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Acetic Acid Recovery from Fast Pyrolysis Oil. An Exploratory Study on Liquid-Liquid Reactive Extraction using Aliphatic Tertiary Amines

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Abstract: Flash pyrolysis oil or Bio-oil (BO), obtained by flash pyrolysis of lignocellulosic biomass, is very acidic in nature. The major component responsible for this acidity is acetic acid, present in levels up to 2–10 wt%. Here, we report an exploratory study on BO upgrading by reactive extraction of acetic acid using long-chain tertiary amines in a batch set-up. Factors affecting the extraction efficiency, such as the type and concentration of tertiary amine and co-solvents, were investigated. More than 90 wt% of the acetic acid could be extracted in a single equilibrium step (BO diluted in THF (26 wt% BO), trioctylamine (TOA) in octane as the extractant phase, T = 20°C). However, the amine has considerable affinity for the BO phase and about 10 wt% on initial intake was transferred to the BO. A considerable improvement was obtained when using the aqueous phase of a thermally treated BO containing 6 wt% acid of acetic acid. In a single extraction step, acetic acid extraction efficiencies up to 75 wt% were achieved without significant amine transfer to the aqueous phase.

Keywords: Acetic acid, bio-oil, biomass, flash pyrolysis, reactive liquid-liquid extraction, tri-*n*-octyl amine

INTRODUCTION

Increased consumption of fossil fuels in the last decades has created considerable environmental problems (e.g. green gas house emissions)

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and resulted in a significant increase in the crude oil price. This has encouraged the exploration of renewable resources like biomass for energy generation. Flash pyrolysis oil, also known as bio-oil (BO), is obtained from lingo-cellulosic biomass using flash pyrolysis technology (1–3). Typical yields are up to 70%-wt of BO. BO is a complicated mixture of a large number of organic compounds belonging to a wide variety of 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 (1–3).

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.* 2–3), caused by the presence of large amounts of organic acids (formic acid, 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 limits its application due to extensive corrosion *a.o.* of the metal surfaces of internal combustion engines.

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 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 also be integrated with an upgrading process for fuel production (Fig. 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. Distillative work-up of pyrolysis oil is known to result in large amounts of solid materials by irreversible polymerization (3). The use of the other techniques is limited as a result of the presence of large amounts of medium molecular weight compounds ($500 < M_n < 3000$) in pyrolysis oil. These are known to cause severe pore blocking of resins and membranes, resulting in a rapid drop in performance (3).

Reactive liquid-liquid extraction (RLLE) of carboxylic acids by suitable extractants 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. 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

1. crude BO derived directly from a flash pyrolysis process, and
2. the aqueous layer of a thermally treated BO.

EXPERIMENTAL SECTION

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). Two different BO samples were used in this study, both obtained by flash pyrolysis of beech wood in a rotating cone reactor (19), but prepared at different process conditions. As a result, the acetic acid concentration for both samples was different. The aqueous fraction of a thermally treated pyrolysis oil was obtained by treatment of BO at 300–340°C and 140 bar pressure. The acetic acid level in the resulting aqueous phase was 6.2 wt%. tri-*n*-Octylamine (TOA) and tri-*n*-dodecylamine (TDDA) were acquired from Acros Organics (98.0% purity). Tetrahydrofuran, o-xylene, hexane, octane, decane, hexadecane, and dodecane (all > 99.0% purity) and pet-ether were purchased from Acros Organics. Ethanol (99%) was obtained from Merck, 2-ethylbutanol (98%) from Janssen Chimica, toluene (99.5%), dichloromethane (99.8%), and chloroform (99.5%) from Lab-Scan Analytical Sciences.

Analyses

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 × 0.32 m × 0.25 μ m) 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 as a result 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 analyses 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.

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 the L-L system.

Table 1. Properties of BO-1 and aqueous phase of thermally treated BO used in this study

Physical property	BO-1	Aqueous phase of thermally treated BO
Water content (%-wt)	30	80
HHV (MJ/Kg)	20	1.5
Density (g/ml)	1.25	0.97
pH	2.5	2.3
Elemental analysis ^a		
C	50.9	13.0
H	7.7	7.8
N	0.2	—
S	—	—
O ^b	41.2	79.1

^a0%-wt on wet basis.^bBy difference.

