects the physical properties (polarity, viscosity) not only of the BO layer but also of the TOA/pet-ether layer (vide infra). This combined effect will affect the extraction process in terms of acetic acid transferred to the TOA-pet ether layer and TOA transfer to the BO layer.

6.3.2.3 Effect of TOA diluents on the extraction process

Initially, dodecane and pet-ether were used as the diluents for TOA. Further experiments with a range of diluents for the TOA phase with different solvent properties (a.o. polarity), were performed to optimize the extraction efficiency and to reduce the amount of TOA in the BO layer at equilibrium. It is well established that amine diluents have a profound effect on the organic acid extraction efficiencies for aqueous systems [14-18]. The experiments were carried out in a batch mode (method B, see experimental section) at room temperature with the BO dissolved in THF (50 vol%) and TOA dissolved in the co-solvent (50 vol%). The phase ratio for both layers was set at a 1:1 ratio.

<table>
<thead>
<tr>
<th>TOA diluent</th>
<th>Number of liquid phases at equilibrium</th>
<th>$\eta_E$ (%)</th>
<th>$\lambda_A$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>2</td>
<td>43</td>
<td>7</td>
</tr>
<tr>
<td>Octane</td>
<td>2</td>
<td>47</td>
<td>6</td>
</tr>
<tr>
<td>Decane</td>
<td>2</td>
<td>38</td>
<td>16</td>
</tr>
<tr>
<td>Dodecane</td>
<td>2</td>
<td>27</td>
<td>21</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>2</td>
<td>24</td>
<td>18</td>
</tr>
<tr>
<td>Methyl iso-butyl ketone (MIBK)</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Toluene</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a. BO in THF (50 %- vol.), TOA in solvent (50 %- vol.).
Employment of MIBK, toluene, o-xylene and chloroform resulted in the formation of a single phase and these solvents are therefore not suitable for our purpose. The use of non-polar solvents (hexadecane, octane, decane and dodecane) gave two distinct liquid phases. These results imply that for BO, strongly a-polar TOA co-solvents are required to create a liquid-liquid system.

The extraction efficiency and the TOA losses are a strong function of carbon number of the hydrocarbon solvent (Table 6-6 and Figure 6-4). The extraction efficiency was highest for octane (47 wt%) and considerably lower for hexadecane (24%). This may be caused by slight changes in the physical properties of the hydrocarbons, affecting the extraction thermodynamics. Such effects have been reported in the literature. For instance, differences in extraction efficiencies were observed when extracting gluconic acid and glycolic acid from aqueous solutions using TOA in various hydrocarbon solvents (hexane, cyclohexane, toluene) [22,23]. The observed trend in extraction efficiencies as a function of the carbon number of the hydrocarbon solvent may also be the result of major differences in TOA distribution between both layers. The amount of TOA in hexadecane (18 wt%) is about three times higher than in octane (6 wt%). The relatively high amounts of TOA in the BO layer when using hexadecane will have a profound effect on the thermodynamics of the extraction process and is expected to lead to reduced acetic acid extraction efficiencies.

![Figure 6-4](image-url)

**Figure 6-4.** Effect of different types of hydrocarbon diluents on the reaction efficiency and TOA losses (BO in THF (50 % vol.), TOA in amine solvent (50 % vol.), room temperature).
On the basis of these data, it can be concluded that octane is the preferred diluent for TOA.

6.3.2.4 Effect of the type of tertiary amine on the extraction efficiency

Two different amines (tri-dodecylamine, TDDA and TOA) both dissolved in dodecane (50 vol%) were tested with BO dissolved in THF (50 vol%). The experiments were carried out in a batch mode (method B, see experimental section) at room temperature. The results are given in Figure 6-5.

![Effect of type of amine on the extraction process](image)

Figure 6-5. Effect of type of amine on the extraction process (amine dissolved in dodecane (50 %-%vol. dilution), BO in THF (50 %-%vol.))

It is evident that TDDA performance is considerably better than TOA. The extraction efficiency is about twice that of TOA and amine distribution between both layers is considerably improved. The latter may be due to the longer hydrocarbon chains of TDDA compared to TOA, leading to a higher affinity for the dodecane-amine layer instead of the more polar BO layer. Improved extraction performance for acetic acid may be the result of this more favorable TDDA distribution. However, effects due to differences in acetic acid-amine complex stability cannot be excluded. It is well known that the distribution coefficients for organic acids
in aqueous-amine extraction systems are a clear function of the molecular structure of the amine and difference up to a factor of 5-10 in distribution factors for lactic acid have been reported [24].

6.3.2.5 Systematic studies for the preferred system

Systematic experiments were performed with BO dissolved in THF and a TOA-octane extraction solvent. This was shown to be the preferred system with respect to extraction efficiencies and TOA distribution. The only exception is the choice of the amine. Although TDDA performed better than TOA, the latter was selected for further optimization as it is considerably (about ten times) less expensive than TDDA. All experiments were carried out in a batch mode (method B, see experimental section) at room temperature.

