

## Research Article

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# Synthesis of insoluble sulfur and development of green technology based on Aspen Plus simulation

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**Abstract:** The continuous process for the production of insoluble sulfur (IS) has been developed to overcome the disadvantages associated with the traditional batch process, such as low automation, discontinuous production, and high consumption of sulfur and  $\text{CS}_2$ . The consumption of  $\text{CS}_2$  in the continuous process is lower than that in the batch process. The recovery of solvent facilitates the recycling of  $\text{CS}_2$  and  $\text{N}_2$  in addition to the closed circulation of the entire system. The key process and recovery parameters of the IS synthesis were simulated using Aspen Plus. Sulfur was completely recovered after high-temperature pyrolysis, and the utilization ratio of sulfur atoms was increased from approximately 50% to more than 95%. Tail gas was comprehensively utilized through compression and cryogenic green treatment. Based on the developed green synthesis process and simulated process parameters, the continuous production of IS was evaluated on an industrial scale of 10,000 metric tonnes. Owing to the continuous characteristics of the production process, the air tightness of the production process was significantly improved, and the quality of the product was more stable than that of the product obtained by the current domestic batch process. The unconverted sulfur could be recycled after recovery, without low-grade sulfur as a by-product. The amount of sulfur used as raw material per unit product was reduced; the comprehensive conversion rate of sulfur to IS exceeded 95%, which significantly improved the utilization rate of sulfur atoms. Through the compression and condensation of the tail gas,

the recovery efficiency of  $\text{CS}_2$  was considerably improved at the same temperature, and compressed  $\text{N}_2$  could be simultaneously obtained. The liquefaction rate of  $\text{CS}_2$  approached 91.78%, which was characterized by obvious greening.

**Keywords:** insoluble sulfur, Aspen Plus simulation, green recycling process, process research

## 1 Introduction

Insoluble sulfur (IS), a high-performance rubber auxiliary material that can replace the use of ordinary sulfur, is a large molecule of sulfur polymerization, named after insoluble in  $\text{CS}_2$ . It is slow to migrate in rubber and can effectively prevent rubber frosting and improve the heat and wear resistance of tires in tire production. Therefore, IS is an essential and important raw material in tire production [1–3].

Currently, there are three methods to produce IS: one-step melting method, high-temperature water method, and continuous method. The first two methods are batch reaction processes (collectively referred to as batch processes). High contents of IS can be obtained after separation, washing, and drying. In the one-step melting method, ordinary sulfur is melted at 130–150°C. Subsequently, the temperature of the mixture is increased to 300–400°C for a certain period; ordinary sulfur is converted into IS, but the conversion efficiency is low [4,5]. IS is extracted after rapid cooling of the solvent, and the product is obtained after drying, crushing, oil filling, and screening. However, the IS produced by the molten one-step process is poorly dispersed and subsequently needs to be crushed. Moreover, the index of the product visibly fluctuates. In the high-temperature water method, the high-temperature sulfur vapour is introduced into an acidic water medium, and the sulfur is cooled to produce IS. The reactant is a mixture of soluble and IS. The mixture is washed, dried, crushed, and extracted to obtain IS. This method involves low production costs [4,6]. However, owing to the use of water for cooling and

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washing, a large quantity of wastewater is generated. Consequently, the market competitiveness is weak.

In the continuous method, common sulfur is melted and rapidly heated to produce superheated steam. Using its pressure, it is injected into the quench liquid at high speed and rapidly cooled. A plastic mixture of insoluble and soluble sulfur is obtained. Subsequently,  $\text{CS}_2$  is used to extract the soluble sulfur in the mixture [7–9]. The products of the continuous process exhibit stable quality and excellent properties. Additionally, the process involves low consumption of raw and auxiliary materials, high degree of automation, and unattended operation on-site.

In this study, the green synthesis process of IS by the continuous method was evaluated to efficiently improve the yield of synthesis, reduce the loss of extractant, and recycle sulfur completely. Aspen Plus software was used to simulate the key processes of the synthesis with the experimental conditions as the boundary, to obtain the optimized process parameters [10,11]. The results of the simulation are used to adjust the operating parameters of the actual production so as to maximize the benefits while meeting the operational targets.

