

**REACTIVE DISTILLATION
OF TRIFLUOROACETIC
ANHYDRIDE**

by

Clare Wunder

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Honors Degree in Bachelor of Chemical Engineering with Distinction

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ABSTRACT

Trifluoroacetic anhydride (TFA anhydride) is an important reagent for the production of a novel class of bio-based surfactants. Current manufacturing methods using trifluoroacetic acid (TFA acid) have been completed on a lab-scale and involve the use of halogens or phosphorous pentoxide; there does not yet exist a continuous method for TFA anhydride synthesis from TFA acid without the aforementioned hazardous compounds. This thesis proposes a two-step process for recovering TFA acid from the production of bio-based surfactants, then synthesizing TFA anhydride through reactive distillation of TFA acid and acetic anhydride. First, it was found that TFA acid can be continuously distilled from the bio-based molecule precursor solution. In this step the heat applied for distillation drives the reaction to near completion, so reagents can be used in a 1:1:1 ratio to minimize waste. 95% of the TFA acid was recovered in a heterogeneous mixture with the heptane solvent, so it can be decanted and purified by distillation for use in TFA anhydride synthesis. Second, it was found that reactive distillation of a stoichiometric ratio of TFA acid and acetic anhydride (2:1) produced TFA anhydride with 94% purity and conversion of 9.0%. Finally, experimental results were used to construct a flowsheet in Aspen Plus, but the heterogeneous azeotropic nature of the first step prevented the use of simulation for predicting results after scale-up. Due to this complication and the low conversion of TFA acid to TFA anhydride, this process will require further investigation before it can be recommended for large-scale production.

Chapter 1

INTRODUCTION

Acid anhydrides are highly useful reagents for carrying out organic synthesis, most notably Friedel-Crafts acylation reactions ^{1,2}. In particular, trifluoroacetic (TFA acid) anhydride is commonly used for adding trifluoro groups onto molecules or generating fatty acid anhydrides for Friedel-Crafts acylation reactions ². TFA acid and TFA anhydride are similar to acetic acid and acetic anhydride in that they are both clear corrosive liquids ^{3,4,5,6}. However, the molecules containing trifluoroacetyl groups have lower boiling points and higher reactivity. Thus, they are more effective for facilitating acylation reactions.

Methods for producing TFA anhydride from TFA acid have been investigated since the 1960's ⁷. However, many synthesis procedures contain harmful chemicals or are unsuitable for scale up to industrial scale due to the formation of unwanted byproducts. For this reason, it is of general interest to identify new approaches to produce pure TFA anhydride from TFA acid using less hazardous materials and a cost-effective method. In this thesis we focus on the separation of TFA acid from a complex reaction mixture (see Figure 1) and the reformation of TFA anhydride using acetic anhydride.

One example of a process where this could be advantageous is in the production of novel bio-based surfactants, such as those prepared by Park et al. using fatty acid anhydrides and bio-based furans ⁸.

The process consumes TFA anhydride and produces trifluoroacetic acid as a byproduct, motivating the need for a process for purifying the TFA acid from the reaction mixture and transforming it, in high yield, to TFA anhydride to be reused multiple times (see Figure 1).

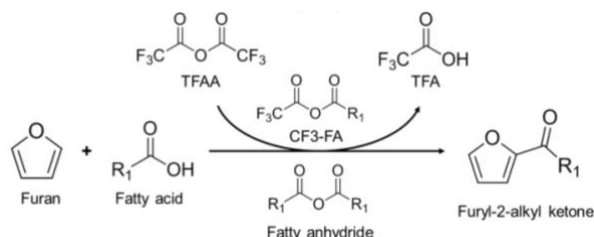


Figure 1. Reaction pathway for furan acylation with fatty acid promoted by trifluoroacetic anhydride at room temperature (TFAA - Trifluoroacetic anhydride, TFA - Trifluoroacetic acid) ⁸.

This can be done, in principle, by adding a new reaction step to convert TFA acid back into TFA anhydride, reducing materials costs and hazardous waste production. Improving the process for making bio-based surfactant molecules would benefit the industry, consumers, and the environment because these specialty molecules maintain the properties necessary for cleaning applications, while also being biodegradable and easily tunable. There are fewer carbon emissions associated with their production because the use of bio-based materials reduces the need for fossil fuel derivatives ⁸.

Traditional Linear Alkylbenzene Sulfonate (LAS) and Alkyl Benzene Sulfonate (ABS) surfactants come from petroleum derivatives ⁹. In contrast, the bio-based surfactants only contain carbon from renewable sources. The furan ring and

fatty acid chains are obtained from plant matter (from xylose dehydration and hydrogenation, and from a number of oil-producing plants), as can be seen in Figure 2.

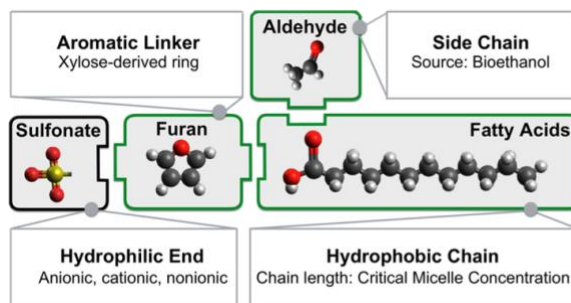


Figure 2. Bio-based surfactant molecule annotated with the sources for each molecular group within the structure ⁸

The bio-based surfactant molecules are currently made from furan, fatty acids, and trifluoroacetic anhydride in a stoichiometric reaction. This reaction follows a Friedel-Crafts mechanism in which furan performs nucleophilic attack on the carbon of a reactive intermediate species which can be either an asymmetric or a symmetric anhydride of the fatty acid, as can be seen in Figure 3. This reaction serves to functionalize the ring with a hydrophobic tail.

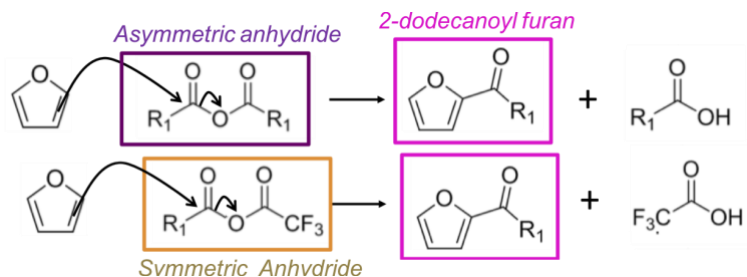


Figure 3. Nucleophilic attack by furan on the reactive anhydride intermediate (top) asymmetric anhydride (bottom) symmetric anhydride

TFA anhydride is essential for producing this asymmetric and/or symmetric anhydride of a fatty acid. The mechanism for this process can be seen in Figure 4.

