

Advanced purification and comprehensive utilization of yellow phosphorous off gas

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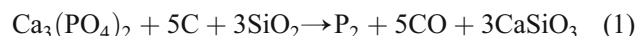
Abstract Yellow phosphorous is an important raw material in the chemical industry. However, during the production of yellow phosphorous, high concentrations of carbon monoxide and other impurities are released. Without appropriate purification and removal, this off gas has potential to cause severe pollution problems once released. Purified yellow phosphorous off gas can be beneficially reused as a raw material in chemical production for synthesis of high value-added chemical reagents. In this paper, the significance of purification and reutilization of yellow phosphorous off gas are explored. The principles, processes, and main characteristics of the technologies for purification and reuse of yellow phosphorous off gas (including technical measurements of impurity reduction, relevant engineering cases, and public acceptance of the technologies) are summarized. In view of the existing problems and scientific development requirements, this paper proposes several recommendations for green production based on the concept of recycle economics. We conclude that advanced purification and comprehensive reutilization can be an effective solution for heavy pollution resulting from yellow phosphorous off gassing.

Keywords yellow phosphorous off gas, purification, comprehensive utilization

1 Introduction

Yellow phosphorus is one of the most important industrial raw materials that are widely applied for preparation of fertilizers, chemicals, detergents, food additives, and fire retardants, etc. In general, yellow phosphorus is produced via electro furnace or blast furnace. Theoretically, about 3000 m³ yellow phosphorous off gas is yielded for one ton

of phosphor production [1–6]. Yellow phosphorous off gas's calorific value can be as high as 1.0×10^7 – 1.1×10^7 J·m⁻³. As shown in Eq. (1), the raw materials for manufacturing per ton yellow phosphorous consist of 8–10 tons of phosphate, 1–1.5 tons of silica, 1.5 tons of coke.



The components of yellow phosphorous off gas are shown in Table 1 [7]. The majority of yellow phosphorous off gas is carbon monoxide, other impurities include S, H₂S, SO₂, COS, CH₄SH, SiF₄, PH₃, P₄, HF, CH₄, CO₂, O₂, N₂, cyanide, and dust [8].

The carbon monoxide content can be as high as 95% after water vapor is removed from yellow phosphorous off gas. In an electro furnace, yellow phosphorus is produced under reduction condition under high temperature. Therefore, the impurities in yellow phosphorous off gas are rather in reduced state than in oxidation state. For instance, phosphate impurities are P₄ and PH₃, sulfur impurities are hydrogen sulfide and organic sulfur, and fluorine impurities are HF and SiF₄ [9]. The sulfur content of phosphate and coke has significant effect on the sulfur content in yellow phosphorous off gas. During the yellow phosphorus production process, condensation treatment was conducted, and the contents of phosphate impurities are largely affected by the temperatures of yellow phosphorus off gas from the condensing tower (Table 2) [10]. When the temperature of the yellow phosphorous off gas that flows out from the condensing tower is under 35°C, the phosphate content in yellow phosphorous off gas can be controlled to less than 1 g·m⁻³, and the condensation efficiency of phosphate can be as high as 99%.

The emission of yellow phosphorous off gas is of great concern due to its impurities and main component, carbon monoxide. Carbon monoxide is an indirect greenhouse gas. The increasing of carbon monoxide concentrate could result in the increase of equilibrium concentration of ozone. In addition, the toxicity of carbon monoxide can do great harm to human health. Therefore, yellow phosphor-

Table 1 Compositions of yellow phosphorous off gas [7]

chemical component	proportion/(vol%)
CO	85–95
CO ₂	1–4
H ₂ O	~ 5
H ₂	1–8
CH ₄	~ 0.3
N ₂	2–5
O ₂	5000
H ₂ S	800–3000
PH ₃	500–1300
SO ₂	~100
COS	~500
CS ₂	~200

Table 2 Changes of phosphate content with different operation temperatures [10]

temperature/°C	phosphate content/(g·m ⁻³)
20	0.170
25	0.287
30	0.472
35	0.572
40	0.775
44.1	1.084

ous off gas must be utilized and recycled for the protection of the environment and human health. So far, besides being used as fuel gas, carbon monoxide is an indispensable chemical material for synthesizing chemical products, such as methanol, formic acid, oxalic acid, dimethylacetamide, and dimethyl carbonate. Obviously, purification and reutilization of yellow phosphorous off gas is important for mono-carbon (C1) chemical engineering [11,12].