6.3.2.6 Effect of the diluent-TOA ratio on the extraction process

A number of experiments were performed with different TOA-octane wt ratio’s at a constant phase ratio of 1 (vol. basis). The results are given in Table 6-7 and schematically represented in Figure 6-6.

<table>
<thead>
<tr>
<th>X_{TOA} (weight fraction)</th>
<th>n_{AA}/n_{TOA}</th>
<th>ηE (%)</th>
<th>λA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>1.0</td>
<td>58</td>
<td>19</td>
</tr>
<tr>
<td>0.45</td>
<td>0.5</td>
<td>59</td>
<td>23</td>
</tr>
<tr>
<td>0.63</td>
<td>0.3</td>
<td>50</td>
<td>23</td>
</tr>
<tr>
<td>0.77</td>
<td>0.2</td>
<td>43</td>
<td>33</td>
</tr>
<tr>
<td>1</td>
<td>0.2</td>
<td>32</td>
<td>52</td>
</tr>
</tbody>
</table>

a. TOA in octane, BO in THF (50 vol%), 1 tot 1 vol. BO-TOA phase ratio
b. Based on initial intakes
The extraction efficiencies are about 60 wt% at TOA wt. fractions below 50%. However, the efficiency drops rapidly when using higher TOA loadings and an extraction efficiency of only 30 % is observed for pure TOA. It is well known in the extraction literature that the diluent concentration has a profound effect on the extraction efficiency and $K_D$. For the aqueous extraction of acetic acid in alamine 336 dissolved in 2-ethylhexanol, an optimum for the $K_D$ was observed at 50% dilution [25]. However, in our system, the extraction efficiency may also be affected considerably by the transfer of TOA from the a-polar organic layer to the BO layer. At TOA loadings above 70 wt%, considerable amounts of TOA dissolve in the BO layer (Figure 6-6). As a result, the extraction efficiency may be reduced considerably due to reaction of acetic acid with TOA in the BO layer.

The distribution of TOA between the BO layer and the octane layer may be calculated using eq 4.
\[ K_{TOA} = \frac{C_{TOA}^{org}}{C_{BO}} \quad (4) \]

The values of \( K_{TOA} \) at different \( X_{TOA} \) values were calculated from the mass balances. For \( X_{TOA} \) values below 0.6, the value for \( K_{TOA} \) is between 3 and 4. However, at higher \( X_{TOA} \) values, the values for \( K_{TOA} \) reduce considerably (0.8 for \( X_{TOA} = 1 \)). Thus, the value for \( K_{TOA} \) is a clear function of the \( X_{TOA} \).

### 6.3.2.7 Effect of dilution of the BO phase on extraction performance

Four experiments with a different acid concentration in the BO phase were carried out by adjusting the THF-BO weight ratio. The extraction was carried out with a TOA solution in octane (50 vol%). A summary of the results is given in Table 6-8.

<table>
<thead>
<tr>
<th>( X_{BO} ) (weight fraction)</th>
<th>( n_{AA}/n_{TOA} ) (mole/mole)</th>
<th>( \eta_E ) (%-wt)</th>
<th>( \lambda_A ) (%-wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.81</td>
<td>0.95</td>
<td>17%</td>
<td>17%</td>
</tr>
<tr>
<td>0.66</td>
<td>0.71</td>
<td>28%</td>
<td>8%</td>
</tr>
<tr>
<td>0.47</td>
<td>0.47</td>
<td>57%</td>
<td>14%</td>
</tr>
<tr>
<td>0.26</td>
<td>0.24</td>
<td>93%</td>
<td>9%</td>
</tr>
</tbody>
</table>

a. \( TOA \) in octane (50 vol%), \( BO \) in THF, room temperature, 1 to 1 phase ratio (vol. basis)

b. Based on initial intakes

The extraction efficiency is a clear function of the BO loading. At higher loadings, the extraction efficiency reduces considerably (Figure 6-6). The highest efficiency (93 %) was observed at \( X_{BO} = 0.23 \) and this is also the highest value obtained in this study. The observed trend that the extraction efficiency reduces at higher BO loadings (i.e., higher acid concentrations in the BO-phase) is in line with literature data on reactive extraction processes of aqueous organic acids using tertiary amines. The acid concentration is known to have a profound effect and generally \( K_d \) is lowered considerably when increasing the acid concentration at constant amine loading [25]. Hence, it is expected that the extraction efficiency will be reduced when working at higher BO loadings. Effects on the extraction efficiency by
concentration dependent transfer of TOA to the BO layer can be excluded for this case as the TOA concentration in the BO-THF layer is about constant at different BO-THF ratio’s (Figure 6-7).