Reactions in a Batch Reactor with Overhead Stirring (Method A)

All experiments were carried out with the BO batch coded BO-1. Properties of BO-1 are given in Table 1 and 2. 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 equipped with 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. Both liquid phases were analyzed and weighed to

Table 2. Type and amounts of organic acids in the various BO samples^a

Type of acid	BO-1 (wt%)	BO-2 (wt%)	Aqueous phase of a thermally treated BO (wt%)
Formic acid	n.d. ^b	n.d. ^b	n.d. ^b
Acetic acid	6.2	1.4	6.22
Propionic acid	0.4	n.d. ^b	0.07
Butanoic acid	0.04	n.d. ^b	n.d. ^b

^aQuantities based on GC analyses.^bNot detectable.

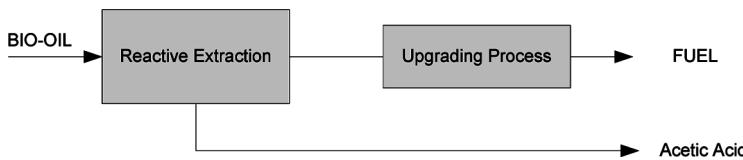


Figure 1. Integrated chemical (acetic acid) and fuel production from BO.

determine the mass balances for the various compounds. Method A was applied to gain insights in the kinetics of the reactive extraction process.

Reactions in Small Glass Vials using External Stirring (Method B)

All experiments were carried out with BO batch coded BO-2. The acid composition of BO-2 is given in Table 2. 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 compounds. Method B was applied to determine the equilibrium composition. For this purpose, it is preferred over method A as it requires less BO, reagents, and solvents.

Terminology and Theory

Organic acid extraction from aqueous mixtures using tertiary amines is a well-established technology. 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 (Fig. 2). Typically, a-polar organic solvents like hexane or kerosene are used for this purpose.

Acid-amine complexes are formed upon reaction (10–18,20). 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 molecule of amine and one molecule of acid, (1,2) complexes and higher aggregates. Due to rapid complex formation, the rate of mass transfer of the organic acid is enhanced (21). This leads to higher extraction efficiencies compared to physical extraction in the absence of an extractant. The locus of the reaction for such an aqueous system is most likely the organic phase, because of the low solubility of TOA in water.

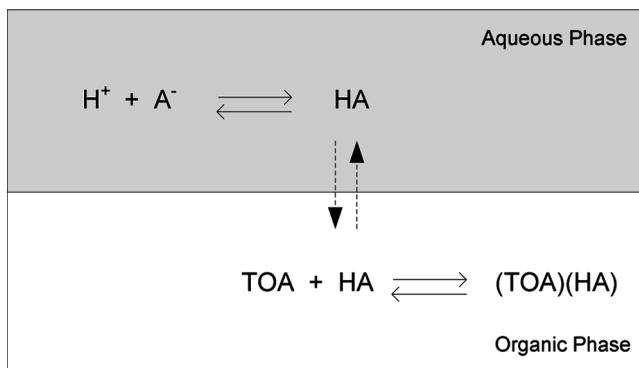


Figure 2. Schematic representation of reactive-extraction of an acid in an aqueous phase using tri-octylamine in an organic phase.

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 arises when extracting organic acids from crude BO with TOA dissolved in an organic phase. BO contains, besides water, hundreds of oxygentated 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 (η_E) and is given by:

$$\eta_E = \frac{m_{AA}^{org}}{m_{AA}^{BO}} \times 100\% \quad (1)$$

Where:

m_{AA}^{org} = amount of acetic acid (g) in the organic phase after extraction

m_{AA}^{BO} = amount of acetic acid (g) in the original BO source before extraction

Another measure for extraction performance is the distribution coefficient (K_D), which is defined as:

$$K_D = \frac{C_{AA}^{org}}{C_{AA}^{BO}} \quad (2)$$

Here C_{AA}^i is the concentration of un-dissociated acetic acid (AA) in phase i . For reactive extractions, 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 during the extraction process is defined as:

$$\lambda_A = \frac{m_{TA}^{BO}}{m_{TA}^{org}} \times 100\% \quad (3)$$

m_{TA}^{BO} = amount of tertiary amine (g) in the BO layer after extraction

m_{TA}^{org} = amount of tertiary amine (g) in the organic phase before extraction