2 Utilization of yellow phosphorous off gas

2.1 Yellow phosphorous off gas as fuel

With a caloric value of about $1.0 \times 10^7 \text{ J} \cdot \text{m}^{-3}$, yellow phosphorous off gas can be used as energy gas for substitution of coke, coal, and diesel oil. However, yellow phosphorous off gas must be purified to remove its impurities, such as phosphate, sulfur, arsenic, and fluorine, etc. In manufacture process of refined yellow phosphorous, purified yellow phosphorous off gas can be employed as fuel of gas boiler [13]. In addition, the heat of yellow phosphorous off gas is also utilized for electric generation. The advantages of direct utilization of yellow phosphorous

off gas as fuel include: simple technique, uncomplicated equipments, energy saving, low cost, and convenient production management. Compared with being used as raw materials of C1 chemical engineering, the economic benefit of yellow phosphorous off gas as fuel is relatively low. Yellow phosphorous off gas is also employed as a heat source in chemical production processes, such as drying and polymerization.

2.2 Resourcification of yellow phosphorous off gas as raw chemical material

As shown in Fig. 1, purified yellow phosphorous off gas can be used for synthesis of a series of chemicals via oxo synthesis, such as formic acid, methanol, sodium formate, methyl formate, oxalic acid, dimethyl ether, and carbonyl chloride, etc. [1]. However, the recycle percentage of yellow phosphorous off gas in China is still less than 40%.

2.2.1 Yellow phosphorous off gas utilized for synthesis of formic acid

From Fig. 2, methyl formate is synthesized by carbonyl synthesis reaction between purified yellow phosphorous off gas and methanol. The maximum conversion efficiency of carbon monoxide is 95%, while the yield efficiency of methyl formate can be as high as 96%. Methyl formate is hydrolyzed into raw formic acid and ethanol, followed by rectification of raw formic acid. The highest yield efficiency of formic acid is 90%. Then the separated methanol can be used as reactant again for synthesizing methyl formate. The overall reaction equation of synthesis of formic acid is as follows:



As shown in Eq. (2), yellow phosphorous off gas and water are consumed as reactants. More importantly, the only product is formic acid, and no other by products can be found in the synthesis process. Therefore, it is a cleaner production technology without the emission of three wastes (waste gas, waste water, and waste residues).

2.2.2 Yellow phosphorous off gas for synthesis of oxalic acid

For decades, yellow phosphorous off gas has already been used for synthesis of oxalic acid. In many plants in China, purified yellow phosphorous off gas was used as substitute of generator gas for synthesis of oxalic acid. Oxalic acid plays an important role in pharmacy and fine chemistry as a tanning agent, rubber auxiliary, metal surface treatment agent, dyeing reductant, complementary color agent, and industrial solvent. It is widely used for synthesis of formate, formamide, and other pharmaceutical products. Oxalic acid can be manufactured via two methods: (1)

