Recovery of trifluoroacetic acid from dilute aqueous solutions by reactive distillation

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Abstract

It is difficult to recover trifluoroacetic acid (TFA) from its dilute aqueous solutions by conventional techniques. This work investigates the feasibility of using reactive distillation to recover TFA through esterification with 2-propanol. A kinetic model is proposed based on batch reactor data. Experiments performed using reactive distillation in batch and continuous modes, show significant recovery. Independent column simulations, based on kinetics and vapor–liquid equilibrium (VLE) developed in this work, agree well with our experimental results. The validated model is further used to obtain suitable design and operating parameters to give nearly complete recovery. A complete process recovery process sheet is suggested based on the results obtained.

Keywords: Trifluoroacetic acid; Isopropyl trifluoroacetate; Reactive distillation; Recovery of chemicals

1. Introduction

Reactive distillation (RD) is the combination of reaction and distillation in a single vessel. Advantages like improved selectivity, increased conversion, better heat control, effective utilization of reaction heat, scope for difficult separations and the avoidance of azeotropes can be realized by application of reactive distillation [1]. Although this technology has been successfully commercialized for the manufacture of certain bulk chemicals, its potential as a separation tool has not been exploited in depth. Reversible reactions such as esterification and acetalization can be looked upon as suitable candidates for this purpose [2]. Acetic acid has been successfully recovered from dilute aqueous solutions through esterification with methanol by employing RD [3,4]. Other acids like lactic acid, adipic acid, myristic acid, succinic acid, chloroacetic acid, glycolic acid and trifluoroacetic acid etc. can also be recovered from their dilute solutions in the same manner with a properly designed RD system.

In fine chemical industries, trifluoroacetic acid (TFA) finds applications as a reagent or as a catalyst. Post-reaction aqueous streams contain typically 1–10% (w/w) acid. TFA is highly corrosive and toxic. It is harmful to human beings as it affects the upper respiratory tract, eyes and skin. Thus, it is outlawed from being disposed via the conventional effluent treatment methods. Furthermore, being expensive, its disposal by neutralization is not recommended. The quantity of the aqueous streams is too large to be neglected despite their small gravimetric acid content. Common industrial separation methods like distillation cannot be utilized because the acid forms a maximum boiling azeotrope with water (20.6 wt.% water, boiling at 105.5 °C) [5]. One way of circumventing this bottleneck problem is to convert the acid to useful products like isopropyl trifluoroacetate (IPTFA) and separate IPTFA from the mixture by distillation. Esters of trifluoroacetic acid are fine chemical intermediates, which are used in the manufacture of pharmaceuticals, agricultural chemicals, liquid crystals, dyes and industrial chemicals [6]. IPTFA is used as a water scavenger and as a solvent in the manufacture of various chemicals [7–10]. It is also used as an intermediate in the preparation of active molecules used in pharmaceutical applications. The preparation of trifluoroacetates by esterification of TFA with various alcohols and other routes of synthesis are described in various patents [6–12].

The esterification of trifluoroacetic acid (Fig. 1) in dilute aqueous solutions is a very challenging task. The presence of large amounts of water, which itself is one of the products, makes this reaction a potential candidate for RD. The simultane-
uous removal of ester may enhance the extent of conversion and hence recovery. However, the boiling points of the components involved are very close to each other (IPA 82°C, IPTFA 74°C, TFA 72°C and water 100°C) and the system is associated with the presence of a minimum boiling azeotrope (IPA–water) and a maximum boiling azeotrope (TFA–water).

Considering the constraints stated above, there is a definite need to explore alternate methods for the recovery of TFA and if possible, convert it to a value added ester, in our case, IPTFA. RD has a potential to achieve both these tasks together and in the present work, we investigate feasibility of this process through experiments and simulations. The reaction kinetics and vapor–liquid equilibrium (VLE) were determined separately and used in RD column simulations to predict its performance and these are compared with the experimental results.

