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Integrated Process-Product Design based on COSMO-SAC model: Application to the Production of 2,2,4-Trimethyl-1,2-H-Dihydroquinoline (TMQ)

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TMQ (2,2,4-trimethyl-1,2-H-dihydroquinoline) is a widely used and effective antioxidant in rubber production technologies. Its product is a kind of mixture which mainly consists of oligomers such as dimer, trimer and tetramer. The quality of TMQ is determined by the content of oligomers, especially dimer. This paper presents a systematic computer-aided molecular design (CAMD) methodology for designing optimal solvents for the synthesis of TMQ reaction system where the function of such solvents is to enhance the yield by optimal selectivity of reaction and extraction of TMQ products. In this work, we proposed an integrated process-product design framework of reaction and extraction solvent design for TMQ product. In this framework, a decomposition-based method is presented, which involves an integrated property estimation method combined group contribution methods with COSMO-SAC (COnductor-like Screen MOdel for Segment Activity Coefficient) and a process model of chemical and phase equilibrium. The results show that the designed solvents are able to improve the yield of dimer.

1. Introduction

In the industry of rubber production, TMQ (2,2,4-trimethyl-1,2-H-dihydroquinoline) is a widely used additive to decelerate rubber aging crack. TMQ product consists of oligomers such as dimer, trimer and tetramer. The quality of TMQ is determined by the content of dimer. Therefore, improving the content of dimmer in TMQ product is the key to improve its quality, and solvent plays an important role in its production. Due to the influence that solvents have on chemical kinetics and thermodynamics equilibrium, different solvents cause diverse product composition. Therefore, it is important to select and design solvents to maximize the content of dimer in the reaction system to improve the quality of TMQ.

Computer aided molecular design (CAMD) is a powerful method to design solvents for specific property requirements. CAMD has been widely used in various kinds of solvents design, such as liquid–liquid extraction (Gani et al., 1983), reaction solvents (Folić et al., 2008, Zhou et al.,2016), ionic liquids (Chong et al., 2014) and so on. In this article, CAMD is applied to design solvents for increasing the yield of dimer. First, we employ group contribution methods（Gani et al., 1983) to quantitatively generate preliminary solvents satisfying the basic constraints in structure and properties. Then we apply the COSMO-SAC (COnductor-like Screen MOdel for Segment Activity Coefficient) model to estimate the activity coefficient of TMQ with preliminary solvents, as group contribution methods are unable to estimate the activity coefficients. In addition, a process model formulated as a set of ordinary differential equations (ODEs) for the modelling of chemical and phase equilibrium is introduced, which is based on the simulation of dynamic evolution of a mixture from non-equilibrium initial composition towards the final equilibrium composition. Next, process simulation using Aspen Plus is implemented to verify the reliability of process model. Finally, the preliminary solvents are evaluated individually by the process model based on the objective of maximizing the yield of dimer.

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2. Design and screening of solvents

In this section, CAMD employed group contribution (GC) property method is used to generate preliminary solvents satisfying the basic structure and property constraints. Then, according to the specified criterions, the final target solvent is selected from the preliminary solvents.

In the first stage of generating preliminary solvents, group candidates which constitute solvent molecules are needed. Considering that groups are chemically inert, the following groups are chosen:

Table 1: Group candidates

Type of groups	Aliphatic groups	Aromatic groups	Cyclic groups
Groups	CH_3, CH_2, CH, C, CH_2=CH, CH=CH, CH_2=C, CH=C, C=C, CH_3CO, CH_2CO, CH_3COO, CH_2COO, CH_3O, CH_2O, CH_2CN, CH_2N	ACH, AC, AC-CH_3, AC-CH_2, AC-CH	CH_2 (cyc) CH (cyc) C=C (cyc)

The structural constraints (Hukkerikar et al., 2012; Liu et al., 2019) are used to ensure chemical feasibility of solvent. Detailed structural constraints are listed as below:

$$\sum_j (2-v_j)n_j = 2m, m = \begin{cases} 1, & \text{for aliphatic molecule} \\ 0, & \text{for monocyclic molecule} \\ -1, & \text{for bicyclic molecule} \end{cases} \tag{1}$$

$$\sum_i n_i \geq 4(1-m)\ , \qquad i \in G\ , \quad v_i \geq 2 \tag{2}$$

$$\sum_i n_i \geq v_j + 1, \qquad i, j \in G \tag{3}$$

$$1 \leq n_j \leq 7, \qquad j \in G \tag{4}$$

$$4 \leq \sum_i n_i \leq 8, \qquad i \in G \tag{5}$$

$$\sum_i n_i = 6n_{ac}, \qquad i \in G_a \tag{6}$$

$$n_{ac} \leq 1-m \tag{7}$$

$$\sum_i n_i \geq 1.01(n_{ac} - 1) + 0.0001\sum_i n_i, \qquad i \in G_{na}, v_i \geq 3 \tag{8}$$

$$3 \times \left(\sum_i n_i - 1\right) + \sum_j n_j + \sum_k n_k \geq 3 - 100 \times (m+1), \qquad i, j \in G_a,\ k \in G_{na},\ v_i \geq 3,\ v_j \geq 4,\ v_k \geq 5 \tag{9}$$

where n_j and v_j are the number and valency of group j, m is the number of rings in the target molecule, n_{ac} is the number of aromatic rings in the molecule, G is the set of groups used in CAMD, G_a is the set of aromatic groups, G_{na} is the set of nonaromatic groups.

