Research Article

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Synthesis of 2,2'-dibenzoylaminodiphenyl disulfide based on Aspen Plus simulation and the development of green synthesis processes

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Abstract: The rubber peptizer 2,2'-dibenzoylaminodiphenyl disulfide is typically synthesized from C_7H_5NS , $NaOH$, H_2SO_4 , and H_2O_2 , but these reactants were replaced with $C_6H_4ClNO_2$, C_2H_6O , Na_2S , S , and $N_2H_4 \cdot H_2O$, and these raw materials effectively improved the synthesis yield, reduced the number of synthetic steps, and made the synthetic process greener. Although the catalyst is difficult to recover, it effectively avoids using ethanol as a volatile organic solvent. The Aspen Plus method was used to simulate the key processes in the synthesis in the experimental conditions as the boundary conditions. The simulation results show that the feed ratio of C_7H_5NS , H_2O_2 , and C_7H_5ClO directly determines the yield of the reaction, and the equivalents of $NaOH$, H_2SO_4 , and Na_2CO_3 indirectly affect the yield of the reaction by changing the reaction environment and controlling the formation of byproducts. The temperature of the ring-opening reaction and the acylation reaction should be maintained within 110–120°C to maximize the yield. The oxidation reaction temperature also directly affects the reaction yield and should be kept below 40°C. The simulation results are consistent with practical industrial production conditions. Based on the developed green synthesis process and the optimal process parameters obtained from the simulation, the industrial-scale production of 10,000 tons of 2,2'-dibenzoyl amino diphenyl disulfide was carried out.

Compared with that of *o*-nitrochlorobenzene, the yield of 2,2'-dibenzoylaminodiphenyl disulfide increased from approximately 72% to more than 90%. Using this method instead of the original synthesis method avoids the use of *o*-nitrochlorobenzene, which is neurotoxic; Raney nickel as the metal catalyst, which is difficult to recycle with existing environmental protection technologies; and ethanol as the organic solvent, which is associated with environmental problems. The amine tail gas that is easily generated in the original synthesis method is not generated in this system, and the drying step is eliminated.

Keyword: rubber peptizer, process synthesis, Aspen Plus simulation, process optimization, clean production

1 Introduction

The peptizers used as rubber additives play a very important role in improving rubber processing and the quality of rubber products. These additives improve the effects of chemical mastication, decrease the time required for mastication, and increase plasticity while having no effect on the aging of rubber products, making them especially suitable for the processing of dense materials [1]. The important raw materials of early rubber peptizers are benzene, aniline, carbon disulfide, phenol, aldehydes, and their derivatives. With the increasing processing requirements for rubber products and the increasing strict environmental protection regulations, research and development involving green plasticizers as rubber additives has attracted substantial interest but remains quite difficult.

Currently, research and development involving rubber peptizers and mainstream production techniques is mainly focused on 2,2'-dibenzoylaminodiphenyl disulfide (hereinafter referred to as DBD). Engels [2,3] combined benzenesulfonyl chloride and its derivatives to form disulfide bonds, which can then be converted to

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diphenyl disulfides by treatment with N_2H_4 and HI/HCl , and then, $\text{N}_2\text{H}_4/\text{NaOH}$ can be added to the disulfide species to form sodium thiophenolate [4]. Chedekel et al. [5] and Adelaere et al. [6] used N_2H_4 to ring-open $\text{C}_7\text{H}_5\text{NS}$ to obtain $\text{C}_6\text{H}_7\text{NS}$ as an intermediate. Ankodia et al. [7] formed disulfide bonds with $\text{C}_6\text{H}_7\text{NS}$ by using H_2O_2 to form a di-disulfide compound (DATA), and DBD was formed as the final product using $\text{C}_7\text{H}_5\text{ClO}$.

