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# Solubility of 2, 5-Di-Tert-Butylhydroquinone and Process Design for its Purification Using Crystallisation

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# ABSTRACT

The solubility of 2, 5-Di-Tert-Butylhydroquinone (DTBHQ) in acetone, ethyl acetate, methanol, and the mixtures of ethanol and water was measured and correlated in the temperature range between 278.95 K to 346.15 K. It was found that the solubility in acetone increases more rapidly with increasing temperature than in other solvents. The data was correlated using the modified Apelblat, Buchowski-Ksiazczak $\lambda$h, and Van't Hoff equations, with the maximum relative average deviation less than 2.74 %. The obtained thermodynamic models were used in designing a crystallisation process and synthesizing a flowsheet for effective purification of crude DTBHQ from the by-product of tertiary butylhydroquinone (TBHQ).

**KEYWORDS**: 2, 5-Di-tert-butylhydroquinone; Evaporative crystallisation; Ethanol; Mixtures of ethanol and water.

## 1. INTRODUCTION

DTBHQ ($C_{14}H_{22}O_2$, CAS No 88-58-4, IUPAC name: 2,5-Di-tert-butylbenzene-1,4-diol) is an important anti-oxidant and anti-aging additive used widely in the polyester industry.[1] It is colourless, of low toxicity, and has shown excellent end-use performance. Its demand has been on the increase in recent years, in particular in the manufacture of transparent or white plastic products. DTBHQ is often made as a by-product during the manufacture of the food additive tertiary butylhydroquinone (TBHQ). The raw DTBHQ needs to undergo decolouring treatment and further purification. The process is complicated by having to achieve multiple objectives including minimization of cost, wastes and use of solvents as well as maximizing the yield and meeting the product quality criterion measured by DTBHQ colour. Process synthesis and optimization could not be achieved purely by computer simulation due to the gap in detailed quantitative knowledge about the colourants and first principle models of decolouring, as well as the lack of thermodynamic models in particular solubility data of DTBHQ in solvents. While the decolouring operation can still be optimized through multiple experiments with the support of the available, despite limited, qualitative knowledge, for the crystallisation operation and for the entire process synthesis, it is almost impossible to achieve the same without thermodynamic data.

The main contributions of the paper are as follows. Firstly, the solubility of DTBHQ in acetone, ethyl acetate, methanol, and the mixtures of ethanol and water with different solvent compositions are measured in the process operational temperature range between 278.95 to 346.15 K using the gravimetric method. Secondly the data was correlated in modified Apelblat, the Buchowski-Ksiazczak $\lambda$h, and the Van't Hoff equations. The data and models were then used in the design and optimization of crystallisation experiments, and in laying out the entire process integrating decolouring and purification operations. Experimental results will be presented, demonstratingthe effectiveness of the process thus synthesized.

## 2. SOLUBILITY MEASUREMENT

### 2.1. Materials

The DTBHQ used in this study was provided by the Guangzhou Taibang Food Additive Technology Co. Ltd., the mass fraction purity is greater than 0.990 as analyzed by gas chromatography (Clarus 500 Gas Chromatograph, PerkinElmer). The mass fraction purity of the solvents used was listed in Table 1. Deionized water was used.

### 2.2. Experimental

Solubility measurement was conducted using gravimetric method. Its main component is a 50 mL jacketed glass reactor equipped with a circulating JULABO thermostatic water bath (FP51, JULABO). The temperature accuracy of the JULABO thermostat is within 0.01 K. The jacketed glass reactor was constantly stirred by a magnetic stirrer to ensure that the solution of DTBHQ in the jacketed glass reactor remains uniform.

The raw material, DTBHQ, was analysed using X-ray powder diffraction (XRPD) and differential scanning calorimetry (DSC). The XRPD patterns were recorded in the range from 5$^o$ to 45$^o$ using diffractometer from Bruker (40KV, 40mA, Cu Ka; Karsruhe, Germany), and the step size and scan rate were 0.005$^o$ and 0.1 s per step, respectively. The DSC instrument was from NETZSCH (NETZSCH DSC 204F1 Phoenix, Germany) with the operation temperature from room temperature to 513.15 K, and the heating rate was set as 10 K min$^{-1}$, and the mass of sample was 3 mg for each measurement.

The XRPD pattern of the raw material DTBHQ is shown in Figure 1, and is found to match the reported XRPD pattern of DTBHQ with a P31C space group[2]. The measured DSC curve for raw DTBHQ is shown in Figure 2, indicating a melting point of 494.05 K and an enthalpy of fusion of 199.9 J/g, which is almost in agreement with reported melting point of 492.15 K to 493.15 K[3]. Therefore, the DTBHQ used in this study was identified as P31C space group, as reported in Cambridge Crystallographic Data Centre.

Measurement of DTBHQ solubility in all solvents followed a procedure similar to the one described below in ethanol and water mixture. Firstly, ethanol and water mixture with a pre-defined ethanol content (w) was prepared in a 1000 mL flask. Then 30 mL solvent was added into the 50 mL jacketed glass reactor at a temperature 5°C lower than set point followed by gradually adding in excess DTBHQ under constant stirring and temperature. After 10 hours stirring at the set point temperature, the magnetic stirrer was stopped. About 3 mL of the upper solution was then withdrawn and put into a weighing bottle (weighed $m_0$) using a pre-heated syringe, the temperature of which was measured using a calibrated thermometer with an uncertainty of 0.1 K and recorded simultaneously. The weighing bottle containing the sampled solution was weighed ($m_1$) quickly and dried in a vacuum oven at 313.15 K. All weighing bottles were covered with a filtered cloth to avoid dust contamination. The weighing bottle was weighed ($m_2$) when the solvent was completely dried. A Mettler Toledo AL204 electronic balance with an uncertainty of 0.1 mg was used to measure all samples.