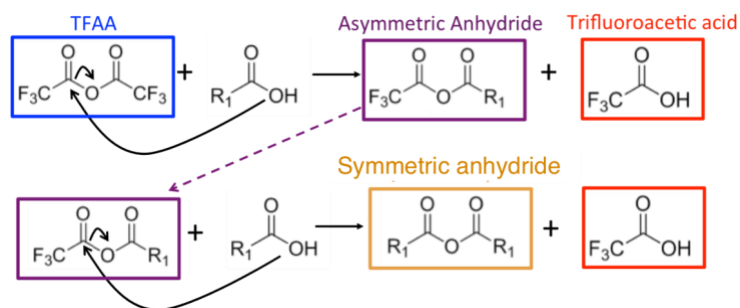


Figure 4. The role of TFA anhydride in the formation of the fatty acid anhydride

The furan head and hydrophobic tail structure created by furan acylation is easily tunable and provides hydrophilic character while the fatty acid tail provides hydrophobic character. This dual functionality promotes interactions with both aqueous and organic liquid phases, which constitutes the basis of surfactant technology. Thus, TFA anhydride facilitates an essential step in formation of the surfactant molecule.

TFA anhydride is expensive. According to Sigma Aldrich it costs about \$110 per kilogram¹⁰. If the high materials cost could be decreased, it would remove an economic obstacle in the path of producing bio-based surfactant molecules on an industrial scale. Therefore, it would be beneficial to develop a cost-effective method for producing the anhydride so that this environmentally friendly product can be more easily manufactured to compete with existing products that are less environmentally friendly.

The production of TFA anhydride from TFA acid can be performed through a variety of routes. One approach is a vapor phase condensation reaction between phosphorus pentoxide (P_2O_5) and trifluoroacetic acid. This reaction produces pure TFA anhydride and generates phosphoric acid as a byproduct^{2,8}. Unfortunately, P_2O_5 is a toxic and corrosive chemical that reacts with water rapidly to form phosphoric acid¹¹. During the process of synthesizing TFA anhydride, the phosphorous pentoxide forms an amalgam with excess trifluoroacetic acid making it difficult to recover unreacted material and the product⁷. This approach is effective at turning TFA acid into TFA anhydride, but the viscous byproduct material and hazardous waste render it impractical for large-scale applications⁷.

A second approach uses trifluoroacetyl chloride and alkali earth metals to form TFA anhydride. This route is economically unfavorable because trifluoroacetyl chloride is an expensive reagent, costing \$894 per kilogram¹². The reaction is industrially difficult because the chlorides are corrosive, requiring special construction materials for the processing equipment. Furthermore, the product ends up contaminated with sodium chloride, which is difficult to separate from the desired anhydride.⁷

A third option is the condensation of trifluoroacetic anhydride from two molecules of $R-CO-O-CO-R'$, where one of the R groups is CF_3 and the other is an alkyl, alkenyl, cycloalkyl, or aryl group composed of 6 or fewer carbon atoms⁷. This method was tested by Amiet et al. and found to be ineffective because the reaction occurs on only one end group of the anhydride and does not progress further.

Amiet and Disdier patented the method of reacting trifluoroacetic acid with an α -halogenated acetic acid and distilling off the trifluoroacetic anhydride⁷. The product

is easily separable from solution, but the yield is very low and halogens such as Cl_2 , Br_2 , or I_2 must be used, posing potential environmental risks.

In this thesis I will focus on the investigation of the reaction of trifluoroacetic acid and acetic anhydride to produce TFA anhydride. This process does not require the use of costly reactants, is highly selective towards the desired product, and produces acetic acid as a byproduct that can be purified and sold for additional profit (see Figure 5). This approach holds potential for economic feasibility because it can be scaled up to industrial scales.

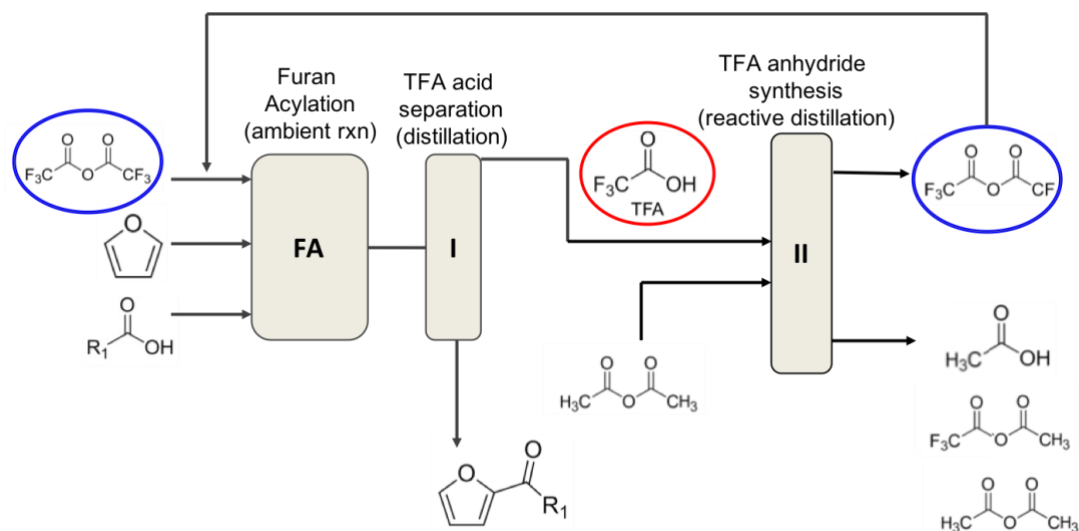


Figure 5. Proposed process for recovering TFA acid from furan acylation and performing reactive distillation of acetic anhydride and trifluoroacetic acid to produce trifluoroacetic anhydride and acetic acid

In the first block, FA, the furan acylation will be performed. TFA acid will be separated from solution by distillation in the second block, which is labelled I. TFA

anhydride will be synthesized by reactive distillation of TFA acid and acetic anhydride in the third block, which is labelled II.

To evaluate the technical and economic feasibility of implementing this step into the existing surfactant synthesis process, the goals of this study are as follows:

1. Conduct laboratory experiments to recover trifluoroacetic acid from a furan acylation reaction medium using reactive batch distillation
2. Characterize the reaction of trifluoroacetic acid and acetic anhydride using a specially designed reactor/column combination
3. Model the process using ASPEN Plus

The reactions will be studied under various conditions to model conversion and selectivity towards the desired products to understand the dependence on starting composition and time.