The synthesis methods are roughly divided into two categories: one is based on $\text{C}_6\text{H}_7\text{N}$ and NaHS , and the target product is synthesized through addition, hydrolysis, oxidation, and acylation [2,3]; the other is the synthesis of *o*-nitrochlorobenzene, using $\text{C}_6\text{H}_4\text{ClNO}_2$ as the raw material, and reacting it with NaHS , Na_2S_2 , $(\text{NH}_4)_2\text{S}$, and Na_2SO_4 to prepare the target product [5,6]. However, both the synthesis methods have common technical problems. On the one hand, the synthesis processes are operationally complicated, have low product yields, and generate several byproducts. On the other hand, in the production process, substantial amounts of “three wastes” are discharged, and they are difficult to handle. The severity of these problems can vary depending on the raw materials. The waste products are highly toxic, explosive, and dangerous substances with a low safety factor. Therefore, the research on new synthetic routes and the development of green synthetic techniques are important for industrial applications.

In this article, $\text{C}_7\text{H}_5\text{NS}$, NaOH , H_2SO_4 , and H_2O_2 replaced $\text{C}_6\text{H}_4\text{ClNO}_2$, $\text{C}_2\text{H}_6\text{O}$, Na_2S , S , and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ as the raw materials for the synthesis. The green synthesis process was optimized to improve the yield, reduce the number of synthetic steps, and effectively solve the problems associated with the poor recyclability of the catalyst while avoiding the use of ethanol as a volatile organic solvent [8]. The Aspen Plus method was used as the boundary conditions for the experimental conditions, and the synthesis was simulated based on its key steps to obtain the best process parameters, and the

simulation results were compared with the actual industrial production process [9–11].

2 Experimental research on green synthesis process for accessing DBD

Currently, the main synthetic route to *o*-nitrochlorobenzene used throughout the world is shown in Figure 1.

The reaction pathway is based on $\text{C}_6\text{H}_4\text{ClNO}_2$, $\text{C}_2\text{H}_6\text{O}$, Na_2S , S , and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, and $\text{C}_6\text{H}_4\text{ClNO}_2$ is a dangerous drug substance. Two intermediate products are formed in this synthetic route, and the two intermediates must be dried and distilled to remove the reaction solvent and then ground to prepare them for the next step. In the pulverization process, some intermediate products are lost in the form of dust, and the generated dust containing the amino and nitro compounds is a sensitization hazard. The entire reaction process requires Raney nickel as the metal catalyst, but it is difficult to recycle with existing environmental protection technologies. The yield of the entire synthesis process is low, and the unique catalytic activity of Raney nickel makes it highly combustible and prone to explosion when exposed to the oxygen in air. The entire reaction process is complicated and difficult to control accurately.

On the basis of the aforementioned problems, a reaction path involving benzothiazole was developed to make the production process greener. Compared with the traditional *o*-nitrochlorobenzene synthesis route, $\text{C}_7\text{H}_5\text{NS}$, NaOH , H_2SO_4 , and H_2O_2 replaced $\text{C}_{10}\text{H}_4\text{ClNO}_2$, $\text{C}_2\text{H}_6\text{O}$, Na_2S , S , and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ as the raw synthetic materials, and H_2SO_4 was used as the activating agent to greatly improve the oxidation performance of H_2O_2 [12,13] and avoid the use of Raney nickel as the metal catalyst. In the reaction pathway, instead of proceeding through two intermediates, only one intermediate was

Figure 1: Synthetic route to *o*-nitrochlorobenzene.

involved in the synthesis of the target product, and the number of reaction steps was reduced, effectively improving the synthesis yield and simplifying the reaction control process. Ethanol was not used at any stage of the reaction process, and the drying step was eliminated to avoid having to recover the ethanol in an environmentally friendly manner.

The developed benzothiazole method is obviously greener, and the reaction yield was increased from 72% to over 90%, while avoiding highly toxic $C_6H_4ClNO_2$, catalytic Raney nickel that is extremely explosive, and the use of ethanol as a solvent. The number of intermediates in the reaction process was decreased from two to one, and the drying process was eliminated, simplifying the tedious control procedures for the entire reaction process. The entire synthesis process effectively solves the problems associated with the *o*-nitrochlorobenzene method, which readily resulted in a human sensitization hazard and posed environmental recycling problems. The developed benzothiazole method and the DBD synthesis process are shown in Figure 2.