Values for η_E and λ_A are determined for each experiment and compared. In the ideal case $\eta_E = 100\%$ and $\lambda_A = 0\%$. In this study, we have set a maximum value of λ_A of 0.5%. This value is based on the anticipated maximum allowable concentration of nitrogen in the pyrolysis oil after acid extraction. When considering an integrated approach (Fig. 1), the pyrolysis oil after acid recovery should be used as a fuel for e.g. in boiler applications. Heavy fuel oil, a typical boiler fuel, contains up to 0.5 wt% of nitrogen. This value was also set as the maximum value for the treated pyrolysis oil. In this exploratory study, the minimum value of η_E was set at 91% ($K_D = 10$). This value is at the high end of the range reported for the reactive extraction of acetic acid using tertiary amines in various solvents ($1 < K_D < 15$) and justified by the fact that the concentrations of acids in pyrolysis oil is high compared to typical aqueous systems (16).

RESULTS AND DISCUSSION

Feedstock Analysis

The characteristics of BO-1 and the aqueous phase of a thermally treated BO used in this study are provided in Table 1.

Various types of organic acids are present in the various BO samples, see Table 2 for details. Acetic acid is by far the most abundant organic acid in the samples.

For comparison, the type and amounts of organic acids for a number of BO samples reported in the literature are given in Table 3.

Table 3. Amount of typical carboxylic acids in various pyrolysis oils from selected suppliers (3)

Acid	BTG (%wt)	Dynamotive (%wt)	Ensyn (%wt)	Pyrovac (%wt)
Formic acid	0.19	0.12	0.12	0.06
Acetic acid	3.18	2.45	4.73	2.24
Propionic acid	0.28	0.32	0.65	0.29

Clearly acetic acid is the dominant organic acid in all samples, in line with our analysis. The actual amount varies considerably, 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 is by far the most abundant acid in BO.

Extraction Studies with Crude BO

The first part of this paper deals with reactive extraction studies on crude BO. First, screening experiments with TOA dissolved in a hydrocarbon solvent will be reported, followed by studies aimed to identify suitable co-solvents to enhance the acetic acid extraction efficiencies. Finally, optimization experiments with the preferred system are given.

Screening Studies using Crude BO

Initial screening experiments were carried out in a batch set-up (Method A, see experimental section) with undiluted BO using TOA dissolved in an a-polar solvent (pet-ether or dodecane), as the extractant phase. The results are summarized in Table 4.

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 4). The results are represented in Fig. 3.

Clearly, equilibrium is reached within less than 1000 s, implying that the results provided in Table 4 are not biased by kinetics and are an intrinsic thermodynamic feature of the system.

Table 4. Experimental overview of screening experiments using BO-1^a

Entry	TOA solvent	TOA fraction in solvent (wt%)	η_E (wt%)	λ_A (wt%)
1	Dodecane	10	5.8	80
2	Dodecane	20	2.7	73
3	Pet ether	50	4.4	78

^aExperimental procedure A was applied, see experimental section for details. T = 20°C, 1 to 1 volume ratio of both phases, 12 h reaction time.

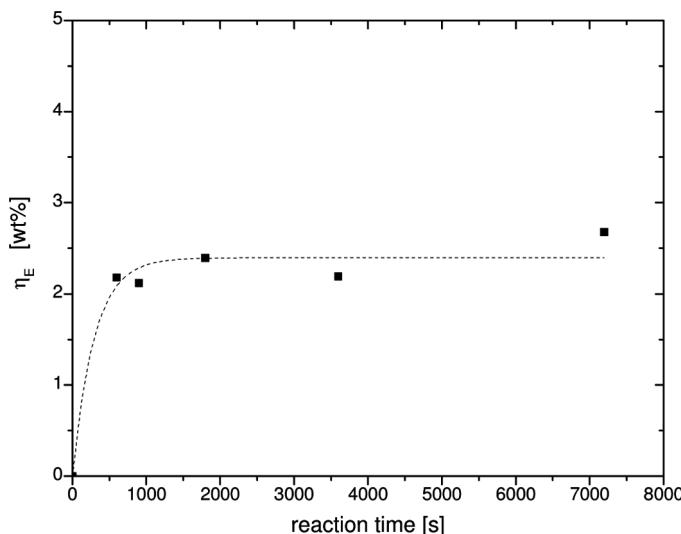


Figure 3. Acid extraction efficiency as a function of time (entry 2 in Table 4). Line for illustrative purposes only.