Chapter 2

PART 1: RECOVERY OF TRIFLUOROACETIC ACID FROM FURAN ACYLATION THROUGH BATCH DISTILLATION

Surfactant synthesis involves the consumption of trifluoroacetic anhydride (TFA anhydride) and the formation of trifluoroacetic acid (TFA acid) as a byproduct of an intermediate acylation step. From this process, our first goal is to separate TFA acid from the reaction solution so that it may be converted back into TFA anhydride, a valuable reagent.

2.1 Safety

Before beginning any experiment, it is imperative that one be aware of the hazards associated with the materials involved and handle them properly. The personal protective equipment required for this project was safety glasses, a flame-retardant lab coat, closed toed shoes, gloves, and long pants. All work was done in a fume hood with the sash pulled down low to avoid inhalation of compounds. Ignition sources were removed from the vicinity of the experiment in order to prevent a fire. All materials were handled with great caution and no chemicals were allowed to come into contact with skin, eyes, or any other part of the body.

Trifluoroacetic anhydride is a clear corrosive liquid. In the event of a spill, it should be absorbed with dry, inert material and prevented from entering drains or sewers. TFA anhydride should be stored in an airtight container (preferably not glass) in a safety storage cabinet⁴. Trifluoroacetic acid (TFA acid) is also a clear corrosive liquid that should be handled with the same approach as TFA anhydride³.

Heptane is a clear liquid that is classified as environmentally damaging, flammable (flash point = -4°C), an irritant, and a health hazard. Symptoms of respiratory exposure can include dizziness, nausea, and drowsiness ¹³.

Furan is highly flammable, with a flash point of -50°C . In the event of a fire, use dry chemical powder or alcohol foam. Ensure that furan containers are cooled and equipped with a ventilation jet to prevent pressure build-up and/or auto-ignition ¹⁴.

Lauric (dodecanoic) acid is corrosive and environmentally damaging. Store in a tightly sealed container in a cool location away from incompatible materials ¹⁵.

Para-xylene is a clear, flammable liquid with a flash point of 25°C . In the event of a fire, one should use dry chemical powder or a water spray ¹⁶. Maleic acid is a white solid that is corrosive and poisonous when dissolved in water ¹⁷. Both of these compounds were used as internal standards for characterization of products with H-NMR spectroscopy.

Deuterated carbon tetrachloride is a proven carcinogen that must be stored in a tightly closed container in a cabinet with adequate ventilation ¹⁸. Deuterated acetonitrile requires similar storage because it is highly flammable (flash point of 2°C) and acutely toxic ¹⁹. Both are used as H-NMR solvents.

2.2 Experimental methods

The reaction setup for the furan acylation step was based on work by Park et al., but a few modifications were implemented to make the setup more suitable for batch distillation applications ⁸. For a solvent, heptane was used in place of hexane because its boiling point is at least 20°C above that of TFA acid, while the latter is about 10°C below that of TFA acid, as can be seen in Table 1 ⁸. It should be noted that heptane is expensive and not commonly used as an industrial solvent, but for the sake

of imitating the reaction conditions of Park et al as closely as possible, it was chosen for this experiment.

Table 1. Boiling points of reagents and products for furan acylation reaction

Species	Boiling point at 1 atm (°C)
trifluoroacetic anhydride	39.2
trifluoroacetic acid	72.4
furan	31.3
heptane	98.4
lauric acid	299

Using a higher boiling solvent makes the solution better suited for distillation because the solvent will not boil over into the distillate before the desired product. and Reducing its quantity from 50 mL to 10 mL lends the system towards distillation applications because there is less liquid to be heated. Energy costs are of high concern in separation processes. The resulting higher concentrations of reagents also increase the rate of conversion. Molar ratios of reagents that were tested are listed in Table 2.

Table 2. Molar ratio of reagents for furan acylation reaction in 10 mL heptane

Furan	Dodecanoic acid	Trifluoroacetic anhydride
1	1.1	1.1
1	1.4	1.6
1	0.80	0.92
1	0.91	0.91

The furan acylation reaction was carried out under ambient temperature, ambient pressure, and with constant agitation for 2 hours. Like the work of Park et al, it showed a color change from clear to dark red/brown in minutes ⁸.

After acylation of the furan was performed, the solution was transferred to a two-neck round-bottomed flask equipped with a distillation apparatus. It was then heated using a hot plate and a glycerol oil bath. The two-necked flask was equipped with a distillation head and an additional round bottomed flask to collect distillate from the condenser. Vapor temperature was monitored throughout the experiment by means of a thermometer placed at the top of the column. This thermometer was insulated with glass wool and foam to prevent error in temperature reading due to heat transfer to the surroundings. The temperature of the reaction solution was monitored by submerging a thermometer in the glycerol bath, assuming that there was adequate heat transfer for the temperature of the bath to be about the same as the temperature of the liquid within the flask.

2.3 Observations and data analysis

Vapor temperature rose to about 60°C for the first cut of distillate and about 2 mL of liquid was collected in the distillate. The distillate separated into two liquid phases, both clear. The top phase was about a third of the volume of the bottom phase. The second cut of distillate came over around 80°C as one homogeneous liquid phase. The bottoms of the solution changed from dark purple to dark brown due to heating.

C-NMR analysis of samples from the distillate with revealed the presence of trifluoroacetic acid as well as heptane in the top and bottom phases of the first cut of distillate. There was only heptane in the second distillate cut. For further discussion on the simultaneous distillation of heptane and TFA acid, see section 2.4.

Samples of the unheated acylated furan solution, both cuts of distillate, and the remaining bottoms of the solution were characterized using $^1\text{H-NMR}$ with an internal standard of p-xylene in deuterated chloroform. The composition of each sample was found using the $^1\text{H-NMR}$ peak integrals of the p-xylene standard, the integral of the peak for TFA acid (10-11.5 ppm) and the volume of the sample. TFA anhydride cannot be seen in $^1\text{H-NMR}$, so conversion was calculated based off of the concentration of TFA acid in each sample.

From the calculated compositions, it was found that 79% of TFA anhydride was converted into TFA acid after the room temperature reaction and before distillation. This is less than the reported TFA anhydride conversion of 91% from Park et al. for a similar reaction⁵. The molar ratios of reagents were 1 furan : 1.3 lauric acid : 1.3 TFA anhydride for this study and 1 furan : 1.3 lauric acid : 1 TFA anhydride for that of Park et al. It is possible the discrepancy in conversion could be due to a slight excess of TFA anhydride in this reaction compared to the original study.