The laboratory adopts the following preparation scheme, and the synthetic route is divided into two steps: in the first step, first, the accurately weighed C_7H_5NS and 32% NaOH are added, the temperature is gradually increased to 110°C and to reflux, and this temperature is maintained for 5 h and the mixture is cooled down before using. H_2O , 98% H_2SO_4 , and 30% H_2O_2 are configured as oxidants and added dropwise to the aforementioned reaction system to control the reaction endpoint pH to 6–7. After stirring for 30 min, the system is cooled to room temperature and the mixture is suction filtered. The mixture is dried to obtain intermediate dithiodiphenylamine (hereinafter referred to as DATA). In the second step, first, the accurately weighed intermediate DATA and the solvents C_7H_8 and Na_2CO_3 are added, the temperature is gradually increased to reflux, and C_7H_5ClO is added to the system dropwise. After the reaction reached the end point, water is added to wash the salt, and the brine is separated while hot. Then, the mother liquor system is cooled to room temperature, and the solid is filtered by suction to obtain

the target product DBD. The experimental results are presented in Tables 1 and 2.

3 Process simulation and optimization of the benzothiazole synthesis

The traditional scale-up process, from the laboratory scale to the industrial production scale, in addition to requiring large investments of time and money, is quite complex. This is not surprising as the relationship between the various synthetic process parameters is complex. It is difficult to scale-up processes to the industrial scale, and it is especially difficult to optimize systems throughout the production process to achieve effective engineering amplification and the ultimate goal.

Since the late 1990s, various process simulation software programs have been widely used in industrial amplification and process optimization control in real-world industrial settings. Among them, Aspen Plus is one of the most common and widely used in the chemical, oil refining, oil and gas processing, petrochemical, and other industries, and it has been widely recognized by the engineering community [12,13]. However, Aspen Plus software has rarely been used to assess the rubber additive production. Therefore, it is necessary to carry out the relevant Aspen Plus simulation on the newly developed benzothiazole-based synthesis (DBD) to optimize the whole production system to achieve a high reaction yield, reduce energy consumption, and make the reaction greener.

With the help of Aspen Plus, the experimental data and a large amount of engineering data were used as boundary conditions to select accurate and reliable physical methods and models [14,15]. By using the sensitivity tool analysis in Aspen Plus, simulation results from different working conditions can be obtained while avoiding problems such as a large experimental workload and simplifying the analysis process. The results

Figure 2: Benzothiazole synthesis route.

Table 1: Effect of reactant ratio on reaction yield

NaOH/C ₇ H ₅ NS	Yield of C ₆ H ₇ NS (%)	H ₂ SO ₄ /H ₂ O ₂	Yield of DATA (%)	C ₇ H ₅ ClO/Na ₂ CO ₃	Yield of DBD (%)
2.0	94.6	1.2	77.2	1.6	73.6
2.5	99.1	1.4	96.8	1.8	85.3
3.0	99.5	1.6	97.1	2.0	92.6
3.5	99.6	1.8	96.7	2.2	94.2
4.0	99.8	2.0	97.1	2.4	94.5

Table 2: Effect of reaction temperature on reaction yield

Alkaline hydrolysis temperature (°C)	Yield of C ₆ H ₇ NS (%)	Oxidation temperature (°C)	Yield of DATA (%)	Acylation temperature (°C)	Yield of DBD (%)
80	80.4	15	97.2	90	58.3
90	87.9	20	97.5	100	88.2
100	94.8	25	97.1	110	95.9
110	98.6	40	95.5	120	95.1
120	99.4	50	86.4	130	93.5

obtained from the simulations can be used as the initial values of the engineering operating conditions, reducing the adjustment interval.

The key to the entire simulation is having a database of known physical and chemical properties. However, currently, a complete database of physical and chemical properties is difficult to obtain. In this article, we use the physical properties of pure substances such as C₇H₅NS, NaOH, H₂O₂, H₂SO₄, Na₂CO₃, C₇H₅ClO, C₇H₈, and H₂O built in Aspen Plus. For the substances C₆H₇NS, DATA, and DBD, which are not in the physical property database, we use physical property estimation to make a preliminary estimation of the missing data and then establish the related calculation methods to obtain the physical and chemical property data. Therefore, relevant calculation methods must be established to determine the physical and chemical properties relevant to the synthesis process [16,18].