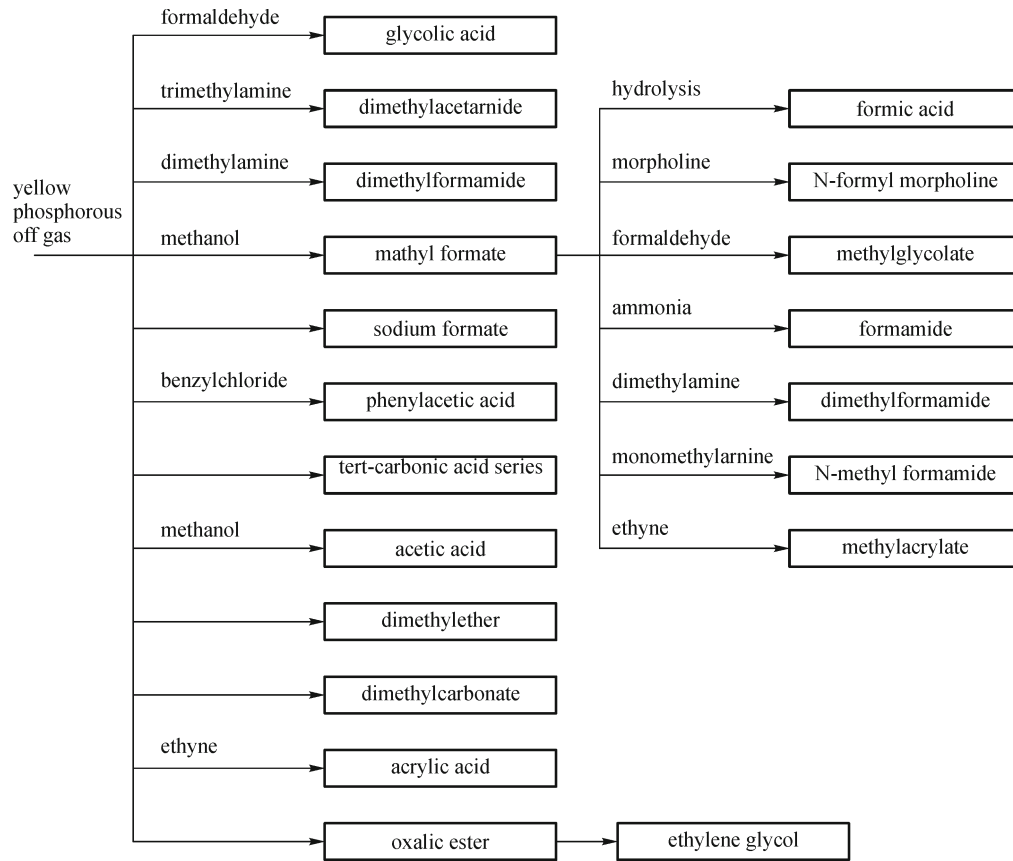


Fig. 1 Chemicals synthesized by using purified yellow phosphorous off gas [1]

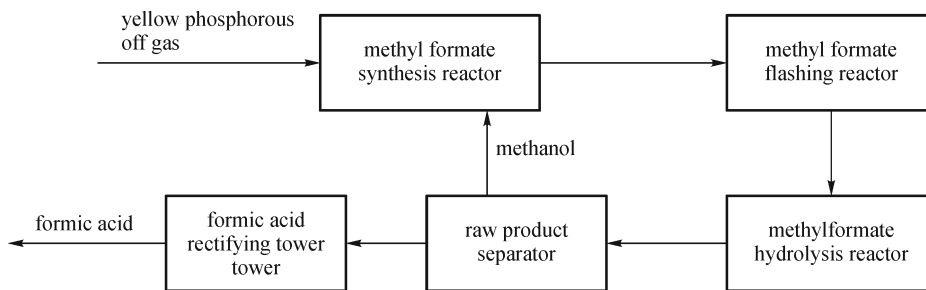
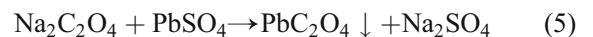
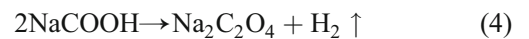


Fig. 2 Schematic drawing of synthesis of formic acid by using yellow phosphorous off gas

synthesis method by using sodium oxalate as reagent, and (2) oxidation method by using carbohydrate as reagent. In general, synthesis method is preferred while yellow phosphorous off gas is applied for manufacturing oxalic acid. Yellow phosphorous off gas can be washed by water to separate the impurities, followed by purification of yellow phosphorous off gas with alkali wash method or activated carbon oxidation process. The reaction between purified yellow phosphorous off gas and sodium hydroxide results in the formation of sodium oxalate. Then, oxalic acid is synthesized through dehydrogenation and acidification according to the following equations:



By using sulfuric acid as a reagent, a by product is sodium sulfate. To reduce the cost and increase the added value of product, industrial phosphoric acid can also be

used as substitute of sulfuric acid for the synthesis of oxalic acid, resulting in the formation of acid phosphates as by products. The prices of sodium dihydrogen phosphate and disodium hydrogen phosphate are higher than that of sodium sulfate. The cost of using per ton phosphate can be lowered by 1000 CNY.