The mole fraction solubility of DTBHQ ($x_1$) in pure solvents and the binary solvent mixture was calculated using eq.1

$$x_1 = [(m_2 - m_0)/M_{\text{solute}}] / \left[\frac{(m_2 - m_0)}{M_{\text{solute}}} + \frac{(m_1 - m_2)w}{M_{\text{solvent}}} + \frac{(m_1 - m_2)(1-w)}{M_{water}}\right] \quad (1)$$

where $M_{solute}$, $M_{solvent}$, and $M_{water}$ are the molecular weight of DTBHQ, solvent, and water respectively, w denotes the mass fraction of ethanol in an ethanol and water mixture, and w is 1 for pure solvent. Every one solubility data point was the average of three parallel measurements under the same condition. It was established that the relative average deviation in the experimental solubility value was less than 3 %.

## 3. RESULTS, DISCUSSION AND CORRELATION

### 3.1 Effects of Temperature and Solvents

The mole fraction solubility of DTBHQ in mixtures of ethanol and water, and pure acetone, ethyl acetate, and methanol in the temperature range from 278.95K to 346.15 K are summarized in Tables 2 and 3. As anticipated the solubility varies with temperature and different solvents, as plotted in Figure 3, where $x_{exp}$ is the mole fraction solubility. It was observed from Figure 3 that the solubility in acetone increases significantly with increasing temperature over the temperature range from 283.35 K to 323.15 K, but for other solvents the increasing trend in temperature is less obvious. It was also observed in Figure 3 that the solubility of DTBHQ in mixtures of ethanol and water drops quickly with increasing water content (1-w) , it becomes very low when w reaches 0.5.

### 3.2 Model Building

Three thermodynamic models were used to correlate the data, namely the modified Apelblat equation, the $\lambda$h equation, and the Van't Hoff model. The model parameters were obtained by calibrating the experimental solubility data using partial least squares (PLS).

Relative average deviation (RAD) was calculated using eq.2 to assess the accuracy of models developed. The relative deviation (RD) between experimental data and predictions was also calculated using eq. 3. The thermodynamic model with the lowest RD and RAD are preferred.

$$RAD = \frac{1}{n}\sum_{i}^{n}\left|\frac{x_{1,i}-x_{1,i}^{fit}}{x_{1,i}}\right| \tag{2}$$

$$RD = (x_1 - x_1^{fit})/x_1 \tag{3}$$

where $x_1$ is the measured mole fraction solubility data, $x_1^{fit}$ is fitted mole fraction solubility by the models, and n is the total number of experimental points in different solvents.

**Modified Apelblat equation.**[5, 6] Eq. 4 is the modified Apelblat equation. To correlate solubility ($x_1$) of DTBHQ in acetone, ethyl acetate, methanol, and ethanol-water mixtures, the parameter values of eq. 4 were given in Table 4. The calculated RD and RAD were summarized in Tables 2 and 3.

$$\ln x_1 = A + B/\,(\mathrm{T}/K) + C\ln(\mathrm{T}\,/K) \tag{4}$$

In eq. 4, $x_1$ is the mole fraction solubility, T is the absolute temperature, and A, B, and C are parameters.

**Buchowski-Ksiazczak $\lambda$h Equation**.[7, 8] The Buchowski-Ksiazczak $\lambda$h Equation, eq. 5, was widely used for modeling solid liquid equilibrium (Buchowski et al[8]):

$$\ln\left[1 + \lambda\frac{1-\mathrm{x}_1}{\mathrm{x}_1}\right] = \lambda\mathrm{h}\left(\frac{1}{T} - \frac{1}{T_m}\right) \tag{5}$$

where $x_1$ is the mole fraction solubility, T is the absolute temperature, $T_m$ is melting point, $\lambda$ and $h$ are model parameters. The values of $\lambda$ and $h$ for eq. 5 were given in Table 5, for different solvents.

**Van't Hoff Equation**. The Van’t Hoff model, eq. 6, is also widely used to model the relationships between mole fraction solubility and temperature, enthalpy of dissolution, and entropy of dissolution[9, 10]:

$$\ln x_1 = -\frac{\Delta \mathrm{H}}{\mathrm{RT}} + \frac{\Delta \mathrm{S}}{\mathrm{R}} \tag{6}$$

where $x_1$ is mole fraction solubility, T is absolute temperature, R is gas constant, ΔH and ΔS stand for enthalpy of dissolution and entropy of dissolution, respectively.

The model parameters of eq. 6, the enthalpy of dissolution and entropy of dissolution of DTBHQ, were calibrated and shown in Table 6, and the RD and RAD between experimental solubility data and fitted solubility were also calculated and given in Table 3 and Table 6, respectively.

It was seen in Table 6 that the enthalpy of dissolution for DTBHQ in all solvents are positive, indicating that dissolution of DTBHQ in these solvents is endothermic, therefore, growth of crystals from the solutions should be exothermic. This is consistent with the phenomenon observed in evaporation crystallisation of DTBHQ that the temperature of solution will rise after nucleation has occurred.

## 4. DTBHQ CRYSTALLISATION DESIGN AND PROCESS SYNTHESIS

Purification of crude DTBHQ from by-product of tertiary butylhydroquinone (TBHQ) can be carried out using cooling, anti-solvent or evaporative crystallisation. As indicated by the solubility data as displayed in Figure 2, only acetone can be used as the solvent if cooling crystallisation is to be considered, since in other solvents the solubility does now show major changes with temperature. But acetone is more expensive than ethanol with a difference in price of about $ 250.00 per ton. Anti-solvent crystallisation, using ethanol as the solvent and water as the anti-solvent, is also an option since as revealed by the data that DTBHQ's solubility in the mixture of 50 % ethanol and 50 % water closes to zero. However, the cost of recovering ethanol, e.g. via distillation, is a factor that must be taken into account, especially considering the fact that ethanol and water can form azeotrope. After having considered all the factors, evaporative crystallisation using ethanol as the solvent was selected as the route for purification of DTBHQ.