The evaluation of the DBD synthesis path developed herein starts with the construction of a reaction force field model and the calculation of the bond order (BO) between any two atoms to determine the instantaneous atom connectivities, as shown in equation (1) [19].

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{lp}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{coa}} + E_{\text{C2}} + E_{\text{triple}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{Hbond}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} \quad (1)$$

The most basic assumption of the BO definition in the reaction force field is that there is a certain

mathematical relationship between the BO and the distance between the atoms. Based on the distance between the atoms, the BO between any two atoms can be directly obtained. In the ReaxFF reaction force field, the bond level BO_{ij} is defined as a function of the interatomic distance r_{ij} , and the bond level is divided into three parts in the chemical sense using the definitions of single bond BO_{ij}, double bond BO_{ij} and triple bond BO_{ij} in the chemical bond contribution, as equation (2) [20].

$$\begin{aligned} \text{BO}'_{ij} &= \text{BO}^{\sigma}_{ij} + \text{BO}^{\pi}_{ij} + \text{BO}^{\pi\pi}_{ij} \\ &= \exp \left[p_{\text{bo1}} \cdot \left(\frac{r_{ij}}{r_o^{\sigma}} \right)^{p_{\text{bo2}}} \right] + \exp \left[p_{\text{bo3}} \cdot \left(\frac{r_{ij}}{r_o^{\pi}} \right)^{p_{\text{bo4}}} \right] \\ &\quad + \exp \left[p_{\text{bo5}} \cdot \left(\frac{r_{ij}}{r_o^{\pi\pi}} \right)^{p_{\text{bo6}}} \right] \end{aligned} \quad (2)$$

The energy of any two groups is represented by a key parameter, such as the bonding function (equation (3) [21]):

$$\begin{aligned} E_{\text{bond}} &= -D_e^{\sigma} \cdot \text{BO}^{\sigma}_{ij} \cdot \exp \left[p_{\text{bo1}} \cdot (1 - (\text{BO}^{\sigma}_{ij})^{p_{\text{bo2}}}) \right] \\ &\quad - D_e^{\pi} \cdot \text{BO}^{\pi}_{ij} - D_e^{\pi\pi} \cdot \text{BO}^{\pi\pi}_{ij} \end{aligned} \quad (3)$$

Gauss View is used to obtain chemical kinetic information and thermodynamic information. According to the Schrodinger equation and the Hartree–Fock equation, combined with the density functional theory (DFT), E_0 is calculated in equation (4)):

$$E_0 = - \sum_a Z_a \int \frac{\sum_i |\theta_i^{ks}|^2}{r_{ia}} - \frac{1}{2} \sum_i \theta_i^{ks} |\nabla_i^2| \theta_i^{ks} + \frac{1}{2} \iint \sum_i \frac{|\theta_i^{ks}|^2 \rho(r_2)}{r_{i2}} dr_1 dr_2 + E_{XC}(\rho) \quad (4)$$

By using the KiSTheIP program, a transition state theory method was first constructed. The calculation of the reaction path degeneracy σ is as follows (equation (5)):

$$\sigma = \sigma(R) \times n(R) / [\sigma(TS) \times n(TS)] \quad (5)$$

$\sigma(R)$ and $\sigma(TS)$ refer to the rotational symmetry numbers of the reactant and the transition state structure, respectively, and $n(R)$ and $n(TS)$ refer to the number of the chiral isomers of the reactant and the transition state structure, respectively. For bimolecular reactants (equation (6)):

$$\sigma = \frac{\sigma_{\text{rot R}}}{\sigma_{\text{rot TS}}} = \sigma_{\text{rot R1}} \times \sigma_{\text{rot R2}} / \sigma_{\text{rot TS}} \quad (6)$$

The thermodynamic and kinetic parameters of the obtained DBD reaction are presented in Table 3.