## 2 Studies on the green synthesis process of IS

Two types of processes are mainly used to produce IS: batch process and continuous process. Currently, batch processes, such as high-temperature water and melting methods, are used for the production of IS in China. However, some drawbacks in the high-temperature water method alter the quality of thermal stability of IS. In contrast to the continuous production process, the melting method involves a lower capacity of equipment, higher consumption of  $\text{CS}_2$ , and underlying risks in production. The IS produced in the continuous process can be recycled continuously. The simultaneous recycling of  $\text{CS}_2$  lowers its consumption below the average level, reduces the cost of the enterprise, and demonstrates a higher degree of automation [11,12]. The product index is stable, and its application performance in rubber is better than that of IS produced by the batch process.

### 2.1 Mechanism of IS generation

When sulfur is cracked by heating, its molecular structure changes very complicated: when the temperature IS lower than  $159^\circ\text{C}$ , ordinary sulfur becomes light yellow

liquid sulfur with a ring structure consisting of eight sulfur atoms after melting by heating. When the temperature exceeds a certain temperature, ordinary sulfur S8 undergoes ring-opening cracking to form an unsaturated sulfur atom chain free radical monomer with electrons at both ends. This free radical monomer forms linear macromolecular chain sulfur through polymerization, which is the main body of IS. The polymerization reaction is reversible, and the degree of polymerization of the polymerization products varies [13]. First, the average molecular weight range of IS was investigated by ideal model iodometric titration, and the experimental results showed that its molecular weight was about 2,800–3,100. Then, the density simulation method based on molecular dynamics combined with experimental methods was used to study the number of sulfur atoms in the polymerized sulfur chain ( $S_n$ ) of IS, and the results showed that  $n = 96$  was appropriate. The following simulation study was based on S96 [14].

Gauss View is used to obtain chemical kinetic information and thermodynamic information. According to the Schrodinger equation and Hartree–Fock equation, combined with density functional theory, the equation is as follows.

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

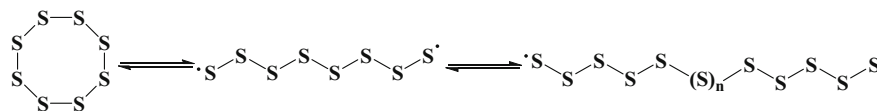
Finally, combining its reaction machine with the existing physical and chemical data (Table 1), Aspen Plus was used to model the IS synthesis process, and sensitivity analysis was used to study the relationship between temperature and IS yield (Scheme 1).

### 2.2 Studies on the recycling process of by-product sulfur

The raw materials of IS are generally common sulfur from mining or recovered products from petroleum and gas

**Table 1:** Reaction thermodynamics and kinetic parameters

|                         | Reaction heat<br>( $\text{kJ}\cdot\text{mol}^{-1}$ ) | Rate constant<br>( $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ ) |
|-------------------------|------------------------------------------------------|--------------------------------------------------------------------------|
| Polymerization reaction | –80.1                                                | $7.58 \times 10^{-8}$                                                    |



**Scheme 1:** Synthetic route to IS.

desulfurization devices. However, the production of IS requires common sulfur of high purity to ensure that the quality of IS is unaffected. The purity requirements are generally greater than 99.95%. The conversion rate cannot always be increased because the polymerization is a reversible equilibrium reaction. Therefore, the IS products obtained by polymerization contain a large quantity of ordinary sulfur in addition to organic compounds mixed in the production process [15]. Therefore, the by-product sulfur cannot be used in the production of IS; the treated by-product generates a low price and subsequently leads to an increase in production costs. At present, the maximum conversion rate that can be achieved by the melt method in the laboratory stage is around 50–60%. The point of the continuous method compared to the melt method mainly lies in the finer particle size and better stability of the product obtained, and since the reaction is reversible, changing the method has little effect on the maximum conversion rate of the substance. In this process, the unreacted common sulfur in the sulfur polymerization reaction is recovered and re-introduced into the system after treatment to participate in the polymerization reaction.