2.2.3 Yellow phosphorous off gas utilized for synthesis of methanol and dimethyl ether

Compared with using natural gas as raw material, the cost of synthesizing methanol by using yellow phosphorous off gas is lowered by approximate 1100 CNY per ton. Synthesis of methanol with carbon monoxide is a mature technology that has been applied widely in chemical industry (Eq. (7)). Hydrogen gas must be prepared from purified yellow phosphorous off gas before it can be used as raw material for synthesis of methanol. Synthesizing methanol by employing yellow phosphorous gives large yellow phosphorous manufactures the advantage of low cost.



The production capability of methanol is $1900 \text{ kt} \cdot \text{a}^{-1}$, and the output is $1300 \text{ kg} \cdot \text{t}^{-1}$. The cost and investment of synthesizing 30 kiloton industrial methanol by using yellow phosphorous off gas can be estimated. The total investment of this project is show in Table 3 [10].

Table 3 Total investment of the project of synthesizing 30kt methanol by using yellow phosphorous off gas [10]

	items	cost (10000 CNY)
1	engineering /including:	4977.0
	(1) constructional engineering	783.0
	(2) equipments	2894.5
	(3) installation	1289.5
2	other expense	510.74
3	reserve fund	274.39
4	interest incurred during construction	95.80
5	current fund loan	473.57
	total	6331.5

The consumption and prices of materials, fuel, and energy are show in Table 4 [10].

The annual profit of this project is 14.88 million CNY. The sale tax and extra charges are 4.24 million CNY. The income tax per year is 4.91 million CNY. The profit after tax per year is 9.97 million CNY. However, it is not recommended for small yellow phosphorous manufactures to produce methanol by using yellow phosphorous off gas because the economic benefit cannot be quite large due to small scale of production.

The synthesized methanol can then be used for preparation of dimethyl ether. Dimethyl ether is a chemical applied as aerosol, spray, refrigerant, solvent, extractant, anesthetic, and catalyst for polymerization, etc. The combustion performance of dimethyl ether is better than that of petroleum due to two reasons: 1) more complete combustion of dimethyl ether without residual; 2) no carbon deposit left after combustion. In residential areas around yellow phosphorous manufactory, dimethyl ether can be a substitute of liquefied petroleum gas as a cleaner fuel. In addition, the combustion performance of petroleum can be improved by mixing dimethyl ether into it. The caloric value of dimethyl ether is higher than that of city gas. Dimethyl ether can be a preferred substitute of automobile fuel. China has already cooperated with Germany for manufacture of dimethyl ether.

2.2.4 Yellow phosphorous off gas utilized for synthesis of methyl formate

In the past, methyl formate was synthesized through esterification reaction between formic acid and methanol. The disadvantages of esterification method are strict operating conditions, high cost, and long technological processes. That method used before has now been innovated by synthesizing methyl formate with the existence of sodium methylate. The purity requirement of carbon monoxide is lowered. Thus, yellow phosphorous off gas can be used for synthesis of methyl formate.

2.2.5 Synthesis of carbonyl chloride by using yellow phosphorous off gas

Carbonyl chloride is also called suffocating gas that can be used as pesticide, dye, and intermediate of pharmaceuticals. It had been used as nerve gas in military. By mixing carbon monoxide, chlorine, and activated carbon, carbonyl chloride can be successfully synthesized. Up to now, no literature is reported on synthesis of carbonyl chloride by using yellow phosphorous off gas in China.