After evaporative crystallisation method was selected, the flowsheet for purification of DTBHQ was then synthesized, as depicted in Figure 4. This process contains three main parts, which are pretreatment, decolouring and evaporative crystallisation. The reported decolouring techniques include using activated carbon, reductive decolourization method.[12] Here reductive decolourization method is preferred due to lower filtering resistance and excellent decolouring performance found in our experiments. First principle and quantitative knowledge of decolouring using reductive decolourization is not yet fully established, so experiments have to be employed to obtain process operational condition. The experimental purification process was as follows: Firstly, the crude DTBHQ with a mass purity of 80 % as measured by gas chromatography was pretreated in the pretreatment tank in which the suspension in hot acidic water was stirred for 30 min at the temperature of 348.15 K. After pretreatment, the slurry was filtered and washed. The pretreated DTBHQ, ethanol and Zn powder were added into the decolouring tank to obtain DTBHQ solution with an initial concentration of 0.4g DTBHQ /g ethanol. Hydrochloric acid solution (37 % in mass fraction) was added into the tank gradually in 30 minutes, then the temperature of reactor was raised to 358.15 K and the solution was kept under reflux for 60 min. The solution was filtered to remove the excess Zn powder prior being introduced to the evaporative crystallisation tank under constant temperature of 363.15 K during 3 hours. The obtained ethanol vapor was cooled and recycled to recovery tank. Finally, the temperature of slurry was cooled down to 298.15 K, and the DTBHQ was obtained by filtering the residual slurry and washing using solvent mixtures of 50 % ethanol and 50 % water.

The quality of the final DTBHQ product was found to be affected the evaporative rate in crystallisation as well as the total amount of ethanol evaporated. The experiment also showed that the colour of final DTBHQ would become red if the total evaporated amount of ethanol comes to a certain value. The maximum allowable percentage for evaporative ethanol was established as 75 % in mass, below it, the colour for DTBHQ product can meet the requirement of the customer.

The yield can be estimated based on mass balance calculations. If the initial solution has a concentration of 0.4 g DTBHQ per g ethanol, there will still be 27 % DTBHQ dissolved in the mother liquor of crystallisation if 75 % ethanol was evaporated. The calculation has used eq.4 with parameters given in Table 4. As shown in Table 7 that the yield of DTBHQ using single stage evaporative crystallisation is 73 %.

To increase the yield, cascade multiple evaporative crystallisation can be considered, as depicted by Figure 5. In such a cascade arrangement, the amount of coloured impurities will no doubt accumulate. Therefore it needs to establish through experiments the optimum number of stages at which the yield is increased to the satisfaction while the requirement on colour of product is still met. The experiments were conducted for an initial feed amount of crude DTBHQ being 0.8kg, as shown in Figure 5. After pretreatment with aqueous hydrochloric acid solution and decolouring using HCl and Zn powder in ethanol solution, the DTBHQ ethanol solution was filtered and introduced to 5L crystallizer-1. After 75 % ethanol in mass was evaporated, the slurry was filtered and 0.467 kg DTBHQ product was obtained, then the filtered mother liquor was introduced to another 5L crystallizer-2. Our result from cascade crystallisation experiments revealed that the colour of DTBHQ product can still meet customer's demand after three stage evaporative crystallizers. The colour of DTBHQ product will grow dark when if a 4th stage evaporative crystallisation is used. The yield for DTBHQ using three cascade crystallizers can be effectively increased from 73 % to 89 %. Therefore three stage crystallisation was used.

## 5. CONCLUSIONS

Solubility of DTBHQ in acetone, ethyl acetate, methanol, mixtures of ethanol and water was measured using the gravimetric method and correlated over a temperature range from 278.95 K to 346.15 K. For the ethanol and water mixture, the mass fractions of ethanol are 1, 0.8998, 0.7992, 0.6501 and 0.4999 respectively. The solubility data was modeled using the modified Apelblat, Buchowski-Ksiazczak $\lambda$h, and Van't Hoff equations, with model parameters obtained by PLS. The maximum RAD was lower than 2.74 %. The enthalpy and entropy of dissolution for DTBHQ in the solvents were calculated using Van't Hoff model. It was observed that solubility of DTBHQ in acetone increases significantly with increasing temperature, while for other solvents the solubility change with temperature is much smaller, eliminating the option of using other solvents other than acetone for cooling crystallisation. It was also noticed that the solubility of DTBHQ in mixtures of ethanol and water drops rapidly to nearly zero when increasing the water content (1-w) to about 50 %. The solubility data provides us three process options for purification of DTBHQ via crystallisation: cooling crystallisation using acetone as the solvent, anti-solvent crystallisation by adding water to DTBHQ - ethanol solution, as well as evaporative crystallisation using ethanol as the solvent. Considering the high cost of acetone and the cost of recovering ethanol from the mixture of ethanol and water, evaporative crystallisation using ethanol as the solvent was selected as the preferred choice.

Centered around the evaporative crystallisation process, the process flowsheet was synthesized that includes three major components: pretreatment, de-colouring, as well as evaporative crystallisation. The synthesis has to meet both requirements on high yield and DTBHQ colour. Combining experiments and theoretical analysis, a three-stage evaporative crystallisation configuration was designed that can meet both the yield requirement and colour.

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## REFERENCES

(1) Sayin, U.; Dereli, Ö.; Türkkan, E.; Yüksel, H.; Birey, M., EPR Study of Gamma Irradiated 2,5-di-tert-butyl-hydroquinone Single Crystals. Radiat. Phys. Chem. **2011,** 80, 38-43.