2. Batch kinetics

2.1. Experimental procedure and analysis

The reaction was studied in a mechanically agitated, glass reactor of 5x10^-4 m^3 capacity. A constant-temperature oil bath was used to control the temperature. The liquid volume in the reactor was maintained at 1.25x10^-4 m^3 in all the batch experiments. The catalyst T-63, a cation-exchange resin, was obtained from Thermax Ltd. (India) (properties: particle size range ~0.3–1.2 mm, exchange capacity: 4.9 mequiv./dry g, temperature stability: up to 130°C). Samples were withdrawn from the reactor at regular time intervals and were immediately cooled with ice to avoid further reaction. Analysis was performed by titration using standard NaOH solution and phenolphthalein as an indicator. Samples were also analyzed using gas chromatograph (GC-MAK-911) equipped with a flame ionization detector (FID). A 25 m long capillary column (BP-1, SGE) was used to separate the components. The injector and detector were maintained at 200°C each. The oven temperature was kept at 68°C initially and was increased further with a ramp rate of 30°C/min to 98°C and maintained there for 4 min. This facilitated best resolution in least time. In few selected runs water concentration was confirmed independently with the help of chromatographic analysis. A gas chromatograph (GC-MAK-911) equipped with a thermal conductivity detector (TCD) with a 2 m long packed column (PoraPak-Q, SGE) was used to separate the components with n-butanol as the standard. The injector and detector temperatures were maintained at 200°C and 150°C, respectively and the oven temperature at 215°C. It was found that all mass balances matched to within 3%. Hence in all the experiments, titration was used to determine the concentration of TFA. The performance of the reaction was evaluated in terms of total conversion of TFA as follows:

\[
\text{conversion} (\%) = \left( \frac{\text{moles of TFA reacted}}{\text{moles of TFA charged}} \right) \times 100
\]

2.2. Results and discussion

Fig. 2 shows the effect of temperature and feed mole ratio of IPA to TFA on the conversion of TFA. It can be seen that the rate of reaction, as expected, increases with an increase in temperature and mole ratio of IPA to TFA. It should be noted that experiments carried out with T-63, showed no significant improvement in the conversion (Fig. 3). Separate batch experiments were also conducted (10 wt.% TFA) with ion exchange resin T-63 as the catalyst (0–25%, w/w of TFA) and this showed a negligibly small increase in the conversion. This is not surprising as the water content of the reaction mixture is exceptionally large and moreover, TFA is a sufficiently strong acid to act as a self-catalyst. Hence, all the further experiments in batch mode and in the RD column were carried out without catalyst.

2.3. Parameter estimation

A kinetic model for the esterification reaction is developed based on the reaction scheme given in Section 1. A concentration-based model was chosen as the reaction takes place in dilute conditions. Eq. (2) gives the proposed kinetic equation for the reacting system, where A, B, C and D represent

\[
\text{rate of reaction (kmol s}^{-1}\text{)} = \frac{A}{B + C + D}
\]
TFA, IPA, IPTFA and water, respectively. The expressions for the temperature dependencies are given by Eqs. (3) and (4):

\[ r = -k_f \left[ C_A C_B - \left( \frac{1}{K_{eq}} \right) C_C C_D \right] \]  

(2)

\[ k_f = k_{f0} \exp \left( -\frac{E_f}{RT} \right) \]  

(3)

\[ K_{eq} = K_{eq0} \exp \left( -\frac{E_{eq}}{RT} \right) \]  

(4)

The objective function to be minimized is expressed as

\[ \min \Theta = \sum_{\text{Data points}} (N_{\text{predicted}} - N_{\text{experimental}})^2 \]  

(5)

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_f ) (l/gmol h(^{-1}))</td>
<td>((3.66 \pm 1.29) \times 10^{12})</td>
</tr>
<tr>
<td>( K_{eq0} )</td>
<td>10000.0 ± 2395.9</td>
</tr>
<tr>
<td>( E_f ) (kJ mol(^{-1}))</td>
<td>96.82 ± 10.51</td>
</tr>
<tr>
<td>( E_{eq} ) (kJ mol(^{-1}))</td>
<td>20.0 ± 7.2</td>
</tr>
<tr>
<td>( \Theta )</td>
<td>(9.926 \times 10^{-3})</td>
</tr>
</tbody>
</table>