3 Purification of yellow phosphorous off gas

3.1 Water washing method

Impurities in yellow phosphorous off gas, such as phosphate, sulfur, arsenic, carbon dioxide, and dust must be removed before it can be used as chemical material. Water washing treatment is effective for removal of dust, mechanical impurities, SiF_4 , H_2S , HF, part of P_4 , tar oil, and phosphorous sludge [14]. Water washing treatment also plays a role in cooling. Yellow phosphorous off gas can be used directly as fuel after water washing pretreatment process. However, neither hydrogen phos-

Table 4 Total cost of materials, fuel, and energy of synthesizing 30 kiloton methanol by using yellow phosphorous off gas [10]

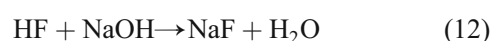
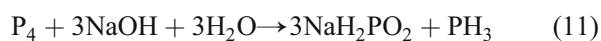
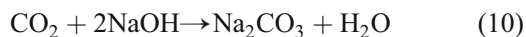
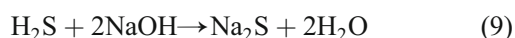
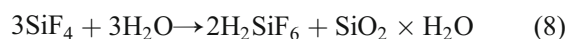
	items	annual consumption	unit price
1	yellow phosphorous off gas	9000 m ³	0.10 CNY·m ⁻³
2	sodium carbonate	45 m ³	1500 CNY·t ⁻¹
3	ADA solution	150 m ³	24000 CNY·t ⁻¹
4	dephosphorization catalyst	30 m ³	6700 CNY·t ⁻¹
5	shifting catalyst	15 m ³	11000 CNY·t ⁻¹
6	synthesis catalyst	18 m ³	23000 CNY·t ⁻¹
7	electron	4800 k·W·h	0.35 CNY·(kW·h) ⁻¹
8	water	210000 m ³	1.2 CNY·m ⁻³
9	water vapor	180 kt	60 CNY·t ⁻¹
10	circulating water	6300000 m ³	0.2 CNY·m ⁻³
11	soft water	150000 m ³	1 CNY·m ⁻³

phide nor hydrogen sulfide can be removed by water washing. The impurities, such as sulfur, fluorine, and arsenic, could be oxidized into toxic gases during the combustion, resulting in secondary pollution.

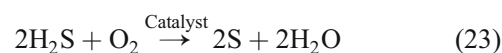
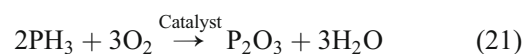
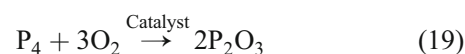
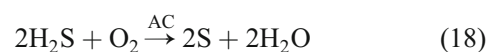
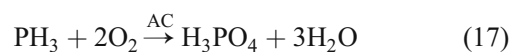
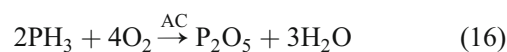
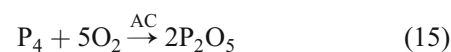
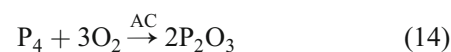
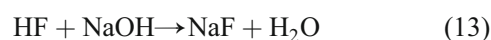
3.2 Water washing-caustic washing method

To remove hydrogen sulfide and carbon dioxide, caustic washing is carried out after water washing by using 10%–15% sodium hydroxide solution. Desulfuration efficiency of caustic washing is in the range of 80%–99%, and defluorination efficiency can be as high as 99%. Carbon dioxide removal efficiency is about 50%. The removal of acidic impurities, such as carbon dioxide, results in the decrease of sodium hydroxide concentration. The purification efficiency of sodium hydroxide solution decreases dramatically with the decrease of sodium hydroxide concentration. New caustic washing solution must be added when sodium hydroxide concentration is decreased to 1%–3%. By causticization, sodium carbonate residual can be transformed into sodium hydroxide for caustic washing in solution. Yellow phosphorous off gas can be used for synthesis of some chemicals, such as oxalic acid and formic acid, which have not high purity requirement for raw feed gas [15,16].

Usually, both water washing method and caustic washing method are applied for purification of yellow phosphorous off gas. The reaction equations are shown in Eqs. (8) to (12).