As the cycle process continues, organic matter accumulates in the sulfur and therefore needs to be removed. The enrichment of alkanes in the by-product sulfur mainly consists of chain breaking and dehydrogenation reactions. The C–C bonds in alkanes are broken by temperature, and the main components of enriched organic matter contain alkanes, cyclic alkanes, aromatic hydrocarbons, and other hydrocarbons. After a complex chemical reaction of high-temperature cracking, the final products of organic matter in sulfur are  $\text{H}_2\text{S}$  and coke particles.

### 2.3 Development of tail gas recycling process

The entire production process of IS is performed under  $\text{N}_2$  to avoid the influence of  $\text{O}_2$  on the product. However, the continuous addition of  $\text{N}_2$  to the system increases the system pressure. Therefore, the excess gas is discharged from the system. The production tail gas is a mixture of  $\text{CS}_2$  and atmospheric  $\text{N}_2$ , which is the main component.

In the tail gas treatment method,  $\text{N}_2$  is condensed and directly discharged into the atmosphere. Therefore,  $\text{N}_2$  is not recycled; this results in its underutilization and subsequently raises production costs. The separation and recovery of  $\text{CS}_2$  and  $\text{N}_2$  from the mixture are essential for environmental protection [16,17], and reduced material consumption and production costs. Additionally, this step is a technical challenge for IS production plants. In the conventional recovery of  $\text{CS}_2$ , frozen water is recycled in the condenser, and  $\text{CS}_2$  is condensed into a liquid. However, the recovery rate of  $\text{CS}_2$  in tail gas by the frozen water method is inadequate owing to the high vapour pressure and volatile characteristics of  $\text{CS}_2$ , and excess  $\text{N}_2$  in the tail gas. Thus, the consumption of  $\text{CS}_2$  is generally high. Tail gas compression and cryogenic design are implemented to reduce the consumption of solvent in the production of IS and facilitate green production. The compressed tail gas replaces pure  $\text{N}_2$  using pressure to supplement the production gas; this can reduce the overall use of  $\text{N}_2$  and the loss of  $\text{CS}_2$  [18].

## 3 Simulation and research of green recovery process of IS

The scale-up process from the laboratory stage to actual industrial production generally follows a comprehensive experimental cycle. For reaction systems, the interaction of various process parameters affects the scale-up to actual industrial production capacities. Since the 1990s, the chemical process simulation system has entered a period of extensive development, where the value of chemical process simulation technology has been recognized and widely used. It is a powerful auxiliary tool for design, research, and production. Chemical process simulations “reproduce” the actual production process on a computer. Therefore, they do not involve any changes in pipelines, equipment, and energy. The designer is provided a considerable degree of freedom to analyse different schemes and process conditions on the computer. Therefore, process simulation considerably saves time and operating costs; it is useful in analysing the planning, research, and development of chemical processes and their technical reliability. Aspen Plus is representative simulation software, which is widely used in

chemical, oil refining, oil and gas processing, petrochemical, and other industries [19–22]. In this study, we simulate the green industrialization of IS based on Aspen Plus in order to obtain more suitable and green process parameters.

### 3.1 Aspen Plus model construction

With relevant experimental data obtained through a literature review as the boundary conditions. The sensitivity analysis module in Aspen Plus is used to select reliable physical properties, methods, and models. Users can use this tool to change one or more process variables and study the impact of their changes on other processes. Additionally, the module is used to analyse and verify whether the solution of the design specification is within the range of manipulated variables [23] to conduct a simulation study of the process. In this simulation, the physical property methods of PR-BM and RK-SOVE and the built-in physical property library of Aspen Plus are used in this article. In conjunction with the operational state, the Aspen Plus simulation makes the following assumptions.

The model shown in Figure 1 is established for the actual production process of IS. The whole system is closed with micro-positive pressure, in order to avoid leakage of materials or  $\text{CS}_2$  into the atmosphere. The RSTOIC module is used first for known chemical reactions.