(2) Ermer, O.; Röbke, C., Crystal Structure of 2,5-Di-tert-butyl-hydroquinone: Polar Stacking of

Nonpolar Hydrogen-Bonded Sheets with Trigonal Symmetry. Angew. Chem., Int. Ed. Engl. **1994,** 33, 1755-1757.

(3) Fujita,S.; Sano,K., Reduction of Quinones and Quinonemonosulfonimides with N,N-diethylhydroxylamine, J. Org. Chem. **1979**, 44, 2647-2651.

(4) Zhang, Y.; Jiang, Y.; Li, K.; Qian, Y., Solubility of β-Artemether in Methanol + Water and Ethanol + Water from (288.85 to 331.95) K. J. Chem. Eng. Data **2009,** 54, 1340-1342.

(5) Apelblat, A.; Manzurola, E., Solubilities of o-acetylsalicylic, 4-aminosalicylic, 3,5-dinitrosalicylic, and p-toluic acid, and Magnesium-DL-aspartate in Water From T=(278 to 348) K. J. Chem. Thermodyn. **1999,** 31, 85-91.

(6) Wang, N.; Fu, Q.; Yang, G., Determination of The Solubility, Dissolution Enthalpy and Entropy of icariin in Water, Ethanol, and Methanol. Fluid Phase Equilibria **2012,** 324, 41-43.

(7) Zhang, Q.; Hu, Y.; Shi, Y.; Yang, Y.; Cheng, L.; Cao, C.; Yang, W., Thermodynamic Models for Determination of the Solubility of Dibenzothiophene in Different Solvents at Temperatures from (278.15 to 328.15) K. J. Chem. Eng. Data **2014,** 59, 2799-2804.

(8) Dun, W.; Wu, S.; Tang, W.; Wang, X.; Sun, D.; Du, S.; Gong, J., Solubility of Ibuprofen Sodium Dihydrate in Acetone + Water Mixtures: Experimental Measurement and Thermodynamic Modeling. J. Chem. Eng. Data **2014**, 59, 3415-3421.

(9) Buchowski, H.; Ksiazczak, A.; Pietrzyk, S., Solvent Activity Along a Saturation Line and Solubility of Hydrogen-Bonding Solids. J. Phys. Chem. **1980,** 84, 975-979.

(10) Song, L.; Gao, Y.; Gong, J., Measurement and Correlation of Solubility of Clopidogrel Hydrogen Sulfate (Metastable Form) in Lower Alcohols. J. Chem. Eng. Data **2011,** 56, 2553-2556.

(11) Mirmehrabi, M.; Rohani, S.; Murthy, K. S. K.; Radatus, B., Solubility, Dissolution Rate and Phase

Transition Studies of Ranitidine Hydrochloride Tautomeric Forms. Int. J. Pharm. **2004,** 282, 73-85.

(12) Shi, X. H.; Wu, X. B.; Dong, L. X. Production Method for Purifying 2,5-di-tert-butyl Hydroquinone. CN 101139260 A, 2007.