A remarkable feature is the large amount of TOA present in the BO layer after the extraction process (Table 4). 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.

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-butanol and dichloromethane) was investigated to modify the properties (viscosity, polarity) of the BO layer with the objective to reduce the TOA solubility in the BO phase and to improve acetic acid extraction efficiencies. An overview of the experiments is given in Table 5.

Employment of 2-ethyl-1-butanol 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.

Table 5. Reactive extractions of BO with TOA using different BO co-solvents^a

BO co-solvent	Phase behavior ^b	η_e (%)	λ_A (%)
THF	L-L	60	39
Ethanol	L-L	29	60
2-ethyl-1-butanol	Miscible	—	—
Dichloromethane	Miscible	—	—

^aBO-2-co-solvent ratio: 50-50 %vol, 20%-vol. TOA in pet ether, T = 20°C, method B.

^bPhase behavior after mixing the BO/co-solvent and TOA/pet-ether phases.

The extraction efficiency for acetic acid was 60% when using THF, which is considerably higher than for ethanol (29%). The amount of TOA ending up in the BO layer is also lowered considerably when using THF (39% versus 60% for ethanol); however, it is still far from acceptable. These numbers are significantly better than for the base case (78%, no BO co-solvent, see Table 4) and clearly shows the benefits of the use of a co-solvent for the BO phase. The exact role of the 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). Furthermore, the concentration of acetic acid is also reduced considerably upon the use of a co-solvent. Dilution is known to affect the extraction efficiencies (25). These combined effects will affect the extraction process both in terms of acetic acid transferred to the TOA-pet ether layer and TOA transfer to the BO layer.

Effect of TOA Diluents on the Extraction Process

Initially, dodecane and pet-ether were used as the diluents for TOA (Table 4). 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 experimental results are given in Table 6.

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 aliphatic hydrocarbon solvents gave two distinct liquid phases. These results imply that very 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 and Fig. 4).

Table 6. Effect of TOA diluents on the extraction process^a

TOA diluent	Number of liquid phases at equilibrium	η_E (%)	λ_A (%)
Hexane	2	43	7
Octane	2	47	6
Decane	2	38	16
Dodecane	2	27	21
Hexadecane	2	24	18
Methyl iso-butyl ketone (MIBK)	1	—	—
Toluene	1	—	—
<i>o</i> -Xylene	1	—	—
Chloroform	1	—	—

^aMethod B, BO-2 in the THF (50%-vol.), TOA in solvent (50%-vol.), 1 to 1 phase ratio, T = 20°C.

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.

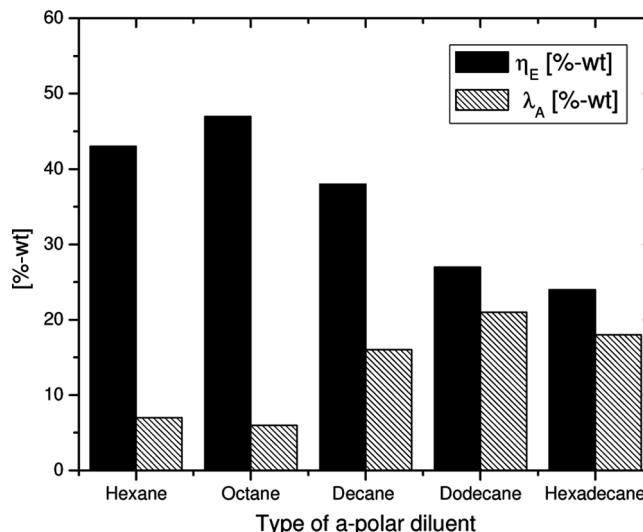


Figure 4. Effect of different types of hydrocarbon diluents on the extraction efficiency and TOA losses (BO in THF (50%-vol.), TOA in amine solvent (50%-vol.), room temperature).