Ordinary sulfur  $\text{S}_8$  reacts with a small number of alkane impurities contained therein at high temperatures to generate small quantities of  $\text{H}_2\text{S}$  and coke, which are subsequently separated by FLASH1 and FLASH2. The obtained pure sulfur undergoes a high-temperature cracking polymerization reaction in reactor R2 and is quenched to generate IS. Typically, the conversion rate of IS is 50–60%. In the extraction kettle,  $\text{CS}_2$  is used as the extractant at normal temperature, and a second extraction method is applied [24,25]. Moreover, some materials are transported by a pump during the actual production process. These materials are not considered during modelling and the steady-state flow is adopted by default. Therefore, there is a gap between the energy loss in the simulation and the actual process. However, the loss of materials is ignored and considered equal to the output of the actual process.

## 4 IS synthesis process Aspen Plus simulation

The investigation of a process generally involves time, concentration, temperature, pressure, and other process conditions. This process is mainly concerned with the effect of temperature on the production process, the effect of  $\text{CS}_2$  dose on the extraction effect of the product, and the temperature and pressure on the liquefaction rate of  $\text{CS}_2$ .

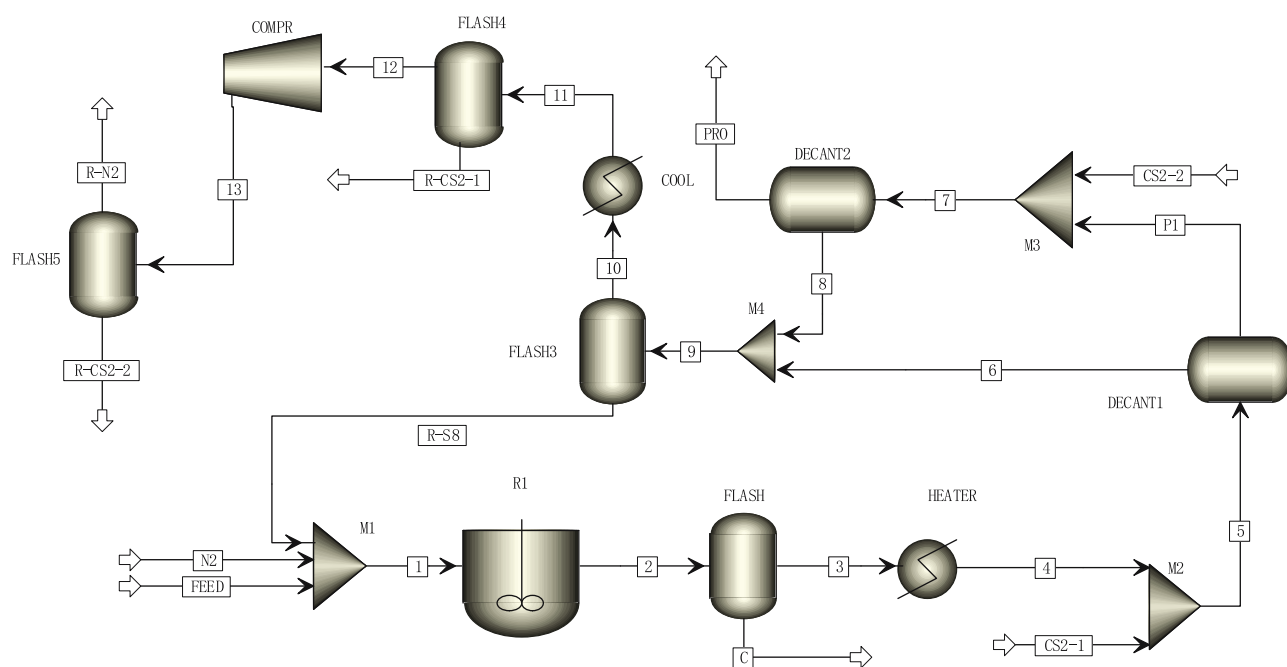
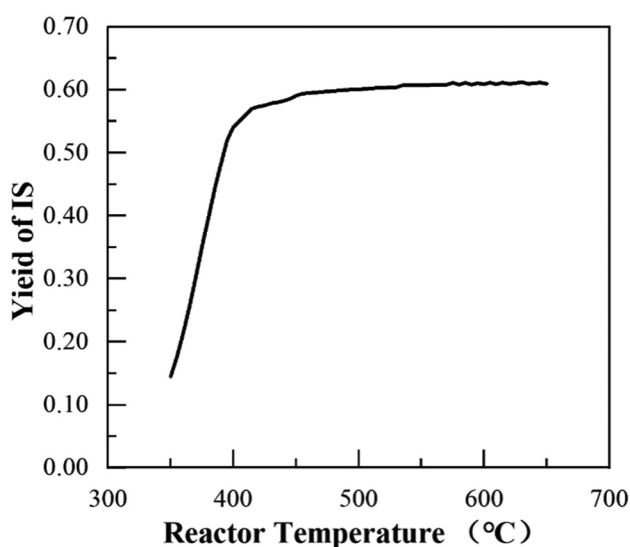