## FIGURES

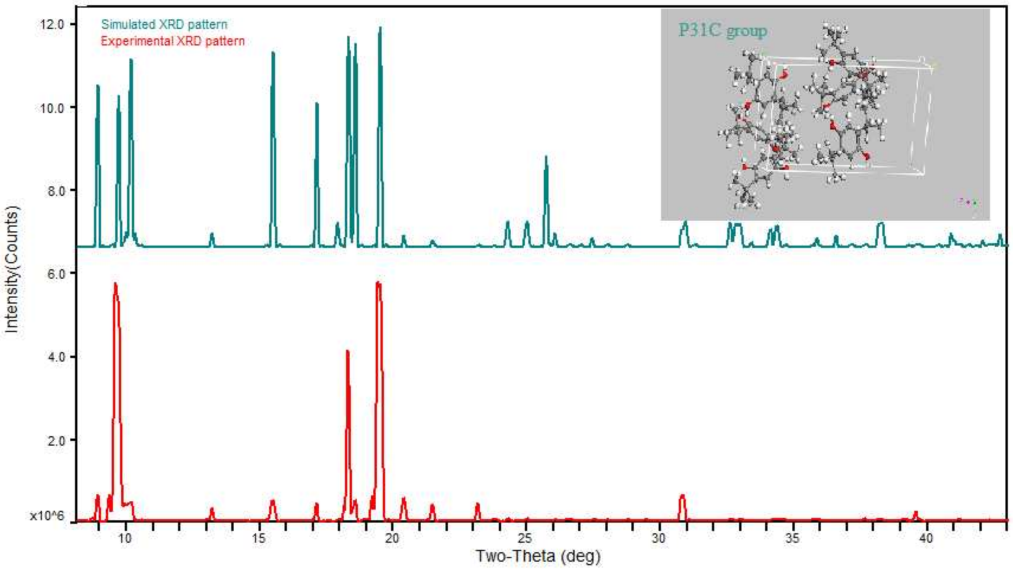


**Figure 1.** XRPD pattern of DTBHQ and simulated from reported crystal structure[2].

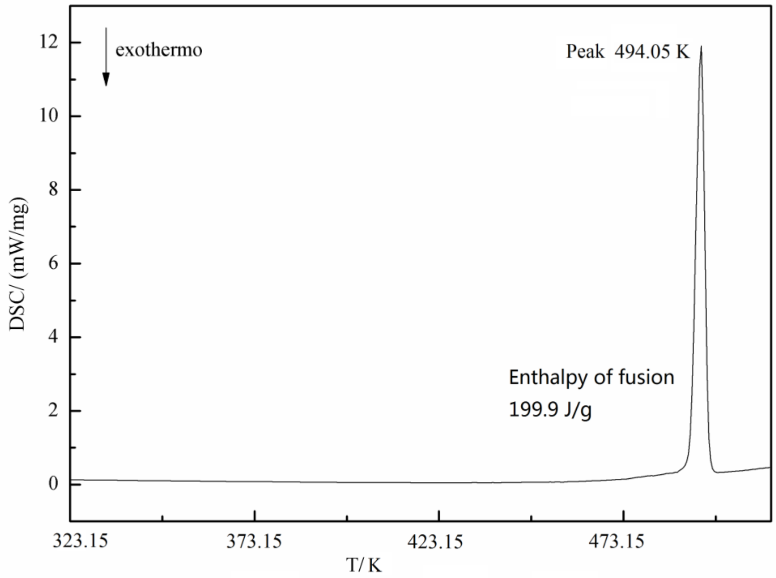


**Figure 2.** DSC curve of DTBHQ at a heating rate of 10 K min$^{-1}$.

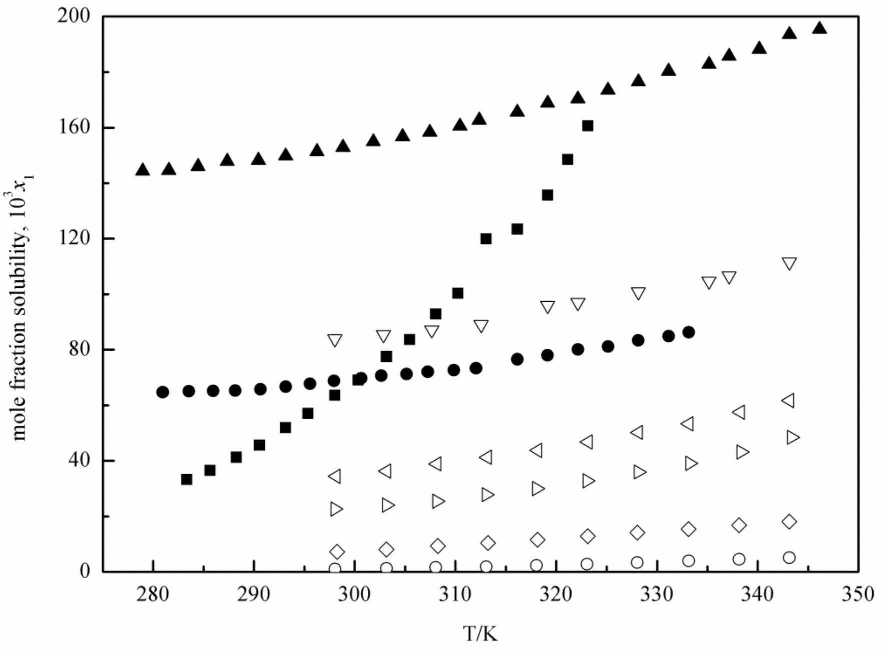


**Figure 3**. Solubility of DTBHQ in acetone, ■; ethyl acetate, ▲; methanol, ●; ethanol, ▽; ethanol + water (w=0.8998), ◁; ethanol + water (w=0.7992), ▷; ethanol + water (w=0.6501), ◇; ethanol + water(w=0.4999), ○.