While the furan acylation reaction did not reach full conversion of TFA anhydride at room temperature, the $^1\text{H-NMR}$ analysis for the bottoms sample after distillation showed an absence of TFA anhydride in the $^1\text{H-NMR}$ spectra, suggesting that the separation drove the reaction to near completion. The overall conversion of TFA anhydride was calculated to be 95.6%. There was only a small amount of TFA acid (0.4 mol%) remaining in the bottoms; 99.7% was recovered from the reaction solution by distillation. The purity of TFA acid collected in the aqueous phase of the distillate was 93%, showing that the main goal of part 1 was met: trifluoroacetic acid was separated from the products of the furan acylation via batch distillation.

2.4 Heterogeneous azeotropic distillation of TFA acid and heptane

The observed vapor temperature of $\sim 60^{\circ}\text{C}$ was below the boiling points of both heptane (bp 98°C) and TFA acid (bp 72°C), indicating that the two species form a low boiling azeotrope. This is an obstacle for obtaining the desired recovery of TFA acid because pure TFA acid cannot be collected directly from the batch distillation. There is no vapor-liquid equilibrium data available for the azeotropic mixture of heptane/TFA acid, but there exist data for an azeotrope between hexane and acetic acid, as well as a reference to "using heptane to azeotrope the trifluoroacetic acid..." found in databases and patents ^{20,21}. Both of these sources suggest that the azeotropic mixture of heptane and TFA acid could exist.

It is important to note that the distillate separates into a heptane-rich top phase and a TFA acid-rich bottom phase. For the composition of each phase of the distillate and the composition of the bottoms, see Table 3.

Table 3. Composition of distillation products for furan acylation solution. Note that mole fractions in the bottoms do not sum to one due to the presence of the remaining reagents.

Sample	Mole fraction heptane	Mole fraction TFA
Top phase of distillate	0.55	0.45
Bottom phase of distillate	0.10	0.90
Bottoms	0.68	0.04

Studies were conducted on a 1:1 molar mixture of heptane : TFA acid and a 3:1 mixture of heptane : TFA acid. The molar ratio of 3:1 was chosen to mimic the molar ratios of solvent and byproduct that are found in the furan acylation reaction. It was determined that an azeotrope forms with a mole fraction of $x_{\text{TFA acid}} = 0.93$ mol/mol and a boiling point of 62°C . Due to the presence of heptane in this bottom

phase of the distillate, it is necessary to include a second distillation step to recover pure TFA acid. Therefore, the setup will require two distillation columns with a decanter between them, as is shown in Figure 6.

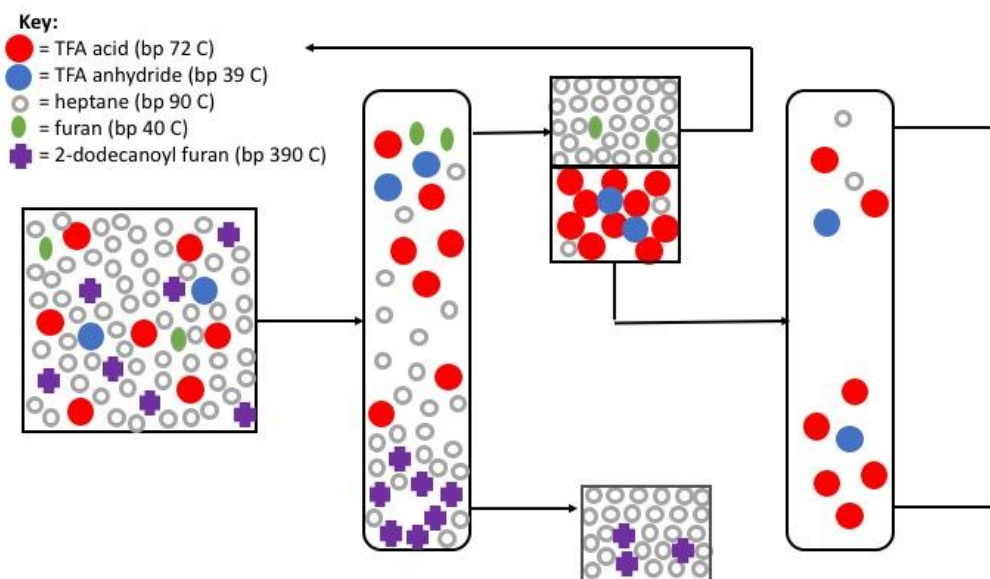


Figure 6. Separation of TFA acid from the acylated furan solution through heterogeneous azeotropic distillation

The square box at the start shows the reaction solution containing the 2-dodecanoyl furan product, the byproduct TFA acid, the heptane solvent, and remaining reagents (furan and TFA anhydride). In the first column, lauric anhydride and the acylated furan product have boiling points at least 200°C higher than that of TFA acid, so both will exit through the bottoms. Heptane will remain mostly in the bottoms, but a fraction will exit as the azeotrope, which is carried out into the distillate. Furan and TFA anhydride both boil around 40°C, so they will exit through

the top of the column. In the distillate, furan will remain mostly in the heptane-rich top layer, while TFA anhydride will be mostly in the acid rich bottom layer. These layers will be separated by decanting. The heptane rich top layer can be recycled for use in the furan acylation reaction. The TFA-acid rich bottom layer from the decanter will be fed into the second distillation column in the separation scheme.

In the second column, the low boiling azeotrope will exit through the top, while pure TFA acid will be collected at the bottom. Ideally, the heptane - TFA acid mixture from the second column can be recycled so that minimal TFA acid will be lost to exit streams. Therefore, TFA acid can be recovered from the furan acylation reaction solution by distillation.

Chapter 3

PART 2: PRODUCTION OF TRIFLUOROACETIC ANHYDRIDE BY BATCH REACTIVE DISTILLATION

The combination of trifluoroacetic acid and acetic acid to form trifluoroacetic anhydride has not been accomplished in prior art; the reaction is thermodynamically unfavorable²². The proposed mechanism is two steps, the first being the formation of an asymmetrical anhydride, and the second being the formation of the full trifluoroacetic anhydride, as can be seen in Figure 7.