Figure 1: Process flowchart for IS production in Aspen Plus.

when the mixture of  $\text{CS}_2$  and  $\text{N}_2$  is separated. Therefore, in this process, the main module consists of the reactor and separator, supplemented by other modules; each module is built sequentially. Independent analysis and optimization are applied to the follow-up module. Subsequently, the most efficient process conditions are determined.

## 4.1 Production process of IS

In the production process of IS, common sulfur and by-product sulfur are mixed and fed into reactor R1, which reacts to produce IS after high-temperature action. During the reaction process, the temperature has a large influence on the product. Figure 2 shows the relationship between the polymerization temperature and the yield of IS. The polymerization temperature has a significant effect on the yield of IS. When the reaction temperature is lower than  $400^\circ\text{C}$ , the yield curve of IS increases rapidly and gradually decreases. When the temperature is in the range of  $420$ – $450^\circ\text{C}$ , the reaction reaches an approximate maximum, and the reaction temperature is no longer the dominant factor in the reaction. As the temperature continues to increase, the yield of IS increases slowly and is stabilized near the maximum, probably because the temperature was too high, and some IS was cracked. In this study, the reaction temperature is  $450^\circ\text{C}$ ; the overall reaction of IS yield is approximately 59.1%.



**Figure 2:** Relationship between the polymerization temperature and the IS yield.

## 4.2 Extraction process

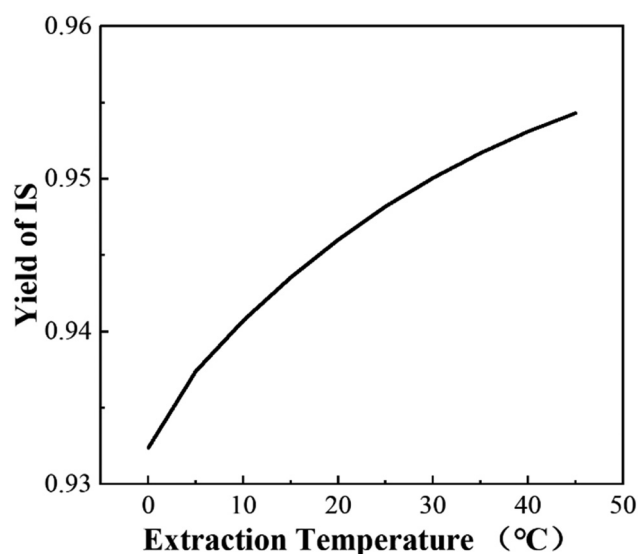
The obtained reaction products were mixed with  $\text{CS}_2$ , and since IS is insoluble in  $\text{CS}_2$ , high-quality IS can be obtained by dissolving the by-product sulfur, but the efficiency of extraction is influenced by temperature and dose.