Table 3: Reaction thermodynamics and kinetic parameters

	Reaction heat (kcal/mol)	Rate constant (cm ³ /molec/s)
Alkaline reaction	19.4	5.80×10^{-9}
Oxidation reaction	-72.5	9.23×10^{-12}
Acylation reaction	-7.61	2.59×10^{-16}

Finally, combining the available physical and chemical data [18], Aspen Plus was used to model the process flow. By using the experimental data for the initial design, sensitivity analysis was used to analyze and optimize the feed and kettle temperatures at each stage. The final simulation optimization maximized the yield of DBD and provided a platform and guidance for determining future operating conditions and optimizing the actual processes.

In the actual production operation, DBD will undergo a series of complex physical and chemical changes. The simulation needs to simplify the model while remaining consistent with the actual situation to simplify the calculation process and ensure the accuracy of the simulation. In this simulation, this article uses the NRTL and ELECNRTL physical properties methods and the built-in physical property library of Aspen Plus.

In combination with the actual operating state, Aspen Plus simulations propose the following assumptions [14]:

- (1) The DBD production process is in a stable operating state in which none of the parameters change with time.
- (2) Because the heat transfer in the reactor is efficient, the temperature distribution in the reactor can be regarded as a uniform.
- (3) Based on the previous experimental results, excess water in the feed does not affect the synthesis process; in addition, when the gasification rate is greater than 0.4, the synthesis can be carried out smoothly. Thus, neither the water content in the feed nor the benzene extraction temperature is considered. The benzene gasification rate should be >0.4.

The model of the actual DBD production process [14] is shown in Figure 3. For reactions with known equations for which the effects of equilibrium and kinetics must be considered [13], the RCSTR module was selected first. C₇H₅NS and NaOH are mixed in MIX1 and then introduced into R1 and heated to reflux. C₆H₇NS is then cooled, and a small amount of CO₂ may be generated by SEP1 and SEP2 removal. The oxidant prepared by using H₂SO₄, H₂O₂, and H₂O is reacted with alkali-releasing outlet stream 5 to obtain DATA in R2, and outlet stream 7 and C₇H₈ are mixed and heated prior to separation in Decanter1. The aqueous phase is discharged through stream WATER1. The oil phase is discharged from stream 10, mixed with C₇H₅ClO and Na₂CO₃ through FSPLIT, and introduced two identical acylation tanks, R3-1 and R3-2, to afford DBD products containing impurities. DBD was purified by washing in Decanter2, crystallization in CRY, and centrifugation in CFUGE. Both the crystals from CRY and the centrifuged C₇H₈ from CFUE were refluxed with MIX6, and fresh C₇H₈ was added [21]. The temperatures of the alkaline hydrolysis reactor, the acylation reactor, and the extraction kettle are high, causing some of the materials to be vaporized. To keep the pressure in the kettle constant, the experimental system was equipped with a reflux condenser, but this was not considered in the model; instead, the reactor pressure was set to 1 atm. The temperature of the reactor is controlled by a protective jacket and a coolant configured by H₂O/C₂H₅OH. At the same time, in the actual production, the logistics of the pump used to transport the material must be considered. When the model is built, it is directly ignored, and the default steady flow is used instead; this results in a difference in energy loss between the actual process and the model, but the material loss is consistent. The neglected losses can be considered equal to actual process outputs.

Figure 3: The process flowchart for DBD production in Aspen Plus.

4 DBD synthesis process aspen plus simulation

General process studies involve reaction concentrations, reaction temperatures, reaction times, and the like. However, in terms of making the process greener, due to the particularities of the synthesis of the DBD reaction, the reaction time must remain within a narrow range, so the feed ratio and the reaction temperature must be directly used to control the product yield and the production of byproducts. Therefore, this process relies most heavily on the reactor module, and the remaining modules are considered as supplements. Each module is built in turn,

and each influencing factor is independently analyzed and optimized and applied to subsequent modules, thereby obtaining the optimal yield of the final product (Figure 4).