The optimization was performed using the batch reactor model in Aspen Custom Modeler, a tool from the standard simulator Aspen Engineering Suite. The values for the estimated kinetic parameters and the sum of the squares of residuals (\(\Theta\)) are summarized in Table 1. Fig. 4 displays the parity plot show-
Table 2
UNIQUAC model parameters

<table>
<thead>
<tr>
<th></th>
<th>TFA</th>
<th>Water</th>
<th>IPA</th>
<th>IPTFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFA</td>
<td>–</td>
<td>−1748.10^a</td>
<td>−710.95^b</td>
<td>−308.40^a</td>
</tr>
<tr>
<td>Water</td>
<td>970.82^a</td>
<td>−</td>
<td>−347.00^c</td>
<td>−231.12^b</td>
</tr>
<tr>
<td>IPA</td>
<td>385.97^b</td>
<td>−54.09^c</td>
<td>−</td>
<td>−110.60^a</td>
</tr>
<tr>
<td>IPTFA</td>
<td>190.22^a</td>
<td>−114.27^b</td>
<td>45.22^a</td>
<td>−</td>
</tr>
</tbody>
</table>

^a Experimental data regression.
^b Reactive.
^c Aspen-Plus.

The comparison of the predictions from the model with the experimental observations.

3. Vapor–liquid equilibria

The vapor–liquid equilibrium (VLE) of this system is difficult to model especially due to the strong tendency of TFA to dimerize in the vapor phase and no data is available in the literature on this aspect to the best of our knowledge. Moreover, since the reaction takes place even in the absence of the catalyst, it is difficult to generate experimental data for the reacting binaries, viz. TFA–IPA and water–IPTFA. The experimental data for all the other binaries was generated using a modified Othmer still [13] and can be found elsewhere [14]. TFA is known to form a maximum boiling azeotrope with water, as indicated in Section 1, which was confirmed through experiments. Out of the various VLE models, only UNIQUAC-HOC predicted the azeotropic composition reasonably accurately. The UNIQUAC model using UNIFAC predictions was used to predict all the other binaries of interest. In order to obtain the TFA–water UNIQUAC parameters, the data from UNIQUAC-HOC model was used to regress parameters of the UNIQUAC model. UNIQUAC parameters used in this work are listed in Table 2. It should be noted that while the fit obtained was not excellent, the model predicted data reasonably well in the region where the composition of TFA was low. This was the case all through our study where the maximum composition of TFA at all points in the column was less than 3–5 mol%. Fig. 5 shows the composition range in which the reactive distillation experiments were conducted. The determination of a comprehensive VLE model, applicable over the entire composition space, may be necessary for TFA solutions of higher concentration as feed and is beyond the scope of this paper.

4. Reactive distillation

Reactive distillation implies concomitant reaction and separation in a distillation column. In a typical RD column, a number of parameters can be varied to achieve the desired extent of reaction and distillation efficiency. A RD column can be run either as a batch reactive distillation (BRD) column or as continuous reactive distillation (CRD) column. BRD is a less expensive and quicker way to experimentally evaluate the applicability of RD
for the process of interest. Fig. 6 shows the schematic of the setup used for the RD experiments in the batch and continuous modes. The next section describes the experimental procedure for both BRD and CRD and the important results.