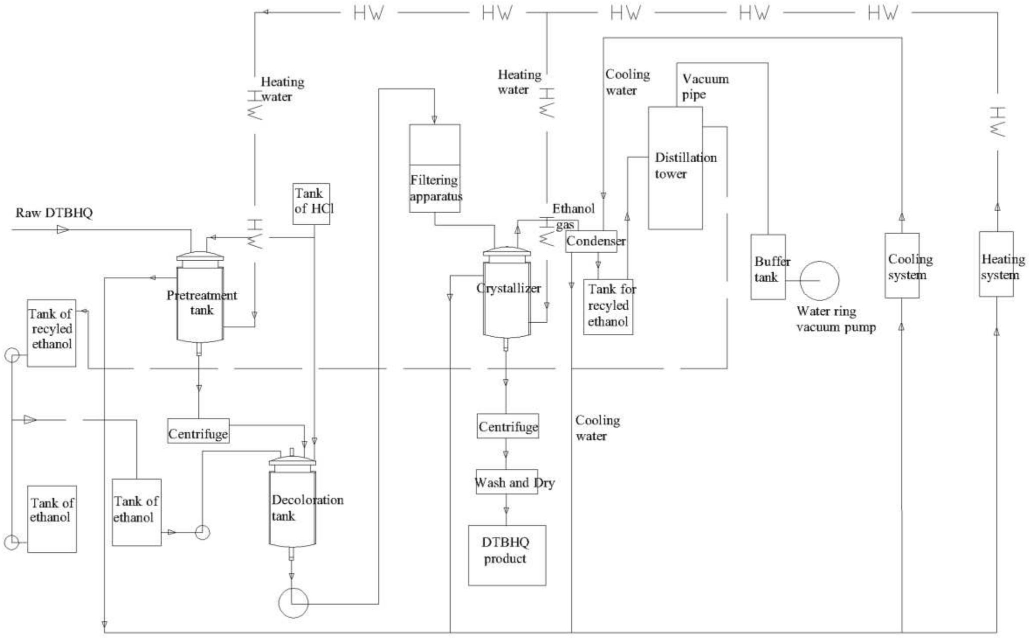


**Figure 4**. Flow sheet of purification of DTBHQ from by-product of TBHQ.

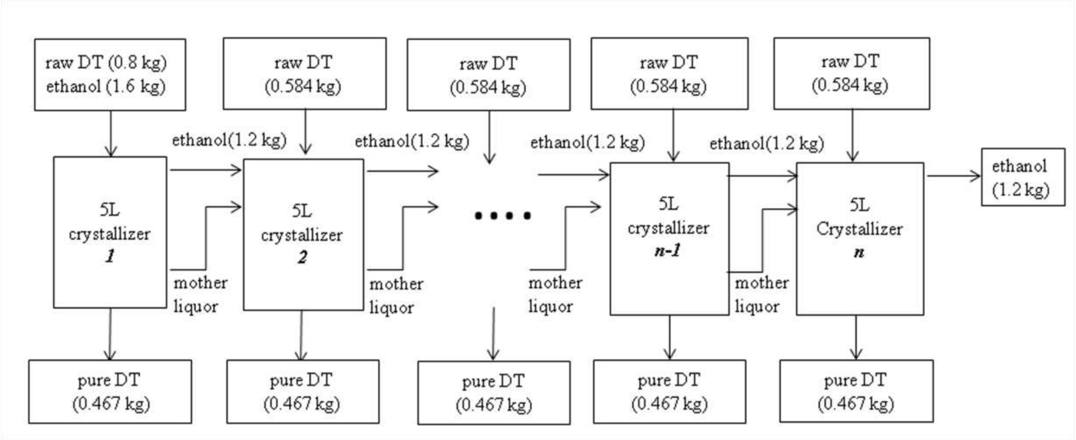


**Figure 5**. Cascade evaporative crystallisation of DTBHQ from by-product of TBHQ.

TABLES

## Table 1. Solvents Used in This Study

| solvent | manufacturer | mass fraction purity |
|---|---|---|
| acetone | Guangzhou Chemical Reagent Factory | analytical purity, >0 %.995 |
| ethanol | Nanjing Chemistry Reagent Co. Ltd | analytical purity, >0.997 % |
| ethyl acetate | Sinopharm Chemistry Reagent Co. Ltd | analytical purity, >0.995 % |
| methanol | Guangzhou Chemical Reagent Factory | analytical purity, >0.995 % |

**Table 2. Solubility of DTBHQ in Acetone, Ethyl Acetate, and Methanol**[a]

| T/K | $10^3x_1$ | $10^2$RD | | | T/K | $10^3x_1$ | $10^2$RD | | |
|---|---|---|---|---|---|---|---|---|---|
| | | eq 4 | eq 5 | eq 6 | | | eq 4 | eq 5 | eq 6 |
| | | Ethyl Acetate | | | | | Methanol | | |
| 278.95 | 144.41 | 0.32 | 4.13 | 4.00 | 280.95 | 64.71 | 0.70 | 4.30 | 4.25 |
| 281.55 | 144.64 | 0.14 | 2.77 | 2.68 | 283.55 | 64.98 | 0.40 | 2.94 | 2.91 |
| 284.45 | 146.03 | 0.05 | 2.04 | 1.99 | 285.95 | 65.13 | 0.11 | 1.55 | 1.54 |
| 287.35 | 147.88 | 0.47 | 1.64 | 1.62 | 288.15 | 65.29 | 0.63 | 0.32 | 0.32 |
| 290.45 | 148.19 | 0.29 | 0.11 | 0.13 | 290.65 | 65.76 | 0.85 | 0.62 | 0.61 |
| 293.15 | 149.77 | 0.14 | 0.31 | 0.27 | 293.15 | 66.7 | 0.45 | 0.84 | 0.82 |
| 296.25 | 151.37 | 0.19 | 0.91 | 0.85 | 295.55 | 67.75 | 0.06 | 0.81 | 0.78 |
| 298.85 | 152.88 | 0.18 | 1.29 | 1.22 | 297.95 | 68.8 | 0.47 | 0.78 | 0.76 |
| 301.85 | 154.95 | 0.04 | 1.49 | 1.40 | 300.65 | 69.68 | 0.39 | 1.19 | 1.15 |
| 304.75 | 156.76 | 0.10 | 1.79 | 1.70 | 302.65 | 70.65 | 0.72 | 1.02 | 0.98 |
| 307.45 | 158.34 | 0.27 | 2.12 | 2.03 | 305.15 | 71.2 | 0.11 | 1.74 | 1.71 |
| 310.45 | 160.55 | 0.25 | 2.18 | 2.09 | 307.25 | 72.04 | 0.07 | 1.82 | 1.78 |
| 312.35 | 162.72 | 0.20 | 1.73 | 1.64 | 309.85 | 72.69 | 0.59 | 2.43 | 2.41 |
| 316.15 | 165.55 | 0.08 | 1.77 | 1.69 | 312.05 | 73.39 | 1.01 | 2.74 | 2.71 |
| 319.15 | 168.79 | 0.50 | 1.18 | 1.11 | 316.15 | 76.56 | 0.54 | 0.76 | 0.74 |
| 322.15 | 170.33 | 0.15 | 1.60 | 1.55 | 319.15 | 78.01 | 0.35 | 0.51 | 0.51 |
| 325.15 | 173.50 | 0.08 | 1.05 | 1.01 | 322.15 | 80.02 | 0.74 | 0.42 | 0.42 |
| 328.15 | 176.54 | 0.17 | 0.58 | 0.57 | 325.15 | 81.09 | 0.15 | 0.18 | 0.17 |
| 331.15 | 180.34 | 0.60 | 0.30 | 0.29 | 328.15 | 83.31 | 0.25 | 1.34 | 1.31 |
| 335.15 | 182.79 | 0.36 | 0.03 | 0.02 | 331.15 | 84.89 | 0.24 | 1.71 | 1.66 |
| 337.15 | 185.74 | 0.06 | 0.83 | 0.76 | 333.15 | 86.29 | 0.21 | 2.34 | 2.28 |
| 340.15 | 188.24 | 0.41 | 1.00 | 0.90 | | | Acetone | | |
| 343.15 | 193.56 | 0.54 | 2.61 | 2.47 | 300.35 | 69.05 | 0.59 | 0.61 | 0.17 |
| 346.15 | 195.42 | 0.38 | 2.45 | 2.27 | 303.15 | 77.55 | 0.13 | 0.23 | 0.46 |
| | | Acetone | | | 305.45 | 83.60 | 1.56 | 1.72 | 0.89 |
| 283.35 | 33.24 | 0.66 | 1.11 | 2.11 | 308.05 | 92.85 | 0.92 | 1.13 | 0.24 |
| 285.65 | 36.50 | 0.77 | 0.33 | 2.90 | 310.25 | 100.27 | 1.41 | 1.63 | 0.75 |
| 288.25 | 41.25 | 0.44 | 0.05 | 1.89 | 313.05 | 119.92 | 6.15 | 5.96 | 6.64 |
| 290.55 | 45.56 | 0.79 | 0.46 | 1.73 | 316.15 | 123.39 | 1.74 | 1.89 | 1.45 |
| 293.15 | 51.94 | 0.96 | 1.19 | 0.50 | 319.15 | 135.7 | 2.54 | 2.56 | 2.56 |
| 295.35 | 57.03 | 0.91 | 1.07 | 0.79 | 321.15 | 148.47 | 0.22 | 0.11 | 0.50 |
| 298.05 | 63.58 | 0.52 | 0.58 | 0.72 | 323.15 | 160.64 | 1.08 | 1.33 | 0.51 |