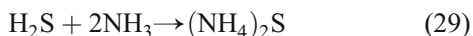
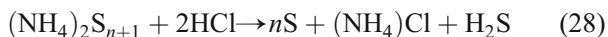
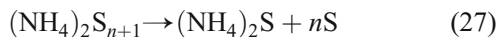
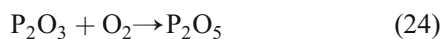


Sodium carbonate in alkaline solution can be transferred into sodium hydroxide by causticization and recycled into purification reaction system. For advanced removal of phosphate and sulfur in yellow phosphorous off gas, activated carbon (AC) catalytic oxidation method is introduced according to the following Eqs [17]:



Regeneration of catalyst is conducted by the following

reactions:



Advanced purification process of yellow phosphorous off gas is shown in Fig. 3. Carbon dioxide and phosphate can be removed when yellow phosphorous off gas is flowed through caustic washing tower-3. Then yellow phosphorous off gas is heated by preheater-6, followed by flowing reactor-7 from bottom to up, resulting in catalytic oxidation of phosphate and sulfur. The oxides of phosphate (phosphorous oxide and phosphorous trioxide) or elemental sulfur are adsorbed on the surface of the catalyst. Before being transported for mono-carbon chemical engineering section, purified yellow phosphorous off gas is cooled down by cooler tower-9.

It is reported that the impregnant-modified AC was proved to be effective for removal of PH_3 and H_2S from yellow phosphorous off gas according to the breakthrough curves. For the modification of PH_3 adsorbent and H_2S adsorbent, $0.10 \text{ mol} \cdot \text{L}^{-1}$ CuAc_2 and 7% of Na_2CO_3 were

proved to be the optimal impregnants, respectively (Fig. 4) [7,18,19].

Wang et al. modified activated carbon by HCl impregnation to enhance the adsorption purification ability [12]. 7% HCl modified adsorbent had the adsorption capacity of $0.041 \text{ g} \cdot \text{g}^{-1}$ when it was applied in the adsorption of PH_3 . The outlet break-point concentration of PH_3 was less than $1 \text{ mg} \cdot \text{m}^{-3}$, which could meet the standard of off gas to be used as the raw material gas to produce C1 chemical products after purification. The purification process was affected by two key factors. One factor was the reaction temperature in the process of using modified activated carbon to adsorb and purify PH_3 . And the other factor was the oxygen content in the gas. The purification efficiency could be significantly improved by raising the reaction temperature or increasing the oxygen content of the gas. After modification, the reduction in the adsorbent's total pore volume mainly occurred in pores below 2 nm in diameter, especially in the range of 0.3–1.5 nm. The pore volume decreased significantly after modification and the decrease in micropore volume accounted for 87% of the total volume change. The surface areas decreased 28%, 29% of which was due to micropore surface decrease after adsorption. When HCl impregnation was applied, HCl significantly increased the performance of carbon as a PH_3 adsorbent whereas the effects of other materials used in this study were much less pronounced. As a result of this process, oxidation products were strongly adsorbed and present in small pores ranging from 0.3 nm to 1.5 nm. HCl that presented in the micropores was likely to act as a catalyst for oxygen activation causing PH_3 oxidation into