4.1. Batch reactive distillation (BRD)

4.1.1. BRD without catalyst

A typical BRD run was performed with 230 g TFA and 2070 g water (i.e. ~10 wt.% TFA) and 1.4:1 molar ratio of IPA to TFA, without catalyst. The setup consists of a reboiler of 3 l capacity with a 1 m tall column (ID: 0.025 m) equipped with a Dean and Stark assembly and condenser (Fig. 6a). The column is packed with non-reactive packings (Hyflux Packings, Evergreen Ltd., Mumbai, India; NTSM = 8). As is seen in Fig. 7, even with this low molar ratio of IPA to TFA about 58% conversion was realized (Run 1 of Fig. 7). In order to further increase the conversion, three successive runs were carried out with stepwise addition of IPA to the same reaction mixture (Runs 2–4, respectively of Fig. 7, IPA to TFA mole ratio: 3:1) and conversion as high as 91% was achieved. Complete conversion can be obtained by further addition of IPA. Only traces of TFA were observed in the condensate throughout the run as TFA forms a maximum boiling azeotrope with water and hence tends to remain in the reboiler. Thus, the results obtained in the batch reactive distillation experiments clearly show the feasibility of RD for recovery of TFA by esterification.

4.1.2. BRD with catalyst packed in the column

As mentioned before, the reaction was observed to be significantly fast even in the absence of a catalyst. However in RD, due to high conversion, it is expected that self-catalysis may not be effective even at lower concentration of TFA. Hence, selected BRD runs with catalyst were performed to identify the need of external catalyst. In a typical BRD run, the reboiler of 500 ml capacity was charged with 10% TFA solution and IPA with 3:1 molar ratio of IPA to TFA. The catalyst (4.1 g) was packed in embedded form in a column placed above the reaction vessel but below the Dean and Stark assembly. It should be recalled that due to azeotrope formation, significant amount of water will also be present at the catalyst site. Fig. 8 shows the conversion of TFA. About 58% conversion of TFA has been realized which is about the same as the case without catalyst reflecting that there is no apparent advantage of using catalyst because of the presence of large amount of water present. Hence, as discussed before, the CRD runs were conducted without catalyst.

4.2. Continuous reactive distillation

CRD experiments were conducted in a column of 0.051 m (ID), 2 m height (Fig. 6b), packed with non-reactive packings (Hyflux Packings, Evergreen Ltd., Mumbai, India). The reboiler was charged with a known quantity of IPA and heating was started. Once the temperature profile was established, TFA and IPA were fed to the column at the desired flow rates at the specified feed points. TFA solution is fed near the top of the column

<table>
<thead>
<tr>
<th>Run no.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reboiler duty (W), including heat losses</td>
<td>200</td>
<td>175</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>Height of reactive section (m)</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>TFA feed solution 5% (w/w) (g h⁻¹)</td>
<td>1309.25</td>
<td>630.35</td>
<td>533.35</td>
<td>363.65</td>
</tr>
<tr>
<td>IPA feed (g h⁻¹)</td>
<td>103.50</td>
<td>117.20</td>
<td>163.85</td>
<td>134.95</td>
</tr>
<tr>
<td>Feed location (IPA, TFA)</td>
<td>3, 9</td>
<td>3, 17</td>
<td>3, 17</td>
<td>3, 17</td>
</tr>
<tr>
<td>IPA/TFA (mol/mol)</td>
<td>3</td>
<td>7</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>Top flow rate (g h⁻¹)</td>
<td>415</td>
<td>122</td>
<td>238</td>
<td>225</td>
</tr>
<tr>
<td>Bottoms flow rate (g h⁻¹)</td>
<td>995</td>
<td>615</td>
<td>443</td>
<td>273</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>14.64</td>
<td>38.50</td>
<td>48.99</td>
<td>57.50</td>
</tr>
<tr>
<td>Error in material balance (%)</td>
<td>Overall</td>
<td>2</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>TFA</td>
<td>0.5</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>
because of the tendency of TFA to form a maximum boiling azeotrope with water which leads TFA to flow down the column. IPA on the other hand is fed close to reboiler and being volatile, it flows in the upward direction facilitating good contact with TFA. The top and bottom flow rates and compositions were measured from time to time. When these were found to be constant over a period of time (>2 h), the overall and individual material balances were verified. This, along with the establishment of a time invariant temperature profile indicated the attainment of steady state (SS). Samples were withdrawn along the length of the column and analyzed as detailed in Section 2.1.