Another explanation for the observed trend of higher efficiencies at lower BO loadings may be related to the distribution of THF between the BO and TOA - octane layer. Mass balance calculations indicate that significant amounts of THF dissolve in the TOA-octane layer and that this effect is more pronounced at higher THF loadings. It may be expected that this affects the extraction efficiencies by changing the physical properties (polarity, viscosity) of the TOA/octane layer.

![Figure 6-7](image)

**Figure 6-7.** $\lambda_A$ (○–○) and $\eta_E$ (●--●) as a function of bio-oil weight fractions in THF. (TOA in octane (50 % -vol.), 1 to 1 phase ratio of the BO and TOA phase, room temperature).

6.3.3 Acetic acid recovery from the aqueous phase of a thermally treated BO

TOA distribution between the BO phase and the extractant phase considerably hampers the extraction process. We anticipated that this problem could be solved by applying an aqueous BO derived fraction enriched in organic acids. An attractive aqueous fraction for this purpose is obtained by thermal treatment of BO at elevated temperatures (>300°C) and pressures (>100 bar) and residence times of around 5 minutes. This results in a phase separation
of the oil, an acidic aqueous phase top layer and a bottom layer rich in other organics (Table 6-1) [26]. The reactive liquid-liquid extraction concept using tertiary amines was applied to recover acetic acid from a typical aqueous phase containing 6.2 wt% of organic acids. Several preliminary extraction experiments were executed with different TOA-diluents (octane, toluene), similar to the experiments reported above. The results of the reactive extractions are compared with previous results found from BO/THF mixtures in Table 6-9.

Table 6-9. Reactive extractions with the aqueous phase of a thermally treated BO. Process conditions: 50 %-vol. TOA in amine solvent.

<table>
<thead>
<tr>
<th>TOA diluent</th>
<th>Acetic acid source</th>
<th>$\eta_e$ (wt-%)</th>
<th>$\lambda_A$ (wt-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octane</td>
<td>Aqueous phase</td>
<td>71</td>
<td>0</td>
</tr>
<tr>
<td>Toluene</td>
<td>Aqueous phase</td>
<td>75</td>
<td>0</td>
</tr>
<tr>
<td>Octane$^b$</td>
<td>BO/THF phase</td>
<td>93</td>
<td>9</td>
</tr>
</tbody>
</table>

$a$. 50 vol% TOA in diluent, room temperature, 1 to 1 phase ratio (vol. basis).

$b$. Optimum conditions: 0.23 wt% BO in THF, 50%-v TOA in octane

The extraction efficiency of the aqueous phase was 71% when using octane as the TOA diluent and slightly higher (75 %) with toluene.

In contrast to the experiments with BO, no TOA was detected in the aqueous phase after reactive extraction. Therefore, acetic acid recovery from the aqueous phase of a thermally treated BO appears feasible and warrants further investigations. A large series of experiments on the extraction of acetic acid from aqueous samples using TOA in different organic solvents were reported by Ziegenfuß and Mauer (1994). This is the basis of work now being carried out.

6.4 Conclusions

Reactive extraction using long chain tertiary amines in combination with various diluents, originally developed and optimized for the extraction of organic acids from aqueous streams, has been applied to extract acetic acid from BO. The physical properties of the BO matrix are considerably different from that of commonly used aqueous systems and this strongly affects the extraction process. A particular drawback is the distribution of TOA
between the BO-phase and the TOA-organic phase. By proper selection of diluents and optimization of loadings, an acetic acid extraction efficiency of 93% could be obtained using TOA in a single equilibrium step with 10 wt% of the TOA ending up in the original BO-phase.

Screening experiments with the aqueous phase from a thermally treated BO were very successful and extraction efficiencies of 75% could be obtained using TOA diluted with toluene. Further experimental optimization studies and modeling activities for the latter system are in progress and will be reported in due course.

6.5 Nomenclature

\[ W_i^j \] Weight of \( j \) in phase \( i \), g
\[ K_D \] Distribution coefficient, M/M
\[ W_{i,t}^j \] Weight of \( j \) in phase \( i \) at reaction time equal to \( t \), g
\[ C_i^j \] Concentration of \( j \) in phase \( i \), M

Subscript and Superscript

AA Acetic acid
aq Original BO phase
org Organic phase
t Reaction time equal to \( t \), min
0 Initial condition or reaction time equal 0, min
TA Tertiary amine
TOA Trioctylamine

Greek symbol

\[ \eta_E \] Extraction efficiency, wt%
\[ \lambda_A \] Amine loss, wt%
6.6 References


[22] Inci, I. Chemical and Biochemical Engineering Quarterly 2002, 16, 185-189.

[23] Inci, I. Chemical and Biochemical Engineering Quarterly 2002, 16, 81-85.