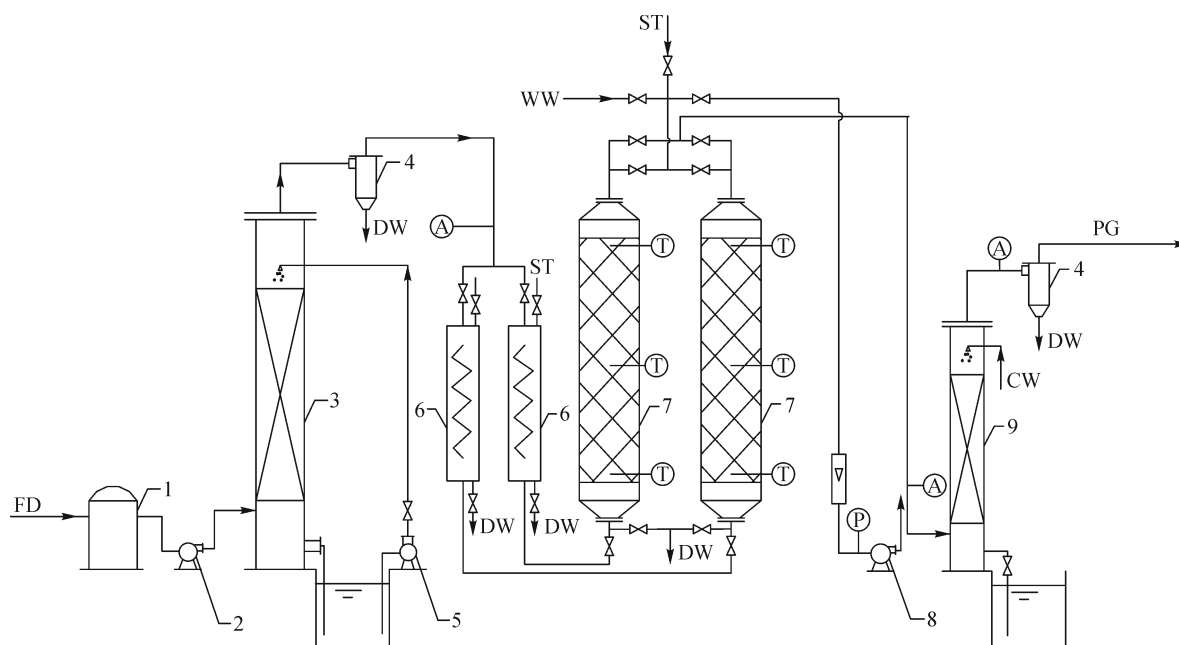


Fig. 3 Schematic of the advanced purification of yellow phosphorous off gas. (1) Water seal; (2) vacuum pump; (3) caustic washing tower; (4) mist eliminator; (5) pump; (6) preheater; (7) reactor; (8) induced fan; (9) cooler; T – thermometer; P – pressure gauge; A – sampling; FD – feed gas; DW – drain water; ST – steam; WW – washing water; CW – cooling water; PG – product gas

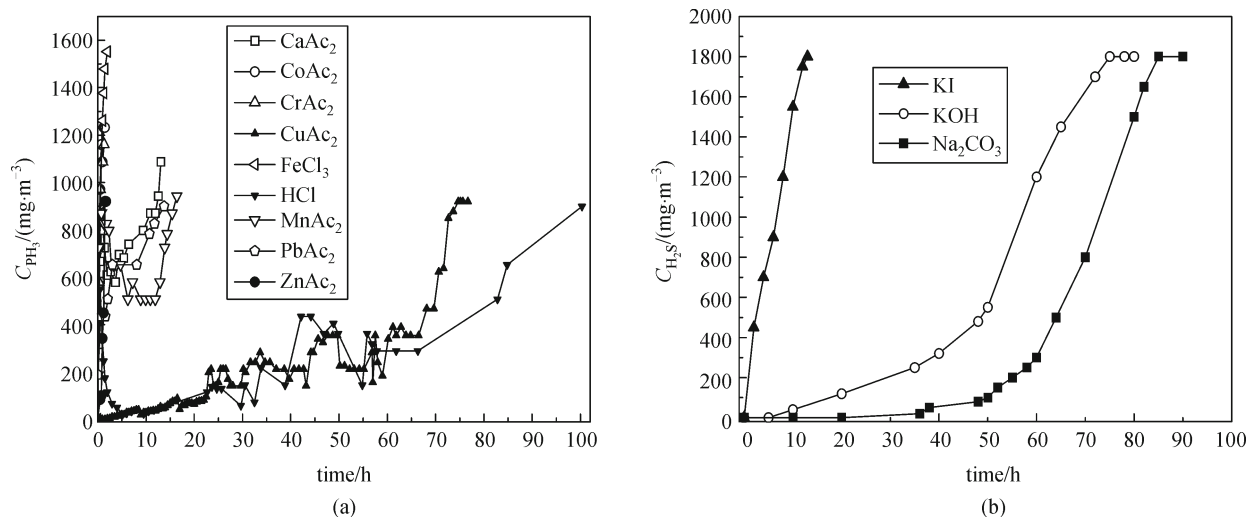


Fig. 4 Breakthrough curves of (a) PH_3 and (b) H_2S on AC modified with different impregnants