4.1 Alkaline hydrolysis

4.1.1 Effect of the NaOH/C₇H₅NS feed ratio on the yield of C₆H₇NS

Figure 5 shows that the C₆H₇NS yield increases linearly as the NaOH/C₇H₅NS feed ratio was increased from 2.4 to 2.7 at a constant initial temperature. At feed ratios of

Figure 4: The main reaction equation in the DBD production process.

2.7–2.9, the C_6H_7NS yield curve gradually levels off. This pattern is mainly due to the effects of stirring; the flow is initially fully incorporated in the reactor, and the reaction is promoted to the maximum extent, but the stirring capacity is limited and there is inhomogeneity in the reactor. As the reaction time increases, the parameters in the detention zone will begin to apply to the retention zone and eventually the homogeneous zone of the reaction, and the yield of C_6H_7NS will change only slightly. When the feed ratio is greater than 3.0, the yield of C_6H_7NS reaches a maximum of 98.7%. NaOH provides the alkaline environment for the C_7H_5NS ring opening, causing NaOH to indirectly affect the synthesis of C_6H_7NS , while the production of C_7H_5NS directly affects the synthesis of C_6H_7NS . As the specific gravity of the NaOH feed increases, almost all of the C_7H_5NS participates in the reaction. Excess NaOH has no effect on the yield of C_6H_7NS , but it does affect the oxidation reaction, resulting in wastage of raw materials. Therefore, the feed ratio of NaOH/ C_7H_5NS was set at 2.9 to allow the collection of C_6H_7NS . This ratio offers almost the same reaction rate while avoiding the wastage of raw materials.

Figure 5: Relationship between NaOH/ C_7H_5NS feed ratio and C_6H_7NS yield.

4.1.2 Effect of the temperature of the alkaline reactor on the yield of C_6H_7NS

The relationship between the temperature of the alkali decanter and the yield of C_6H_7NS is obtained. The effect of the temperature of the alkali dehydration on the yield of C_6H_7NS is significant. When the temperature in the kettle was $<120^\circ\text{C}$, the yield of C_6H_7NS gradually changed with the increasing temperature. At $120\text{--}130^\circ\text{C}$, the reaction yield reached its maximum, and temperature is no longer

the dominant factor influencing the reaction outcome. As the temperature was further increased, the yield of C_6H_7NS remained constant at the maximum. In this study, the optimal reactor temperature was 120°C , and the optimized conditions for the alkali hydrolysis reaction resulted in a C_6H_7NS yield of 99.5% (Figure 6).

Figure 6: Relationship between the temperature of the alkali hydrolysis reactor and the yield of C_6H_7NS .

4.2 Oxidation reaction

4.2.1 Effect of the oxidant feed ratio on data yield and pH in the kettle

As shown in Figure 7, C_6H_7NS has a significant effect on H_2O_2 under acidic conditions, and the $-S-H$ bond breaks to form an $S-S-$ bond. H_2O_2 participates in the oxidation reaction, and H_2SO_4 does not participate in the reaction

Figure 7: Relationship between the feed ratio of H_2SO_4/H_2O_2 and the DATA yield and pH in the kettle.

but controls the pH in the reactor. When the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ feed ratio was <1.25 , the DATA yield increased slowly, and the reaction environment became alkaline. When the feed ratio was between 1.25 and 1.4, the pH in the kettle changed rapidly from alkaline to an acidic. The yield of DATA increased linearly, and the slope of the production curve increased as the reaction rate increased. When the feed ratio was further increased, the yield of DATA reached its maximum and stabilized. The $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ feed ratio of 1.4 was selected.

4.2.2 Effect of the oxidation reactor temperature on the DATA yield

As shown in Figure 8, the temperature has a large influence on the DATA yield. Temperature $\leq 35^\circ\text{C}$ favored the formation of DATA and provided the maximum yield; as the temperature increases, the yield of DATA began to decrease. When the temperature was $>45^\circ\text{C}$, the yield of DATA decreased rapidly and reached less than 10% at 60°C . The simulation results suggest that H_2SO_4 is generated by the oxidant, and the water encounters a large amount of heat from the exothermic reaction in the autoclave, and the oxidation reaction proceeds more smoothly at low temperatures. Therefore, the temperature inside the reactor should be strictly controlled, and the reactor should be precooled. In this article, the temperature of the autoclave was 25°C , and the optimized conditions of the oxidation reaction afforded a DATA yield of 98.2%.