### 4.2.1 Effect of extraction temperature on the IS yield

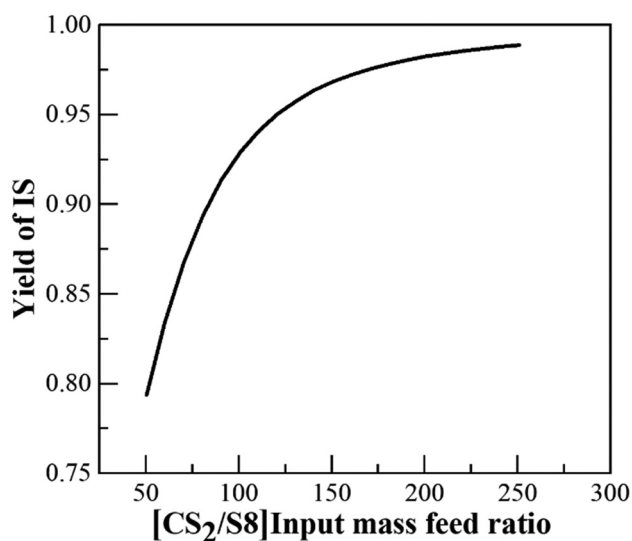
Controlling the temperature significantly influences the yield of IS. The lower limit of the extraction temperature is set to  $0^\circ\text{C}$ ; extremely low temperatures are not conducive to extraction efficiency and result in higher costs. The upper limit is set to  $45^\circ\text{C}$ ;  $\text{CS}_2$  will vaporize at temperatures above  $46.5^\circ\text{C}$ . The effect of extraction temperature on the content of IS was studied by varying the temperature. Figure 3 shows that the efficiency of  $\text{CS}_2$  in the product increases with the increase in temperature. The extraction efficiency is 94.60% at  $25^\circ\text{C}$  and 95.01% at  $30^\circ\text{C}$ . In this study, the extraction temperature is  $30^\circ\text{C}$ , and the final mass fraction of IS is 95.01%.

### 4.2.2 Effect of extractant dosage on extraction efficiency

Two-stage extraction was used to improve the extraction efficiency. Figure 4 shows that the mass fraction of IS increases with the increasing amount of extractant at the set temperature. The yield of IS was low, not reaching 90% when the feed ratio of  $\text{CS}_2/\text{S8}$  is less than 100. The



**Figure 3:** Relationship between the extraction temperature and the IS yield.



**Figure 4:** Relationship between the extraction dosage and the IS yield.

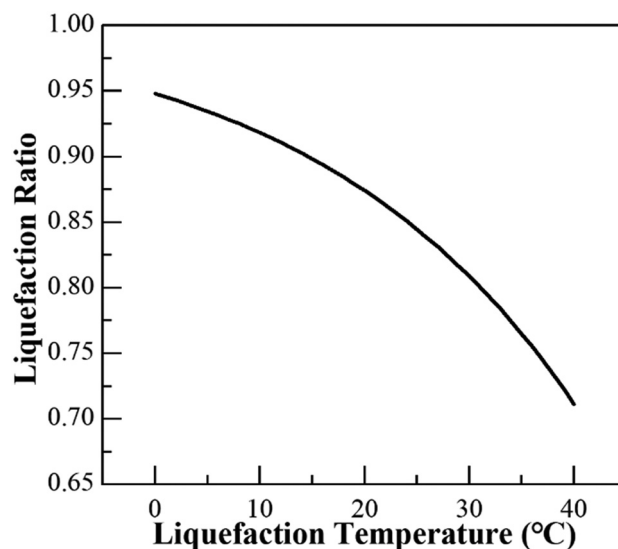
extraction rate increases slowly when the feed ratio of CS<sub>2</sub>/S8 is greater than 175. Increasing the amount of CS<sub>2</sub> would result in high production costs. The feed ratio of CS<sub>2</sub>/S8 was set at 150 to allow the collection of IS. This ratio offers a product of 95.01%, while avoiding the waste of raw materials.

### 4.3 Tail gas recovery process

CS<sub>2</sub> and N<sub>2</sub> in the tail gas are compressed, but CS<sub>2</sub>, as a condensable gas, can be liquefied at the right temperature and pressure and will exist in a different phase from N<sub>2</sub>, so that the two can be separated. Therefore, the effect of temperature and pressure on the liquefaction rate of CS<sub>2</sub> is investigated separately.