Table 3 summarizes the representative experimental runs with input parameters and the conversion levels achieved. As can be seen from the table, higher residence time and/or mole ratio of IPA to TFA results in an increase in the conversion (from 14 to 57%). The performance of the RD column was simulated independently using the RadFrac module of Aspen Plus which uses an equilibrium stage model. The assumptions and the model equations can be found elsewhere [15]. Also, the RateFrac module from Aspen Plus, which uses a non-equilibrium model, was employed to simulate the column performance [15]. This non-equilibrium model uses segmentation of the column height to carry out the simulation [16] with the optimal number of segments giving best accuracy and speed of calculation. The details of the parameters used for the two models are shown in Table 4.

Fig. 9 shows the comparison between the experimental observations and model predictions. It should be noted that no catalyst was used in these runs.

Table 4
Parameters used for simulation in the RadFrac and RateFrac models

<table>
<thead>
<tr>
<th>Property</th>
<th>RadFrac</th>
<th>RateFrac</th>
</tr>
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<tbody>
<tr>
<td>Property model</td>
<td>UNIQUAC</td>
<td>UNIQUAC</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>0.5384</td>
<td>0.5133</td>
</tr>
<tr>
<td>Reboiler duty (W)</td>
<td>102.5</td>
<td>102.5</td>
</tr>
<tr>
<td>Stages</td>
<td>18</td>
<td>24</td>
</tr>
<tr>
<td>Feed stage (TFA, IPA)</td>
<td>3, 17</td>
<td>4, 20</td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Reactions (stages)</td>
<td>2–17</td>
<td>3–23</td>
</tr>
<tr>
<td>Holdup (g)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Distillate rate (g h⁻¹)</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Condenser temperature °C</td>
<td>80.39</td>
<td>80.38</td>
</tr>
</tbody>
</table>

It can be seen that both the models show good agreement with the experimental observations. The RadFrac model, thus validated, was used to make further predictions. It can be seen from Fig. 9(b) that RD is capable of maintaining the concentration of IPTFA in the column at a minimal level thereby enhancing the conversion, and hence recovery, as compared to conventional reactors.

4.3. Parametric studies

It is very difficult and also not advisable too, to cover a very wide range of operating parameters through experimentation. Hence, the experimentally validated simulation model was used to predict the behavior of the RD column for this reaction and
to predict the conditions that may favor the maximum possible conversion and hence the recovery. In a typical RD column, the number of reactive stages, relative feed locations, reboiler duty and reflux ratio are the important parameters that dictate the overall performance. Simulation results are discussed in the following sections.

4.3.1. Effect of number of stages

One way of obtaining conversion close to 100% is to increase the reactive stages of the column thereby providing large residence time and efficient separation. The experimental column consisted of 18 stages in all. In the simulation five stages were provided for the rectifying and stripping sections each and the number of stages in the middle reactive section was increased one at a time. Fig. 10 shows that the conversion is very sensitive to the change in the number of stages. It can be observed that as many as 70 total stages are required to achieve conversion of the order of 96.4%. Thus it is theoretically possible to obtain 100% conversion at the cost of additional number of stages. This is obviously advantageous since the streams from the RD column would be essentially free of TFA and thus complete recovery would be achieved. Seventy stages were used for further parametric studies.

4.3.2. Effect of feed location of TFA and IPA

The feed location of the reactants influences the conversion, as the reactive zone height would vary with a change in the feed points. With the given number of stages and the location of IPA feed, as shown in Fig. 11, lowering the TFA feed below about 30 stages decreases the conversion. A similar study was carried out for IPA feed location. Typically for a column with total 70 stages and TFA and IPA feeds at stages 9 and 67, respectively from the top offers 96.64% recovery.