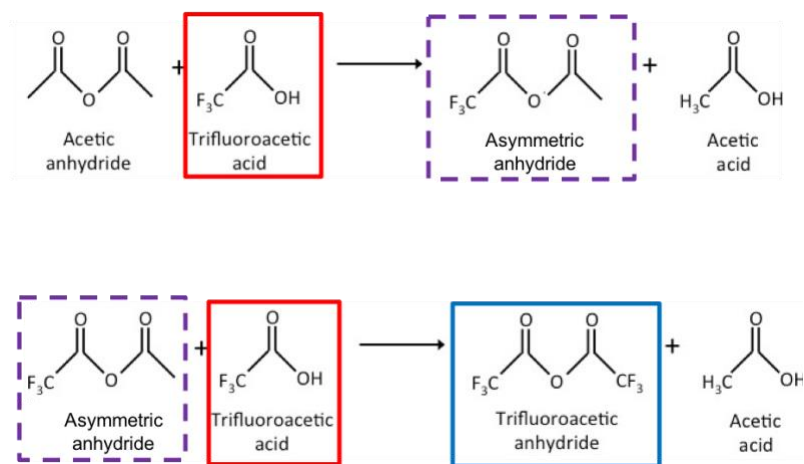


Figure 7. Proposed two step mechanism for synthesis of TFA anhydride from TFA acid and acetic anhydride

The first step quickly forms a stable asymmetric anhydride²². The second step is less thermodynamically favorable, so reactive distillation was chosen for this

application to continuously remove product and drive the reaction forwards. Montiel-Smith et al. investigated a process for forming the asymmetric anhydride through a 1:1 reaction of trifluoroacetic acid and acetic anhydride ². The two step reaction pathway for forming the asymmetric anhydride then the symmetric anhydride is also described in work by Bourne et al ²³. Montiel et al obtained a conversion of 20% of TFA acid into the symmetric anhydride in about 15-20 minutes, showing that the first step of the proposed mechanism (for forming TFA anhydride) proceeds almost instantaneously. However, their goal was to form said asymmetric anhydride and they did not look into the use of separations in tandem with reactions. Reactive distillation technology could offer significant advantages for the case of synthesizing TFA anhydride from this unfavorable reaction because it will remove product as it is formed, driving the reaction forward.

An advantage of using acetic anhydride to form TFA anhydride instead of using P₂O₅ is that the reaction with acetic anhydride produces acetic acid as a byproduct. Acetic acid is easy to separate from TFA anhydride by distillation because there is a large difference in boiling points. In addition, this compound is less corrosive than phosphoric acid and has many applications. After purification, this byproduct will not pose a waste treatment cost, but rather profit due to additional sales.

3.1 Safety

For safety information on trifluoroacetic acid and trifluoroacetic anhydride, see Chapter two. Both acetic anhydride and acetic acid are clear, corrosive liquids. Acetic anhydride is also flammable. Both must be handled with extreme care and stored in

tightly sealed containers in chemical safety cabinets. The anhydride belongs in flammables storage while TFA acid should be stored as a corrosive material. ^{5,6}

3.2 Experimental methods

A 2:1 molar ratio of trifluoroacetic acid : acetic anhydride was combined in a 50 mL two-neck flask with a stir bar. This molar ratio matched the stoichiometric ratio of the reaction. A distillation apparatus consisting of a 12 inch column with a condenser was secured to the top neck of the flask containing the reagents. An additional flask (50 mL, single neck) was connected to the condenser to collect the distillate; it was cooled in an ice water bath that was refreshed throughout the course of the experiment. Cold ice water was used for cooling the condenser of the distillation head. The reaction was stirred and heated for 6 hours under ambient pressure.

3.3 Results and Discussion

Throughout the course of the reaction, the clear liquid solution in the bottoms flask slowly turned brown. According to Montiel-Smith et al, this is common of reactions producing asymmetric anhydrides with carboxylic acids because the application of heat causes some compounds to degrade ².

A vapor temperature of ~40°C corresponded with collection of clear liquid distillate. This temperature is close to the boiling point of trifluoroacetic anhydride (bp 39°C) at 1 atm. The temperature profile for the vapor over the course of the distillation can be seen in Figure 8.

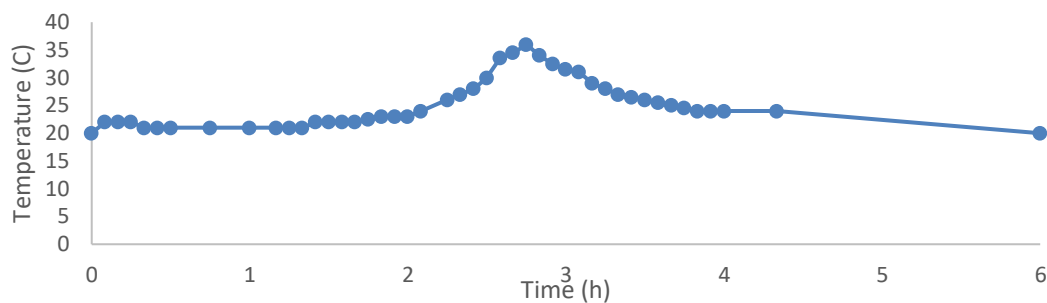


Figure 8. Vapor temperature of over time for reactive distillation of TFA acid and acetic anhydride in a 2:1 molar ratio

After 0.3 mL of clear distillate was collected, the vapor temperature dropped down to 25°C and no more liquid accumulation was observed in the condenser. The distillate that was collected was analyzed with $^1\text{H-NMR}$ and C-NMR in deuterated chloroform.

The concentration of TFA acid in each sample was determined with $^1\text{H-NMR}$, using a p-xylene internal standard and a solvent of CDCl_3 . Qualitative confirmation of the presence of the anhydride in the distillate was obtained through C-NMR via observation of TFA anhydride's characteristic peak around 150 ppm. The conversion for this reaction was calculated to be about 9% based on the change in moles of TFA acid from the initial solution to the final bottoms and distillate.

Two distillation setups were tested for running this reactive distillation. One involved the use of a multistage, 12 inch column while the other consisted of a single stage column about 1 inch in length. Distillation with the larger column required at least four hours of heating, whereas distillation with the smaller column required two. The asymmetric anhydride was not observed in the H-NMR analysis of the distillate from the experiments using the larger column, showing that only TFA acid and TFA

anhydride were recovered. However, the asymmetrical anhydride was observed in the distillate of experiments performed with the shorter column. This likely indicates that the heating rate was too great for the smaller column to work effectively, so proper separation based on boiling points was not achieved.

The asymmetric anhydride was observed in the bottoms, regardless of distillation setup. This is to be expected because full conversion of TFA acid to TFA anhydride was not achieved, so the remaining trifluoroacetyl groups were present as other compounds in solution. Further adjustment of the heating rate and column length could reduce the amount of time needed to recover TFA anhydride, while also maintaining the desired distillate purity. This would be important to pursue for scale-up because energy usage is important for optimizing utilities costs associated with industrial separations.

In summary, reactive distillation can be used to produce TFA anhydride from TFA acid and acetic anhydride. Conversion and recovery are low, but there is room for optimization of heating rate and column length.