#### 4.3.1 Effect of temperature on liquefaction rate of CS<sub>2</sub>

As shown in Figure 5, under the initial set pressure, the temperature control significantly influences the liquefaction rate of CS<sub>2</sub>. When the temperature is lower than 10°C, the liquefaction rate of CS<sub>2</sub> is higher. With the increase in temperature, the liquefaction rate of CS<sub>2</sub> begins to decrease significantly. Particularly, the increase in temperature greatly increases the molecular activity of CS<sub>2</sub>, which reduces its tendency to liquefy. Therefore, lower temperatures result in higher liquefaction yields. However, considering the actual industrial production, the temperature is controlled at 10–15°C to avoid significant

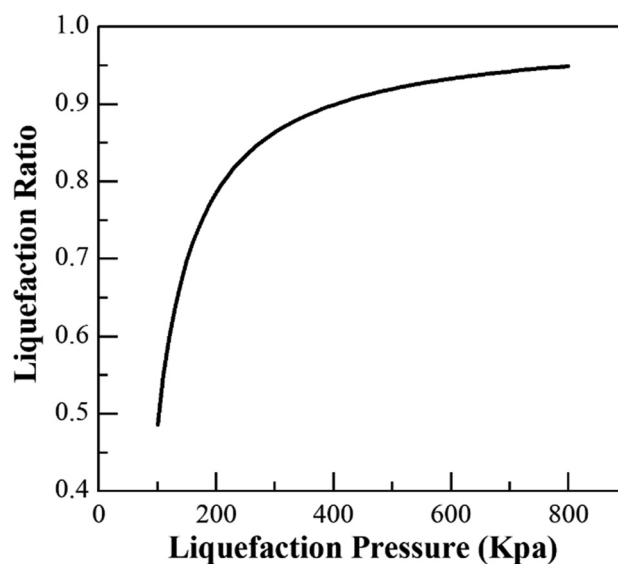


**Figure 5:** Relationship between the temperature and the liquefaction rate of CS<sub>2</sub>.

waste of energy in the recovery process. The liquefaction rate of CS<sub>2</sub> approaches values above 90%. In this study, 12°C is considered the separation temperature of CS<sub>2</sub>, which optimizes the liquefaction rate of CS<sub>2</sub> in the entire separation process.

#### 4.3.2 Effect of pressure on liquefaction rate of CS<sub>2</sub>

Figure 6 shows that the pressure considerably influences the liquefaction rate of CS<sub>2</sub>. At the set temperature, the