4.3.3. Effect of reflux ratio and reboiler duty

For a column with a given number of stages, an increase in reboiler duty increases the vapor flow in the column thereby increasing the liquid that is refluxed to the column. In this system the water concentration is large and hence, the increase in

Fig. 10. The effect of number of stages on conversion. Base case is Run 4 of Table 3 (indicated by square).

Fig. 11. The effect of TFA feed location on conversion with a 70-stage column.

Fig. 12. Effect of reboiler duty: (a) IPA concentration; (b) conversion. Number of stages: 70; reflux ratio: 0.75.
Reboiler duty increases the water concentration further in the column thereby decreasing the IPA concentration (Fig. 12a) and hence the conversion. Fig. 12b shows that when the reboiler duty is increased, the conversion drops drastically. Thus the column needs to be operated at minimum possible reboiler duty.

A similar study was conducted for the reflux ratio and it was observed that, under otherwise similar conditions, increasing the reflux ratio decreases the conversion (Fig. 13a and b). This is because with increase in reflux ratio not much enhancement is observed as we already have sufficient number of stages. On the contrary, with an increase in the reflux ratio, the IPTFA-rich distillate is fed back to the column (Fig. 13a) thus reducing the overall ester removal rate and hence the conversion (Fig. 13b).

Based on the parametric studies some important recommendations for obtaining high conversion values have been drawn. These include large number of stages, low reboiler duty, low reflux and IPA and TFA feed locations as far away from each other as possible but leaving sufficient stages for non-reactive distillation.

Fig. 13. The effect of reflux ratio on (a) IPTFA concentration; (b) conversion. Number of stages: 70; reboiler duty: 150 W.

5. Proposed complete recovery system

While the simulations indicate that close to 100% conversion may be realized, because of the use of excess IPA and the large amount of water in the feed, the top stream from the RD column contains mainly IPA, water, IPTFA and traces of TFA. If 100% conversion of the acid is assumed, then the acid concentration of the top stream can be safely neglected. The ester from this stream needs to be recovered further if desired in pure form. The major issues are (1) IPA forms an azeotrope with water, and (2) the IPTFA content of the stream is low (\(\sim 4\) mol%). Aspen Split was used to predict the residue curve map (RCM) for the ternary system of IPA, water and IPTFA (Fig. 14).

It can be seen that for the given feed composition, the separation of IPTFA is feasible. The same was brought about with simulation in RadFrac in Aspen Plus. The top stream from the RD column was fed to a normal distillation column consisting of 63 stages.

Fig. 14. Residue curve map (RCM) for the system IPA–water–IPTFA.

Fig. 15. The column profile for the atmospheric distillation column. Reboiler duty: 180 W; feed stage: 34.
The feed location was optimized to be at the stage 34. The column profile is shown in Fig. 15. It can be seen that it is possible to recover the ester almost completely. Recovery of 99.1% is predicted through simulation. It should be noted that a very high reflux ratio (131) is necessary. This is anticipated as the IPTFA content of the feed stream itself is very small and a high purity distillate is intended. The proposed flow sheet for the complete recovery process is given in Fig. 16. It must be noted that the backward hydrolysis of IPTFA under uncataysed conditions in the distillation column is assumed to be negligible. To suppress hydrolysis, if any, the distillation may be performed at reduced pressure which would reduce the temperature of the column. Further cost estimation may be performed to evaluate the economic viability of this alternative.

6. Conclusion

Reactive distillation is a promising tool for the recovery of TFA from its dilute aqueous solution through formation of IPTFA, a useful intermediate. The studies on batch kinetics indicate a need to remove product of the reaction to surpass the reaction equilibrium limitations. The vapor–liquid equilibrium characteristics are favorable for the effective in situ separation of IPTFA by distillation. Experiments performed in batch and continuous reactive distillation systems offer increased conversion. Both, equilibrium stage and non-equilibrium stage models can explain the experimental data reasonably well. It was confirmed through simulation that a properly designed recovery system can yield greater than 97% recovery.

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References