[a] Standard uncertainties U are U(T) = 0.05K; U(p)=0.07 kPa; U($x_1$)=0.0006

**Table 3. Solubility of DTBHQ in Ethanol (w) + Water (1-w)**

| T/K | $10^3x_1$ | 100*RD | | | T/K | $10^3x_1$ | 100*RD | | |
|---|---|---|---|---|---|---|---|---|---|
| | | eq 4 | eq 5 | eq 6 | | | eq 4 | eq 5 | eq 6 |
| | w=1.0000 | | | | | w=0.7992 | | | |
| 298.05 | 83.89 | 0.92 | 2.23 | 2.16 | 298.05 | 22.65 | 0.26 | 7.33 | 7.15 |
| 302.85 | 85.42 | 0.02 | 0.44 | 0.42 | 303.15 | 24.06 | 0.08 | 3.28 | 3.24 |
| 307.65 | 87.10 | 0.94 | 1.11 | 1.09 | 308.15 | 25.43 | 1.18 | 0.87 | 0.87 |
| 312.55 | 89.03 | 1.77 | 2.38 | 2.35 | 313.05 | 27.79 | 0.50 | 1.22 | 1.15 |
| 319.15 | 95.99 | 1.55 | 0.71 | 0.76 | 318.05 | 29.93 | 0.03 | 2.94 | 2.84 |
| 322.15 | 96.94 | 0.59 | 0.26 | 0.22 | 323.05 | 32.74 | 0.46 | 2.78 | 2.66 |
| 328.15 | 100.8 | 0.49 | 0.16 | 0.12 | 328.15 | 36.01 | 0.83 | 1.89 | 1.81 |
| 335.15 | 104.71 | 0.53 | 0.59 | 0.59 | 333.25 | 39.10 | 0.59 | 2.05 | 2.02 |
| 337.15 | 106.57 | 0.16 | 0.00 | 0.02 | 338.35 | 43.15 | 0.81 | 0.28 | 0.30 |
| 343.15 | 111.51 | 0.11 | 1.09 | 1.02 | 343.35 | 48.47 | 0.50 | 3.61 | 3.49 |
| | w=0.8998 | | | | | w=0.6501 | | | |
| 298.05 | 34.38 | 0.03 | 3.03 | 2.88 | 298.25 | 7.17 | 0.84 | 2.79 | 2.89 |
| 303.15 | 36.27 | 0.47 | 0.80 | 0.74 | 303.15 | 8.07 | 0.50 | 2.35 | 2.35 |
| 308.15 | 38.93 | 0.64 | 0.57 | 0.57 | 308.25 | 9.29 | 0.75 | 0.43 | 0.38 |
| 313.15 | 41.25 | 0.24 | 0.73 | 0.68 | 313.05 | 10.39 | 0.19 | 0.77 | 0.76 |
| 318.15 | 43.79 | 0.14 | 1.60 | 1.51 | 318.05 | 11.56 | 0.09 | 1.12 | 1.18 |
| 323.15 | 46.74 | 0.13 | 1.67 | 1.58 | 323.05 | 12.79 | 0.78 | 1.33 | 1.33 |
| 328.15 | 50.21 | 0.36 | 0.88 | 0.82 | 328.15 | 14.18 | 0.13 | 1.76 | 1.82 |
| 333.15 | 53.33 | 0.41 | 1.03 | 0.99 | 333.25 | 15.40 | 0.65 | 0.32 | 0.36 |
| 338.25 | 57.49 | 0.03 | 0.42 | 0.38 | 338.35 | 16.87 | 0.22 | 0.24 | 0.23 |
| 343.15 | 61.67 | 0.15 | 1.77 | 1.65 | 343.35 | 18.16 | 0.84 | 1.38 | 1.40 |
| | w=0.4999 | | | | | w=0.4999 | | | |
| 298.05 | 1.04 | 4.81 | 5.77 | 5.58 | 323.05 | 2.80 | 0.71 | 1.79 | 1.68 |
| 303.15 | 1.26 | 0.79 | 6.35 | 6.43 | 328.05 | 3.37 | 1.19 | 3.56 | 3.44 |
| 308.05 | 1.60 | 1.25 | 0.63 | 0.87 | 333.15 | 3.94 | 1.02 | 2.54 | 2.59 |
| 313.05 | 1.89 | 2.65 | 2.65 | 2.65 | 338.15 | 4.52 | 0.44 | 0.66 | 0.62 |
| 318.05 | 2.30 | 2.61 | 0.87 | 0.74 | 343.15 | 5.10 | 0.78 | 2.55 | 2.59 |

[a]Standard uncertainties U are U(T) = 0.05K; U(p)=0.07 kPa; U($x_1$)=0.0006; U(w)=0.00004