Chapter 4

PART 3: ASPEN MODEL OF PROCESS FOR INDUSTRIAL APPLICATION

This procedure is a proposed improvement for an existing industrial process. Therefore, it would be beneficial to simulate the recovery of acid and conversion into the anhydride on a large scale to gain insight into the economics and energy requirements for producing trifluoroacetic acid on a large scale. Aspen Plus was used to assemble a process flow diagram of the proposed two-step process for TFA acid separation and TFA anhydride synthesis (see Figure 9). From this simulation, mass balances over the whole system were obtained and the results were compared with those of experimental observations.

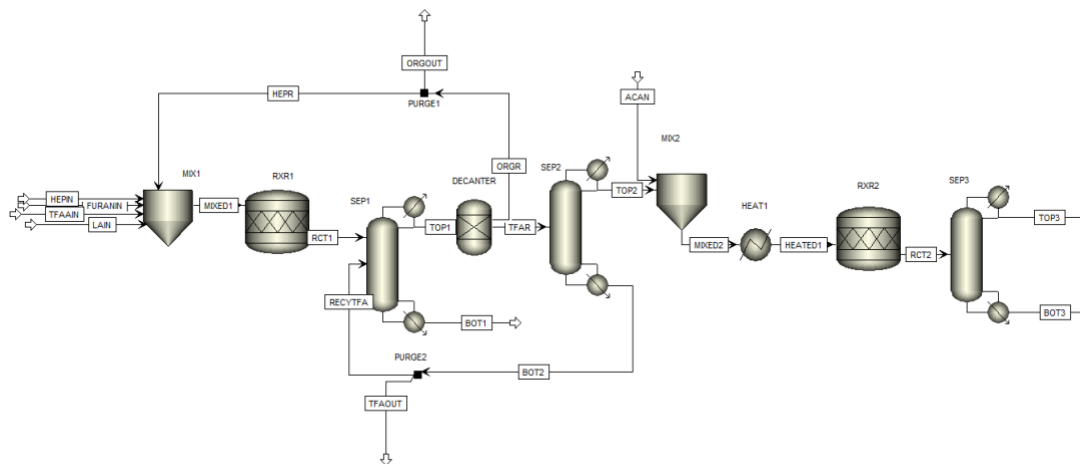


Figure 9. Aspen Plus flowsheet for process of furan acylation and reactive distillation to form trifluoroacetic anhydride

4.1 Flowsheet setup

The physical and thermodynamic properties of each component in the simulation were calculated using the UNIQUAC method, but reaction conversions and stoichiometry were set based on the experimental findings from the studies on furan acylation and trifluoroacetic anhydride synthesis by reactive distillation.

Molar stoichiometry of 1:1:1 is recommended for the reagents of the furan acylation reaction to minimize waste of materials. It was assumed that the heat from distillation would drive this reaction to near completion, so having the reagents in their stoichiometric ratio achieved satisfactory conversion and was the most efficient setup. The flow rate of furan, trifluoroacetic anhydride, and lauric acid (dodecanoic acid) were each set to 1 kmol/s. The n-heptane solvent was set at 200 L/s. After the reagents were mixed, a stoichiometric reactor modeled the furan acylation reaction to achieve conversion of 96% with a residence time of 30 minutes.

While experimental results showed only 79% conversion in the room temperature furan acylation reaction, the value was entered as 96% because it was assumed that whatever reagent had not reacted by this time would go towards full conversion by the heating of the distillation separation. 96% was the observed conversion after distillation in experiments.

The residence time was also based off of experimental observations. An exotherm was observed during the first half hour of reaction, followed by a decline in temperature and minimal change in the color of reaction solution. In the work of Park et al, it was also shown that TFA anhydride reached near full conversion within the first thirty minutes under ambient conditions with similar reactant ratios⁸. Therefore, it is likely that most of the reaction is completed in the first 30 minutes.

After the furan acylation reactor, RXR1, TFA acid was removed from the solution by distillation. The goal of this separation structure is to remove 99% of the n-heptane solvent before proceeding to the next step so that it will not interfere with TFA anhydride synthesis. The heterogeneous azeotropic distillation was modelled using two 10 stage RADFRAC columns, SEP1 and SEP2. SEP1 had a reflux ratio of 10 and a distillate to feed ratio of 0.2. The system was designed to reach vapor-liquid-liquid equilibrium (VLLE) at the condenser.

4.2 Results and discussion

This first separation produced TFA of 90.8 mol% purity. The second distillation, SEP2, was also 10 stages with a reflux ratio of 10 and a distillate to feed ratio of 0.5. This second column output 99.9% pure TFA acid so that the separation structure achieved the removal of n-heptane.

The impurity of the TFA acid after the first separation is due to TFA anhydride, furan, and n-heptane. The TFA anhydride impurity is not of concern. It is good to distill unused anhydride from solution so that the trifluoroacetyl group will be recovered. If there is any water present in the system, the anhydride will be hydrolyzed to form TFA acid, contributing to higher recovery of TFA acid. The presence of furan in the distillate is expected in this simulation because it has a low boiling point. However, this will not likely be observed in real world distillations because TFA acid acts as a catalyst for furan hydrolysis to form 2,3-butanedione and can react with other species in solution to form heavy byproducts that will not boil up into the distillate ²⁴. 2,3-butanedione has a higher boiling point than furan and would not be found in the distillate ²⁵. These side reactions were not accounted for in the simulation, which is why the presence of furan differs between Aspen Plus and

experimental observations. In the decanting step, the furan was removed with heptane in the organic recycle stream so that none continued on through the rest of the process.

During lab experimentation, it was observed that TFA acid and heptane distilled over as a heterogeneous, low-boiling azeotrope. The distillation column was designed for an azeotropic system with vapor-liquid-liquid equilibrium at the condenser. Two outlet streams were located at the first stage (the condenser) to constitute the organic-rich and aqueous-rich distillate phases. However, using the UNIQUAC method, Aspen Plus does not recognize TFA acid and n-heptane as forming an azeotropic mixture under atmospheric pressure. Nor does the software recognize that TFA acid and n-heptane form an immiscible mixture. This was observed with both the UNIQUAC. NRTL-RK was also tested because it should be accurate for modeling hydrocarbons and polar species. However, it was unable to recognize the azeotrope and phase separation of the heptane-TFA acid mixture. For this reason, the distillate outflows could not be separated into aqueous-rich and organic-rich phases. Instead, the distillate was modelled as a single outflow.

A separator block (DECANTER) was used to simulate phase separation and collection for the TFA acid-rich outflow (TFAR) and organic rich outflow (ORGR) by using a separator block to recover 99% of the TFA acid and 0.34% of the heptane in stream TFAR. These were the experimentally observed recoveries of each species in the bottom phase of the distillate during Part I. This stream went on to SEP2 while the organic rich stream (ORGR) was returned to SEP1 for further purification.