Figure 8: Relationship between the oxidation reactor temperature and the DATA yield.

4.3 Acylation reaction

4.3.1 Effect of $\text{C}_7\text{H}_5\text{ClO}/\text{Na}_2\text{CO}_3$ feed ratio on the DBD yield

As shown in Figure 9, because $\text{C}_7\text{H}_5\text{ClO}$ directly participates in the acylation reaction, the specific gravity of the feed directly affects the DBD yield. When the feed ratio of $\text{C}_7\text{H}_5\text{ClO}/\text{Na}_2\text{CO}_3$ was <1.9 , the yield of DBD increases linearly; when the feed ratio was 1.9–2.1, the yield of DBD gradually increased to its maximum value; when the feed ratio was further increased, the DBD yield remained almost constant. This trend was caused by the fact that NaOH is formed as a byproduct in the acylation reaction, the specific gravity of the feed of $\text{C}_7\text{H}_5\text{ClO}$ is increased, and the amount of HCl is also increased, and the amount of Na_2CO_3 is insufficient to neutralize the generated HCl, which restricts the DBD yield. Therefore, the $\text{C}_7\text{H}_5\text{ClO}/\text{Na}_2\text{CO}_3$ feed ratio of 2.1 was chosen.

Figure 9: Relationship between the feed ratio of $\text{C}_7\text{H}_5\text{ClO}/\text{Na}_2\text{CO}_3$ and the DBD yield.

4.3.2 Effect of acylation reactor temperature on product DBD yield

As shown in Figure 10, when the temperature was lower than 100°C , the yield of DBD increased linearly; from 110°C to 112°C , the slope decreases and the yield reaches its maximum. However, when the temperature is further increased, the yield of DBD begins to decrease. On the one hand, the temperature may be above the optimum reaction temperature, which shifts the reaction equilibrium to the left, and the DBD is gradually consumed. On the other hand, it may be that the temperature being

too high favors the side reaction, and the increase in the formation of byproducts affects the DBD yield. In this article, the temperature of the acylation reactor was 110°C, and the optimized acylation reaction conditions afforded a DBD yield of 96.4%.

Figure 10: Relationship between the acylation reactor temperature and the DBD yield.

4.4 Crystallization

Figure 11 shows that when the temperature of the crystallization kettle is low, a large amount of C_7H_8 is present in the DBD, and the crystallization effect is poor. When the temperature is $>120^\circ\text{C}$, the purity of the DBD in stream 18 can reach 95%, and the content of C_7H_8 is less than 0.5%, and the crystallization effect is better. For the optimization of C_7H_8 feed flow in the crystallization stage, we first explored to determine the optimal feed equivalent of C_7H_8 without

Figure 11: Relationship between the crystallizer temperature and the purity of the DBD and the C_7H_8 in stream 18.

introducing a recycle stream and then used the optimization module in Aspen Plus to optimize the toluene loss as the optimization goal. The introduced recycling logistics is selected as the tear logistics, and the recycling logistics is optimized to ensure the maximum recovery rate of C_7H_8 and ensure low-emission green production.

The stream exiting the crystallization vessel contains a small portion of C_7H_8 . Therefore, it is necessary to centrifuge this stream to remove the C_7H_8 impurities in the DBD, and the separated C_7H_8 can be recycled. Under normal centrifuge operation conditions, the conversion rate of the final product (DBD) is 92.5%, which meets the quality requirements for the final product.