Property constraints (Liu et al., 2018), including boiling point, melt point, Lethal Concentration 50 (LC_{50}) and solubility are listed orderly as follows:

$$410K \leq 244.7889 \times \mathrm{Ln}\sum_i n_i T_b \leq 440K \tag{10}$$

$$298K \leq 143.5726 \times \mathrm{Ln}\sum_i n_i T_m \tag{11}$$

$$\sum_i n_i LC_{50} \leq 4mg\,/\,L \tag{12}$$

$$16Mpa^{1/2} \leq 20.7339 \times \mathrm{Ln}\sum_i n_i S_P \leq 20Mpa^{1/2} \tag{13}$$

where n_i is the number of group, i, T_b, T_m, LC_{50}, S_p are relative group contribution value of boiling point, melt point, LC_{50} and solubility respectively (Marrero and Gani, 2001).

A number of preliminary solvents are generated by the solution of the above MINLP model. Then in the second stage of solvents screening, criterions are set for the screening solvents. The first criterion is that solvents generated by CAMD exist in PubChem database, which ensures the existence of the molecules (solvents). The second criterion is maximization of dimer and minimization of water in extraction phase of process model, which is discussed in section 3. The results are shown in Section 4.2.

3. Process model: Chemical and phase equilibrium

3.1 COSMO-SAC model

In the reaction model, the activity coefficients are predicted with COSMO-SAC (Conductor-like Screen Model for Segment Activity Coefficient) (Lin and Sandler, 2002). COSMO-SAC is based on continuum solvation model used in quantum-mechanics (QM) calculations. Comparing to group contribution (GC), one significant advantage is that COSMO-SAC can provide the prediction of activity coefficients without the need of binary interaction parameters, which require large experimental data sets of thermodynamic properties, to make robust parameter estimates for many types of molecular structures. Meanwhile, GC method cannot estimate activity coefficients of TMQ in mixtures for the lack of interaction parameters. Therefore, COSMO-SAC is a more suitable approach for TMQ system.

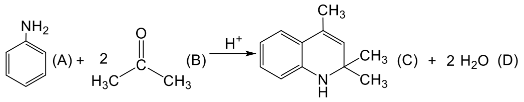
The prediction of activity coefficients with COSMO-SAC contains two steps:

1. QM-calculations are performed for each pure component using density function theory (DFT) and continuum solvation model (CSM). Based on the 3D structure of each component, molecular geometry and energy are optimized through DFT-CSM calculations. The output results contain cavity volumes (V_{COSMO}) and the screening charge density which describes charges of discretized surface of a molecule.
2. The screening charge density in the first step is transformed into a histogram (σ-profile). Based on the σ-profile and V_{COSMO}, COSMO-SAC model is applied to calculate the activity coefficients of each components in a mixture.

3.2 The Ordinary Differential Equations (ODEs) of chemical and phase equilibrium

In the reaction process, chemical and phase equilibrium between two or more phases are usually solved by diverse mathematical approaches (Zinser et al.,2016). Gibbs free energy minimization is applied to handle reaction equilibrium and the equality of the chemical potentials of all components is the most common approach for phase equilibrium at constant pressure and temperature. Zinser et al. (2016) proposed a dynamic method for computing thermodynamic equilibrium including chemical equilibrium and phase equilibrium. The method is based on the solution of a set of ODEs which can handle chemical and phase equilibrium simultaneously. Zhou et al. (2016) applied the ODEs approach to calculate esterification reaction including both chemical and phase equilibrium, however, there are still some redundant mathematical model equations in their formulation, which make their model complex and slow in simulation. Therefore, an improved model formulation is presented based on simultaneous chemical and phase equilibrium and a simplified ODEs model formulation in rate-based two-phase reaction system, which describes the composition distribution of all components.

The main synthesis reactions for TMQ include condensation reaction (Eq(14)) and polymerization reactions (Eqs(15)-(17)) with abbreviations for each compound are given.