While the first column had heptane coming out the base and the mixture of heptane and TFA acid exiting the top, the second column should have TFA acid exiting through the bottoms and the low boiling n-heptane TFA acid azeotrope exiting

through the top. However, since this low-boiling azeotrope is not recognized, Aspen predicts that the majority of heptane will leave the column as a heavy boiling component. Due to this limitation, the simulated process uses the distillate from the second column (TOP2) instead of the bottoms (BOT2) to feed the TFA anhydride synthesis reactor. This is not accurate to the true nature of the system, but it is practical for modelling the separation and achieving the purity of TFA acid required for moving forwards.

After exiting SEP2, the TFA acid stream was mixed with acetic anhydride and the mixture entered a second reactor (RXR2) to model the synthesis of TFA anhydride through reactive distillation. The reaction and distillation for this synthesis were performed separately. Ideally, they would be modelled to occur simultaneously, as was observed in experimentation. This flow sheet approximates the behaviors of the system.

This simulation has a slight excess of acetic anhydride so the ratio is 1.89 : 1 instead of the recommended 2 : 1 molar ratio. In a real-world application, some of the acetic anhydride might be lost to hydrolysis or other side reactions, so this slight excess could potentially be beneficial for the process. The conversion of TFA acid to TFA anhydride was set to be 99%, which assumes that the reaction time is faster than the residence time in the column. The higher conversion assumption used in the simulation is also based on the continuous nature of the process. Reagent is constantly being replenished so the distillation will not peak then fade out, as was observed for the batch distillation in Part II, and more of the TFA acid will be recovered. The experiments from Part II showed a reaction time between four and five hours. With column optimization, this time could be reduced so that species will react before they

leave through the top or bottom streams. Given that TFA anhydride (bp = 39°C) has a much lower boiling point than the next lowest boiling component, TFA acid (bp = 72°C), it will come out the top of the column in high purity. Any asymmetric anhydride (bp ~ 98°C) that is formed will be somewhere in the middle of the column, where it can react to form the symmetric TFA anhydride and acetic acid, which will travel to the top and bottom of the column respectively. Acetic anhydride will react to near completion and the resulting acid will exit through the bottoms of the column.

The distillation of this part of the process was simulated in a DSTWU distillation module (SEP3). TFA anhydride was recovered with 99.9 mol% purity as the distillate product. Acetic acid was recovered in 95.8 mol% purity from the bottoms stream. Further adjustment of reflux ratios and column dimensions will be required to optimize the recovery of acetic acid so that it meets the purity requirements for sale as a reagent grade chemical (must be 99% or higher).

According to the Aspen Plus simulation, the TFA anhydride formed in this process was 93.7% of that which initially entered. This conversion was calculated on a molar basis. A stream table of the major inputs and outputs of the system can be seen in Figure 10. Said table includes the inflow of TFA anhydride for furan acylation and the outflow of TFA anhydride from the reactive distillation column to illustrate the overall recovery of TFA anhydride. This table also displays the input and output of acetic anhydride and acetic acid to show conversion of the reagent and recovery of the salable byproduct. More detailed records of the molar flow rates of all species can be found in Appendix A.1. Specifications for the distillation columns can be found in Appendix A.2.

	Units	TFAAIN	TOP2	TFAOUT	ORGOUT	ACAN	TOP3	BOT3
From			SEP2	PURGE2	PURGE1		SEP3	SEP3
To		MIX1	MIX2			MIX2		
Substream: MIXED								
Phase:		Liquid	Liquid	Liquid	Mixed	Vapor	Liquid	Liquid
Component Mole Flow								
ACETI-01	KMOL/SEC	0	0	0	0	0	0	1.89338
TRIFL-01	KMOL/SEC	0	1.91251	0.0415826	0.00428368	0	1.91251e-06	0.0191231
ACETI-02	KMOL/SEC	0	0	0	0	1	0	0.0533079
N-DOD-01	KMOL/SEC	0	0	0	0	0	0	0
N-HEP-01	KMOL/SEC	0	5.50332e-05	0.000918793	0.026178	0	6.1345e-11	5.50332e-05
FURAN	KMOL/SEC	0	0	0	0.00826488	0	0	0
2-DOD	KMOL/SEC	0	0	0	0	0	0	0
TFAA	KMOL/SEC	1	0	0	0.00826432	0	0.937225	0.00946692
WATER	KMOL/SEC	0	0	0	0	0	0	0
Mole Flow	KMOL/SEC	1	1.91256	0.0425014	0.0469909	1	0.937227	1.97534
Mass Flow	KG/SEC	210.03	218.077	4.83348	5.40998	102.09	196.846	123.319
Volume Flow	CUM/SEC	0.121568	0.161801	0.00365158	0.371781	2.44831e+06	0.124694	0.133706
Temperature	K	298.15	344.949	345.332	343.083	298.15	341.433	413.763

Figure 10. Stream table of major inflows and outflows in Aspen Plus simulation of the process for synthesizing TFA anhydride using byproduct TFA acid from furan acylation

It should be noted that due to the limitations of Aspen's thermodynamic models, the separation of TFA acid from the acylated furan solution is not completely accurate. Manual entry of the separation of TFA acid and heptane in the decanter unit was used to correct for this limitation as best as possible with the given software.

Overall recovery of TFA anhydride can be optimized by fine tuning the recycle structure that recaptures TFA acid from the n-heptane rich streams in the first separations structure, consisting of SEP1 and SEP2. The purges for the two recycle streams only return 80% of their contents to the system, so some TFA acid is lost in the exit streams. A larger column for TFA anhydride synthesis (SEP3) would offer the benefit of producing purer acetic acid in the bottoms. Purer distillate and bottoms products would bring higher profit through sale of desired product and sale of byproducts respectively.

In the event that more information could be gathered on the composition of the distillation of acylated furan reaction solution and the combination of TFA acid and acetic anhydride at the given separations, the recycle structure could be modified to recover more byproduct acid (TFA acid).

One must consider that this also requires the safe removal of the surfactant precursor molecule. In the case that this desirable molecule can be removed from the bottoms of the first distillation, then the recovered TFA acid - heptane mixture can be purified and reused in the first step of this process.

4.3 Future work

With respect to Part I and Part II, it would be of great interest to test the furan acylation reaction and TFA distillation with a different solvent to see if the heterogeneous azeotrope can be avoided. Furthermore, it will be important to take TFA acid recovered from the first step and test its use in TFA anhydride synthesis.