**Table 4. Correlated Parameters in eq. 4 for DTBHQ in Ethanol (w) + Water (1-w), Acetone, Ethyl Acetate, Methanol**

| Solvent | w | A | B | C | 100*RAD |
|---|---|---|---|---|---|
| Ethanol | | -51.9464 | 1775.9668 | 7.6353 | 0.71 |
| Ethanol (w) + Water (1-w) | 0.8998 | -98.7654 | 3388.9811 | 14.7481 | 0.26 |
| Ethanol (w) + Water (1-w) | 0.7992 | -215.3010 | 8545.0475 | 32.0989 | 0.53 |
| Ethanol (w) + Water (1-w) | 0.6501 | 107.8496 | -7121.3351 | -15.6049 | 0.46 |
| Ethanol (w) + Water (1-w) | 0.4999 | 21.0726 | -13902.2213 | -31.8303 | 1.62 |
| Acetone | | 77.5189 | -6685.2997 | -10.1539 | 1.26 |
| Ethyl Acetate | | -58.4059 | 2225.8388 | 8.6109 | 0.25 |
| Methanol | | -91.3302 | 3578.3562 | 13.4527 | 0.43 |

**Table 5. Correlated Parameters in eq. 5 for DTBHQ in Ethanol (w) + Water (1-w), Acetone, Ethyl Acetate, Methanol**

| Solvent | w | $\lambda$*$10^4$ | h | 100*RAD |
|---|---|---|---|---|
| Ethanol | | 829.3585 | 8955.4819 | 0.90 |
| Ethanol (w) + Water (1-w) | 0.8998 | 745.8337 | 19073.4817 | 1.25 |
| Ethanol (w) + Water (1-w) | 0.7992 | 808.8434 | 23096.4099 | 2.62 |
| Ethanol (w) + Water (1-w) | 0.6501 | 377.8601 | 55897.2435 | 1.24 |
| Ethanol (w) + Water (1-w) | 0.4999 | 337.9336 | 105123.7507 | 2.74 |
| Acetone | | 33629.5873 | 1171.3574 | 1.29 |
| Ethyl Acetate | | 1330.1610 | 4130.8561 | 1.50 |
| Methanol | | 576.0714 | 10337.8067 | 1.45 |

**Table 6. Correlated Parameters in eq. 6 for DTBHQ in Ethanol (w) + Water (1-w), Acetone, Ethyl Acetate, Methanol**

| Solvent | w | $\Delta H$ | $\Delta S$ | 100*RAD |
|---|---|---|---|---|
| Ethanol | | 5584.9942 | -2.0488 | 0.87 |
| Ethanol (w) + Water (1-w) | 0.8998 | 11279.4692 | 9.5676 | 1.18 |
| Ethanol (w) + Water (1-w) | 0.7992 | 15021.1457 | 18.2877 | 2.55 |
| Ethanol (w) + Water (1-w) | 0.6501 | 17335.5488 | 17.3056 | 1.26 |
| Ethanol (w) + Water (1-w) | 0.4999 | 29443.0929 | 42.1270 | 2.72 |
| Acetone | | 29638.7260 | 76.4716 | 1.46 |
| Ethyl Acetate | | 3826.4611 | -2.7111 | 1.43 |
| Methanol | | 4594.3061 | -6.7720 | 1.42 |

**Table 7. Mass Balance of DTBHQ during Cascade Evaporative Crystallisation**

| | Input raw material | Product | Dissolved DTBHQ in mother liquor | Total yield[1] |
|---|---|---|---|---|
| Crystallizer-1 | 0.8 kg raw DTBHQ[2]<br>1.6 kg ethanol | 0.467 kg | 0.173 kg[3] | $\frac{0.467\text{kg}}{0.8\text{kg}*0.8}$=73 % |
| Crystallizer-2 | 0.584 kg raw DTBHQ | 0.467 kg | 0.173 kg | $\frac{0.467\text{kg}+0.467\text{kg}}{(0.8\text{kg}+0.584\text{kg})*0.8}$=84 % |
| Crystallizer-3 | 0.584 kg raw DTBHQ | 0.467 kg | 0.173 kg | $\frac{0.467\text{kg}+0.467\text{kg}+0.467\text{kg}}{(0.8\text{kg}+0.584\text{kg}+0.584\text{kg})*0.8}$=89 % |

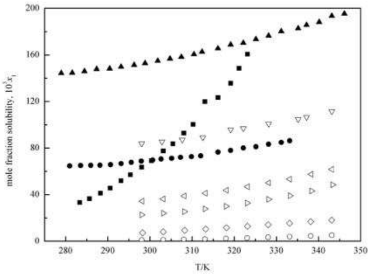
[1]. Total yield is calculated using the total DTBHQ product obtained by all DTBHQ in raw material;

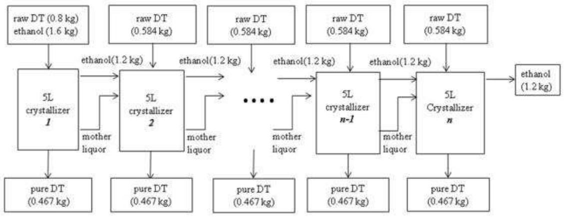
[2]. The mass fraction of DTBHQ in raw material is 0.8 measured by Gas Chromatography;

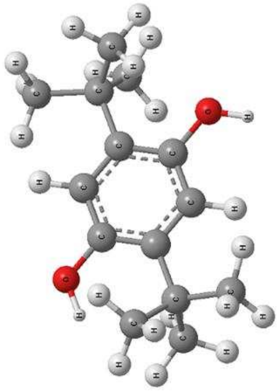
[3]. The calculated solubility value of DTBHQ in pure ethanol at 298.15 K using eq.4 was used.

# Solubility of 2, 5-Di-Tert-Butylhydroquinone and Process Design for its Purification Using Crystallisation

**Yang Zhang[1, 2], Jing Jing Liu[2], Lei Zhang[1], Xue Zhong Wang[2, 3]***







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