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.

On the basis of these data, it can be concluded that octane is the preferred diluent for TOA. However, the values for η_E and λ_A are still below the target values.

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 results are given in Fig. 5.

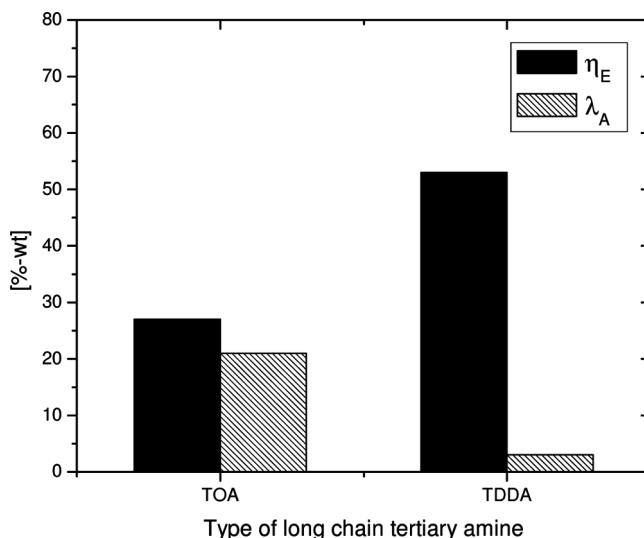


Figure 5. Effect of type of amine on the extraction process (amine dissolved in dodecane (50%-vol. dilution), BO in THF (50%-vol.), method B).

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 differences up to a factor of 5–10 in distribution factors for lactic acid have been reported (24).

Systematic Studies

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 (vide supra). 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.

Effect of the Composition of the TOA Phase on the Extraction Process

A number of experiments were performed with different TOA-octane wt ratio's at a constant volumetric phase ratio of 1. The results are given in Fig. 6. 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 values for the extraction efficiency and the 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 (Fig. 6). As a result, the extraction efficiency may be reduced considerably due to reaction of acetic acid with TOA in the BO layer.

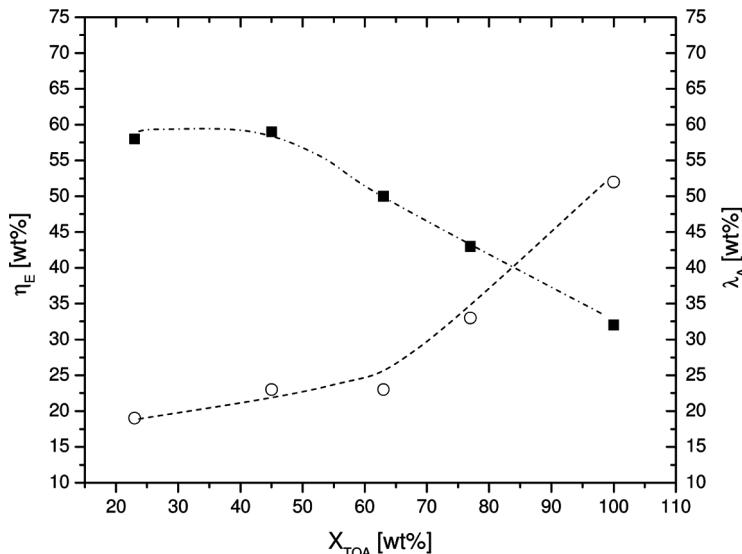


Figure 6. Influence of X_{TOA} on η_E (■) and λ_A (○). Lines are for illustrative purposes only. Conditions: BO-THF (50%-vol.), TOA in octane, room temperature, phase ratio of 1.0 (vol. basis), experimental method B.

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%). The results are graphically represented in Fig. 7.