This study has not considered the effects of heating and separation on the bio-based surfactant molecule precursor. An investigation should be made into whether or not the desired product molecule is altered during this procedure. If this molecule is modified beyond use, then a different method must be found for separating TFA acid from the initial furan acylation reaction solution.

Further study using the reactive distillation module in Aspen could provide valuable insight into the scale up of the process. The assumption of 99% conversion in the reactive distillation is a large statement to make because this requires a large reflux ratio that could be economically infeasible. More accurate representation of phase envelopes and optimization of column parameters will be required before a decisive recommendation can be made on implementing this process at an industrial scale.

Chapter 5

CONCLUSIONS

The proposed two-step process for TFA anhydride production by reactive distillation of TFA acid and acetic anhydride is technically feasible. TFA acid can successfully be recovered as a biphasic distillate from the reaction solution of furan acylation. The TFA acid-rich bottom phase of the heterogeneous distillate can be decanted and distilled again to remove residual heptane and obtain pure TFA acid. By using reactive distillation, TFA acid and acetic anhydride can be combined to produce TFA anhydride as a distillate product with 99.9% purity and overall recovery of 9%. Both the initial separation step and the reactive distillation step can be completed in less than a day and can be implemented as continuous processes, lending them towards application in large-scale production. Both steps also offer the advantage of operating under mild temperatures and ambient pressure. The reactive distillation process to form TFA anhydride also forms a salable byproduct, offering further economic benefits. Drawbacks to the proposed process are that the conversion of TFA acid to TFA anhydride energy intensive. Aspen modeling showed overall recovery of 93.7% of the TFA anhydride that entered the system, due to the absence of azeotropic behavior in the model and the assumption that in a continuous system, the synthesis step goes to 99% conversion. More rigorous experimentation and simulations should be conducted to better understand the heterogeneous azeotropic distillation in the first step and to optimize the conversion in the second reactive distillation step.

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APPENDIX

A.1 STREAM TABLES FROM ASPEN PLUS SIMULATION

Table 4. Aspen Plus stream results for materials balance

Component Mole Flow: (kmol/s)	Stream:																
	FURANIN	HEPIN	HEPR	LAIN	MIXED1	TFAIN	ORGR	ORGOUT	TFAR	TOP2	BOT2	TFAOUT	ACAN	MIXED2	RCT2	TOP3	BOT3
acetic acid	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.893384	0	1.893384
trifluoroacetic acid	0	0	0.0171347	0	0.0171347	0	0.0214184	0.00428368	2.120422	1.912509	0.2079132	0.0415826	0	1.912509	0.019125	1.91E-06	0.0191231
acetic anhydride	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0.0533079	0	0.0533079
dodecanoic acid (lauric acid)	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0
n-heptane	0	1.362092	0.1047122	0	1.466804	0	0.1308903	0.026178	0.004649	5.50E-05	0.00459396	0.000918793	0	5.50E-05	5.50E-05	6.13E-11	5.50E-05
furan	1	0	0.0330595	0	1.033059	0	0.0413243	0.00826488	0	0	0	0	0	0	0	0	0
2-dodecanoyl furan	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
trifluoroacetic anhydride	0	0	0.0330572	0	1.033057	1	0.0413216	0.00826432	0	0	0	0	0	0	0.9466921	0.9372252	0.00946692
water	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total:	1	1.362092	0.1879637	1	4.550056	1	0.2349546	0.0469909	2.125071	1.912564	0.2125071	0.0425014	1	2.912564	2.912564	0.9372271	1.975337

A.2 ASPEN PLUS SPECIFICATIONS

Table 5. Aspen Plus specifications for design of distillation column SEP1

RadFrac	
Name	
Property method	1-Sep
Use true species approach for electrolytes	UNIQUAC
Free-water phase properties method	YES
Water solubility method	STEAM-TA
Number of stages	3
Condenser	10
Reboiler	TOTAL
Number of phases	KETTLE
Free-water	3
Top stage pressure [bar]	NO
Specified reflux ratio	1.0125
Calculated molar reflux ratio	10
Calculated bottoms rate [kmol/sec]	10
Calculated boilup rate [kmol/sec]	2.36003065
Calculated distillate rate [kmol/sec]	29.0665936
Condenser / top stage temperature [K]	2.36003065

Condenser / top stage pressure [N/sqm]	343.482341
Condenser / top stage heat duty [Watt]	101250
Condenser / top stage subcooled duty	-989534328
Condenser / top stage free water reflux ratio	23.6003065
Reboiler pressure [N/sqm]	101250
Reboiler temperature [K]	392.77709
Reboiler heat duty [Watt]	1074522260
Basis for specified distillate to feed ratio	MOLE
Specified distillate to feed ratio	0.5
Basis for specified bottoms to feed ratio	MOLE
Basis for specified boilup ratio	MOLE
Calculated molar boilup ratio	12.3161933
Calculated mass boilup ratio	7.58103515

Table 6. Aspen Plus specifications for design of distillation column SEP2.

RadFrac	
Name	2-Sep
Property method	UNIQUAC
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Number of stages	10
Condenser	TOTAL
Reboiler	KETTLE
Number of phases	3
Free-water	NO
Top stage pressure [bar]	1.0125
Specified reflux ratio	5
Calculated molar reflux ratio	5
Calculated bottoms rate [kmol/sec]	0.21250714
Calculated boilup rate [kmol/sec]	11.4915683
Calculated distillate rate [kmol/sec]	1.91256427
Condenser / top stage temperature [K]	344.948971
Condenser / top stage pressure [N/sqm]	101250
Condenser / top stage heat duty [Watt]	-441801665
Condenser / top stage subcooled duty	
Condenser / top stage reflux rate [kmol/sec]	9.56282135
Reboiler pressure [N/sqm]	101250
Reboiler temperature [K]	345.33167

Reboiler heat duty [Watt]	442218481
Basis for specified distillate to feed ratio	MOLE
Specified distillate to feed ratio	0.9
Basis for specified bottoms to feed ratio	MOLE
Specified bottoms to feed ratio	
Basis for specified boilup ratio	MOLE
Calculated molar boilup ratio	54.0761514
Calculated mass boilup ratio	54.1618533

Table 7. Aspen Plus specifications for design of distillation column SEP3.

DSTWU	
Name	3-Sep
Property method	UNIQUAC
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Number of stages	30
Reflux ratio	60
Light key component recovery	0.99
Heavy key component recovery	0.0001
Distillate vapor fraction	0
Minimum reflux ratio	2.53662074
Actual reflux ratio	60
Minimum number of stages	17.5682582
Number of actual stage	18.1525127
Feed stage	13.0099137
Number of actual stage above feed	12.0099137
Distillate temperature [K]	341.433256
Distillate to feed fraction [K]	413.763018