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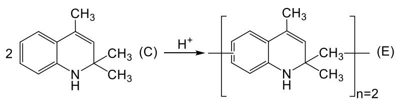

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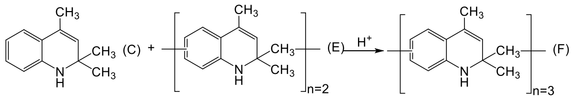

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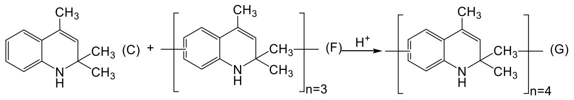

(17)

The reactions are carried out in a batch process. With the existence of solvent, the reaction system is divided in two parts, extraction phase and raffinate phase (Figure 1). The extraction phase is initialized with solvent and the raffinate phase is initialized with reactants. The synthesis reactions of TMQ happen in both of the two phases.

All components including reactants, products and the solvent are transferred between extraction and raffinate phase driven by the difference of chemical potential when the computation starts. To accelerate the reaction, in the end, the solvent and oligomers are almost in the extraction phase and water is the primary component in the raffinate phase.

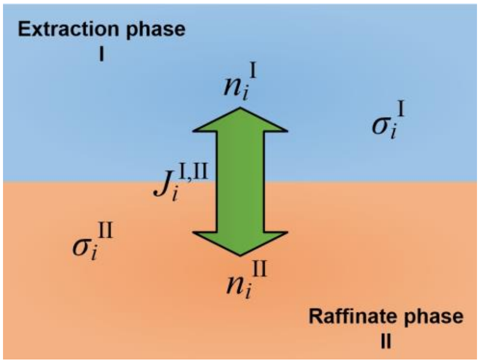

Figure 1: The schematic diagram on reaction model

Mass transfer rate expressions between phases

$$J_i^{I,II} = k_{trans}(x_i^I\gamma_i^I - x_i^{II}\gamma_i^{II}) \qquad i \in (A,B,C,D,E,F,G) \tag{18}$$

where J is the mass transfer rate between two phases, k_{trans} is the rate constant of mass transfer, γ is the activity coefficient, x is the molar composition, I and II represent extraction phase and raffinate phase respectively, A, B, C, D, E, F, and G are reactants and products as depicted in Eqs(14)−(17). According to Zinser et al. (2016), k_{trans} is set to 1. The J becomes zero at thermodynamic equilibrium, then the chemical potentials are equal between two phases, which describes phase equilibria.

Reaction rate expressions of components

$$2\sigma_A^P = \sigma_B^P = -\sigma_D^P = -2k_1x_A^P\gamma_A^P(x_B^P\gamma_B^P)^2 \qquad p \in (I,\ II) \tag{19}$$

$$\sigma_C^P = k_1x_A^P\gamma_A^P(x_B^P\gamma_B^P)^2 - k_2(x_C^P\gamma_C^P)^2 - k_3x_C^P\gamma_C^Px_E^P\gamma_E^P - k_4x_C^P\gamma_C^Px_F^P\gamma_F^P \tag{20}$$

$$\sigma_E^P = k_2(x_C^P\gamma_C^P)^2 - k_3x_C^P\gamma_C^Px_E^P\gamma_E^P \tag{21}$$

$$\sigma_F^P = k_3x_C^P\gamma_C^Px_E^P\gamma_E^P - k_4x_C^P\gamma_C^Px_F^P\gamma_F^P \tag{22}$$

$$\sigma_G^P = k_4x_C^P\gamma_C^Px_F^P\gamma_F^P \tag{23}$$

where σ is the accumulation rates of components during reaction, the activity coefficients γ can be predicted with COSMO-SAC, k_1, k_2, k_3 and k_4 are respectively rate constants of the reactions of Eqs. (1)−(4). The reaction rate constant values are not available in any literature. But the distribution of products involving dimer, trimer and tetramer is illustrated in literatures (Qian Q. H., 2003). So, the rate values are estimated by the distribution of oligomer. The values are not absolutely accurate, however, the trend in the distribution of products are evaluated and the results agree with the literature values. Here, the reaction rate constant values are set to 176, 114, 16 and 8, respectively. In our future work, these rate constants will be calculated and verified by QM methods.

The chemical and phase equilibrium is formulated as a set of ODEs:

$$\frac{dn_i^I}{dt} = -J_i^{I,II} + \sigma_i^I \tag{24}$$

$$\frac{dn_i^{II}}{dt} = J_i^{I,II} + \sigma_i^{II} \tag{25}$$

The Eqs. (25) and (26) are driven by chemical potential difference between each component. The thermodynamic equilibrium of a system is finally achieved when all driving forces become zero. When the chemical potential differences are zero, the chemical potentials between two phases are equal, which describes phase equilibria.