**Figure 6:** Relationship between the pressure and the liquefaction rate of CS<sub>2</sub>.

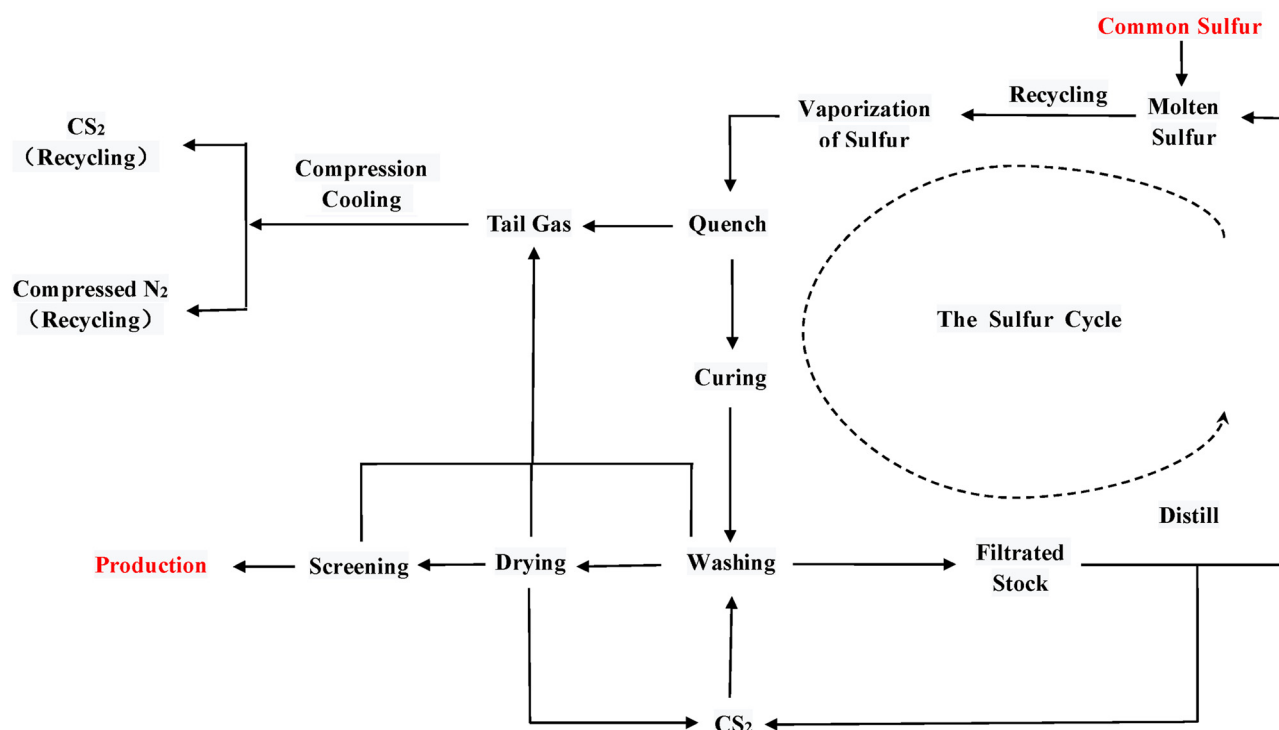


Figure 7: Diagram of IS production system process.

liquefaction rate of CS<sub>2</sub> increases with the increase in pressure. For pressures lower than 400 kPa, the liquefaction rate of CS<sub>2</sub> increases rapidly with the increase in pressure; the rate decreases gradually when the pressure is higher than 600 kPa. In this study, the pressure of the entire cryogenic recovery unit is set to 450 kPa, and the liquefaction rate of CS<sub>2</sub> in tail gas is approximately 91.78% using compression and cryogenic separation at 12°C.

## 5 Green process cycle

Based on the Aspen Plus simulation of the IS production process, a continuous and green production process is developed. The by-product sulfur is completely recycled, as shown in Figure 7. The process mainly consists of reaction, extraction, compression, condensation, and other auxiliary systems. Liquid sulfur after high-temperature cracking and polymerization reaction forms IS. The extraction step uses CS<sub>2</sub>; relatively pure CS<sub>2</sub> is obtained after separation. Subsequently, the product is obtained after washing and drying. The extracted common sulfur is recycled into the reaction system for participation in the next reaction cycle. After separation, most of the CS<sub>2</sub> is in a liquefied form. The tail gas undergoes cryogenic compression,

and liquefied CS<sub>2</sub> is directed into the tank. Following the extraction step, supplementary N<sub>2</sub> gas participates in the process cycle. The results of the simulation reduce the debugging interval and provide reference values for the actual operation parameters of IS production in Shandong Yanggu Huatai Chemical Co., Ltd., China.

## 6 Conclusions

The actual process model of continuous production of IS is established using Aspen Plus. The simulation and optimization results provide a suitable reference for the actual operation. The model can reasonably predict the different working conditions of the IS production process.

The process of producing IS was studied by simulation with Aspen Plus software, from which the utilization rate of sulfur atoms was greatly improved from about 50% in the current intermittent method to more than 95%. Through the process of CS<sub>2</sub> extraction of common sulfur, the extractant feed volume-to-mass ratio, temperature, and pressure analysis was optimized between the process modules by the control variable method, from the optimization results; it can be learned that the product with a mass of more than 95% can be obtained at

a feed ratio of 150 for CS<sub>2</sub>/S8 and an extraction temperature of 30°C. By compressing and condensing the tail gas, the pressure of the deep cooling and compression device is controlled at 450–500 kPa, and the temperature is controlled at 8–10°C. The recovery efficiency of CS<sub>2</sub> is greatly improved so that the liquefaction rate of CS<sub>2</sub> reaches 91.78%, and the consumption of unit IS is greatly reduced through recycling. Moreover, while recovering CS<sub>2</sub>, compressed nitrogen can be obtained at the same time, which realizes the green recycling of tail gas.

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**Author contributions:** Liang-liang Zhou: investigation, methodology, and writing – original draft; Xiao-lai Zhang: conceptualization, investigation, and supervision; Wen-bo Wang: data curation; Meng-cheng Du: formal analysis; De-long Ma: project administration.

**Conflict of interest:** The authors state no conflict of interest.

**Data availability statement:** Available data are presented in the manuscript.

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