5 Clean synthetic process

On the basis of the previous generation of production process experience, we have developed 10,000 ton 2,2'-dibenzoyl-amino diphenyl disulfide based on the laboratory synthesis stage of DBD, the pilot test stage, and the Aspen Plus process simulation stage. The industrial production process and the device are as shown in Figure 12. The process consists mainly of a purification system for the reaction system, the intermediate products and the final products, as well as a toluene circulation system, a heat exchanger, and other auxiliary systems. C_7H_5NS is mixed with NaOH and heated to reflux to form C_6H_7NS as an intermediate. At the end of the reaction, a preformulated oxidant is added at low temperature to control the formation of DATA. Then, this solution is mixed with toluene and heated to reflux. The aqueous phase is separated in the extraction vessel, and the residual oil phase is mixed with C_7H_5ClO and Na_2CO_3 and heated to reflux in the acylation reactor [7] to obtain DBD containing impurities; the DBD is purified by washing and crystallization. The final product (DBD) is obtained by centrifugation. Toluene separated during the crystallization and centrifugation steps can be recycled and is fed together with fresh toluene into the extraction vessel.

The simulation results in this article provide initial values for the actual operating parameters for the production of DBD as a rubber additive by Shandong Yanggu Huatai Co. Ltd, which reduces the debugging interval. Compared with the synthesis of *o*-nitrochlorobenzene (72%), the yield of 2,2'-dibenzoylaminodiphenyl disulfide is increased to over 90%. The use of this method instead of the original synthesis method avoids the use of *o*-nitrochlorobenzene, which is neurotoxic, and catalytic Raney nickel, which is difficult to recycle with existing environmental protection technologies, and the

Figure 12: Diagram of the industrial process for producing DBD.

Table 4: The simulation results are compared with the enterprise parameters

Operating conditions and results	Materials and equipment	Simulation parameters	Actual parameter	Deviation from actual
Feed rate (kg/h)	Benzothiazole	≥ 800	875	-75
	32% sodium hydroxide	2,250–2,400	2,285	-35
	30% hydrogen peroxide	≥ 350	401	-51
	98% sulfuric acid	≥ 650	641	+9
	One water intake	1,500	2,000	-500
	Methylbenzene	2579.1	1,885	+694.1
	Sodium carbonate	≥ 800	1,000	-200
	Benzoyl chloride	≥ 400	412	-12
	Secondary water intake	$\geq 2,500$	1,500	+1,000
Operating parameters (°C)	Alkaline hydrolysis kettle	≥ 120	125	-5
	The oxidizing kettle	≤ 35	< 40	-5
	The acylation kettle	110–115	110	0
	Crystallization axe	110	110	0
Product production (kg/h)	Stream 21	1289.7	1,200	+89.7
Product yield		92.5%	90%	+2.5%

environmental problems associated with the volatile amine tail gas easily generated in the original synthesis method. The drying step is eliminated, and the use of ethanol as an organic solvent is avoided, making the overall reaction greener.

6 Conclusion

The model of the actual production process of DBD established using Aspen Plus is consistent with the

actual operation data of the project. The model can reasonably predict different working conditions for the DBD production process.

While controlling other variables, the feed amount and the temperature of each process module were analyzed and optimized, and the feeds can be further optimized. The feed ratio between the best streams is 2.9 for NaOH/C₇H₅NS, 1.4 for H₂SO₄/H₂O₂, and 2.1 for C₇H₅ClO/Na₂CO₃. The temperature optimization results show that the temperatures of the alkali hydrolysis reactor, oxidation reactor, and acylation reactor should

be controlled at $\geq 120^{\circ}\text{C}$, $\leq 35^{\circ}\text{C}$, and $110\text{--}115^{\circ}\text{C}$, respectively, and the temperature of the crystallization kettle should be controlled at $>110^{\circ}\text{C}$.

The practical 10,000 ton DBD production process showed that the reaction yield can reach over 90% while still avoiding the use of neurotoxic *o*-nitrochlorobenzene and the use of catalytic Raney nickel, which is difficult to recycle using existing environmental protection technologies. The original synthetic method is prone to crucial environmental problems related to the amine tail gas. The drying step is eliminated, and the use of ethanol as an organic solvent is avoided, making this a greener reaction method. The comparison between the simulation results and the actual feed quantity, operation parameters, DBD output, and yield is presented in Table 4.

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