The extraction efficiency is a clear function of the concentration of acetic acid in the BO layer. At higher concentrations, the extraction efficiency reduces considerably. The highest extraction efficiency (93 %) was observed at $X_{BO} = 0.23$ and this is also the highest value

Table 7. Reactive extractions with the aqueous phase of a thermally treated BO^a

TOA diluent	Acetic acid source	η_E (%)	λ_A (%)
Octane	Aqueous phase	71	0
Toluene	Aqueous phase	75	0
Octane ^b	BO/THF phase	93	9

^a50 vol% TOA in diluent, room temperature, 1 to 1 phase ratio (vol. basis).

^bOptimum conditions: 0.23 wt% BO in THF, 50 vol% TOA in octane

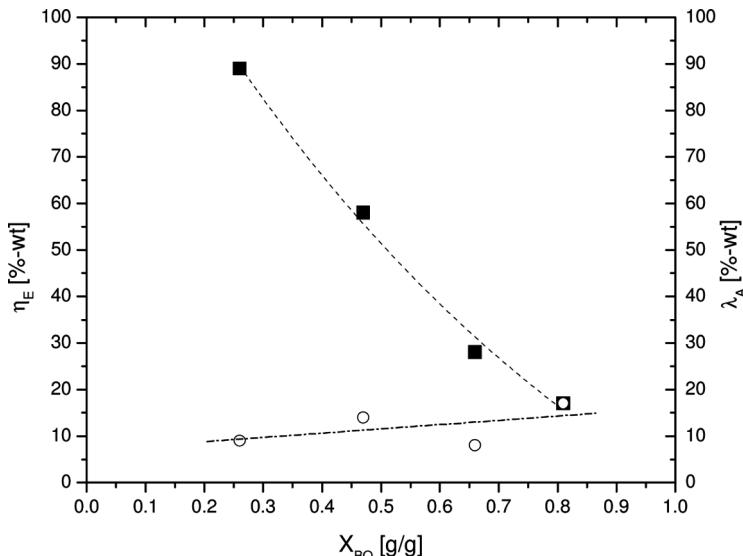


Figure 7. Influence of X_{BO} on η_E (■) and λ_A (○). Lines are for illustrative purposes only. Conditions: TOA in octane (50%-vol.), 1 to 1 phase ratio of the BO and TOA phase, room temperature, experimental method B.

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 (Fig. 7).

Acetic Acid Recovery from the Aqueous Phase of a Thermally Treated BO

TOA transfer from the extractant phase to the BO-phase reduces the attractiveness of acetic acid recovery from BO using the reactive extraction concept. 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 was obtained by thermal treatment of BO at elevated temperatures ($>300^{\circ}\text{C}$) 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 (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 for crude BO. The results of the reactive extractions are provided in Table 7 and compared with previous results found for BO/THF mixtures.

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, TOA was not detected in the aqueous phase after reactive extraction. Therefore, acetic acid recovery from the aqueous phase of a thermally treated BO appears more feasible than the use of crude BO and warrants further investigations.

CONCLUSIONS

The proof of concept for the recovery of acetic acid from BO by reactive extraction using long chain tertiary amines in combination with various diluents has been demonstrated. By proper selection of co-solvents and optimization of loadings, an acetic acid extraction efficiency of 93% could be obtained using TOA in a single equilibrium step. In this best case, 10 wt% of the TOA ended up in the original BO-phase. This is a disadvantage of the method as it complicates the recovery and recycle of the expensive TOA and makes the BO fraction less attractive for further applications. To reduce TOA transfer to the BO layer, screening experiments with the aqueous phase from a thermally treated BO were performed. Extraction efficiencies of 75% could be obtained using TOA diluted with toluene. TOA transfer to the aqueous phase was not observed. Further experimental optimization studies and modeling activities for the latter system are in progress and will be reported in due course.

NOMENCLATURE

AA	Acetic acid
BO	Bio-oil, fast pyrolysis oil
C_j^i	Concentration of j in phase i , M

HHV	Higher heating value, MJ/kg
K_D	Distribution coefficient, M/M, defined in eq. 2
m_j^i	Amount of component j in phase i , g
TA	Tertiary amine
TDDA	Tri-n-dodecylamine
THF	Tetrahydrofuran
TOA	Tri-n-octylamine
X_i	Weight fraction of component i

Greek Symbols

η_E	Extraction efficiency, wt%, defined in eq. 1
λ_A	Amine loss, wt%, defined in eq. 3

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