It should be noted that the TMQ reactions happen in a liquid system where the effect of gasification on reaction will not be taken into consideration under the reaction temperature. Homogeneous liquid reactions happen when solvents are not added to reaction system. Two phases will form when the solvent is added.
Aspen Plus simulation is a widely used commercial process simulator and is used here to validate the rationality of the ODEs model. COSMO-SAC is used as the property method in the Aspen Plus simulation. All the results are given in Section 4.1.

4. Results and discussion

4.1 Comparison of results between the ODEs model and Aspen Plus

The initial amounts of aniline and acetone are 1 kmol and 2 kmol, respectively. The reaction temperature is 383 K and the reaction time is 7 hours. The end composition of components in TMQ solvent-free system is shown in Figure 2.

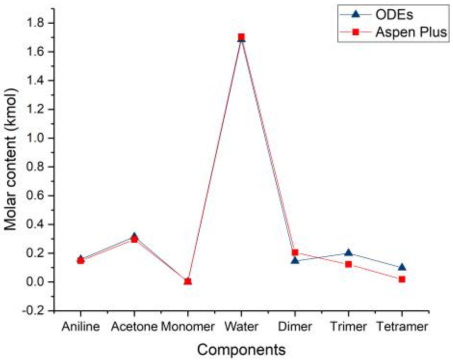

Figure 2: The comparison of results between ODEs and Aspen Plus

The compositions calculated by ODEs and Aspen plus are consistent from the comparison, especially in the condensation reaction. The dimer, trimer and tetramer are not entirely consistent. This is because the different COSMO-SAC version used. The COSMO-SAC used in the ODEs model is modified by Chen (Chen et al., 2016)and the version used in Aspen Plus is revised by Lin (Lin and Sandler, 2002), therefore the deviation is allowed.

4.2 The results of solvents screening

The solvents comply with the two criteria are selected, as shown in Table 2. The raffinate phase is initialed as aniline and acetone with 1 kmol and 2 kmol respectively. The extraction phase is initialed as pure solvent with 1 kmol. The value and unit of initial feed have no effects on final results. The molar quantities used in this text exemplify the applicability of the process model to illustrate that solvents have positive influence on reaction. Actually, the molar quantities can be set to arbitrary value. The reaction temperature and time are same as above. All these solvents have positive effect on TMQ synthesis improving the yield of dimers. In solvent-free reaction, the yield of dimer, trimer and tetramer are respectively 0.14580 kmol, 0.19983 kmol and 0.09897 kmol. The comparison between reactions with and without solvent is shown in Table 2.

Table 2: The yield of dimer, trimer, tetramer and water with adding solvents in extraction phase

Number of solvents	Solvent	Dimer (kmol)	Trimer (kmol)	Tetramer (kmol)	Water (kmol)	Increased percentage of dimer (%)
1	Isopropyl benzene	0.23822	0.24152	0.07827	0.01822	63.39022
2	Ethylbenzene	0.23770	0.24291	0.07722	0.01900	63.03304
3	Toluene	0.23588	0.24477	0.07602	0.02025	61.77990
4	Isopropyl Butyrate	0.21383	0.23981	0.08338	0.08030	46.65931
5	1-Methylpropyl Ester	0.21110	0.23914	0.08406	0.09432	44.78419
6	Ethyl Pentanoate	0.20977	0.23925	0.08372	0.09941	43.87535
7	Butyl Propionate	0.20952	0.23949	0.08353	0.10515	43.70140

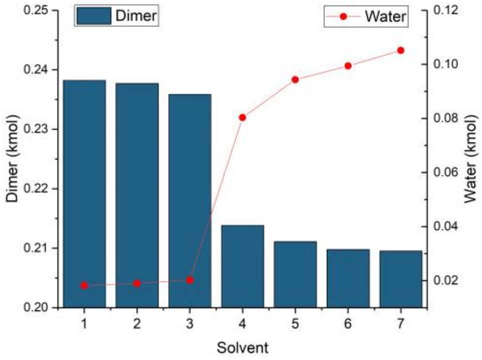

Figure 3: The yield of dimer and water with adding solvents in extraction phase

As can be seen, the yield of dimers is increased due to the effect of solvents. Aromatic solvents are best among all of them, which have less water content and much higher yield of dimers.

5. Conclusions

Computer-Aided Molecular Design (CAMD) methodology for identifying optimal solvents for the synthesis of TMQ reaction system is proposed to improve the yield by optimal selectivity of reaction and extraction of TMQ products. In this work, we used the developed model (Eqs(1) – (25)) for the design of solvents. For the solution of this model, two-stage strategy is needed. In the first stage, Eqs(1) – (13) is used first to generate feasible solvents, and then, in the second stage, Eqs(14) – (25) are used for further screening from the generated solvents, and the final optimal one is selected based on the objective function. Among these designed solvents, toluene, is already used in the industry, which demonstrated the rationality of this methodology. From the proposed design method, better solvents have been found which can improve the quality of TMQ besides toluene.

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