H_3PO_4 and P_4O_{10} . Therefore, impregnated activated carbon can be used in further purification of low concentration phosphine [12,20].

In general, yellow phosphorous off gas cannot be used as feed gas by traditional caustic washing method and water washing method due to relatively high concentration of impurities. Compared with traditional purification method, the advantages of advanced purification method include: 1) impurities in yellow phosphorous off gas reach the standard of being used as raw feed gas, and 2) purified yellow phosphorous off gas can be recycled (phosphor content $< 10 \text{ mg} \cdot \text{m}^{-3}$, sulfur content $< 10 \text{ mg} \cdot \text{m}^{-3}$, arsenic hydride content $< 0.5 \text{ mg} \cdot \text{m}^{-3}$, hydrogen cyanide $< 5 \text{ mg} \cdot \text{m}^{-3}$) [21].

3.3 Catalytic oxidation method for purification of yellow phosphorous off gas

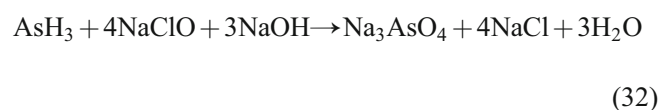
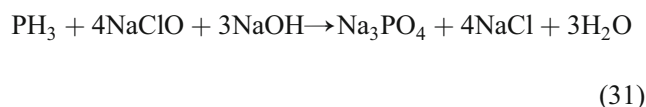
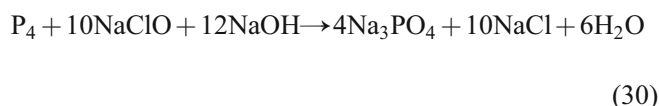
Catalytic oxidation method is used for higher dephosphorization efficiency and desulfuration efficiency, and conducted after water washing and caustic washing treatments [24]. By introducing fresh air into reaction system, oxygen content is increased to about 1%. Phosphate and sulfur impurities are oxidized into P_2O_3 , P_2O_5 , and S, respectively, on the surface of fixed bed catalyst at 110°C . 1 kg catalyst is able to purify 700–1,000 m^3 yellow phosphorous off gas. Equally, 2.5–4 kg catalyst is used for purification of 1 ton yellow phosphorous off gas [23,24]. The spent catalyst during oxidation processes can be regenerated. The by products of catalytic oxidation include sulfur and phosphoric acid (purity $> 20\%$). Dephosphorization efficiency increases with the increase of reaction temperature and oxygen content.

In addition, catalytic oxidation method can be combined with caustic washing method for higher dephosphorization efficiency and desulfuration efficiency. For instance, the

desulfuration efficiency of caustic washing is 88.1%–90%, and that of catalytic oxidation method is 85%–90%. The desulfuration efficiency is increased to 99% by using caustic washing-catalytic oxidation method.

3.4 Sodium hypochlorite oxidation method

Sodium hypochlorite solution acts as an adsorbent in sodium hypochlorite oxidation method for removal of phosphate arsenic in yellow phosphorous off gas (Eqs. (30) to (32)).



Purified by sodium hypochlorite oxidation method, concentrations of phosphate and arsenic can be as low as 0.0001% [25].

3.5 Purification of yellow phosphorous off gas by temperature swing adsorption and pressure swing adsorption

To lower energy consumption, temperature swing adsorption (TSA) and pressure swing adsorption (PSA) are employed for purification of yellow phosphorous off gas (Fig. 5(a) and 5(b)). Flow chart shown in Fig. 5(a) can be chosen for purification of yellow phosphorous off gas with

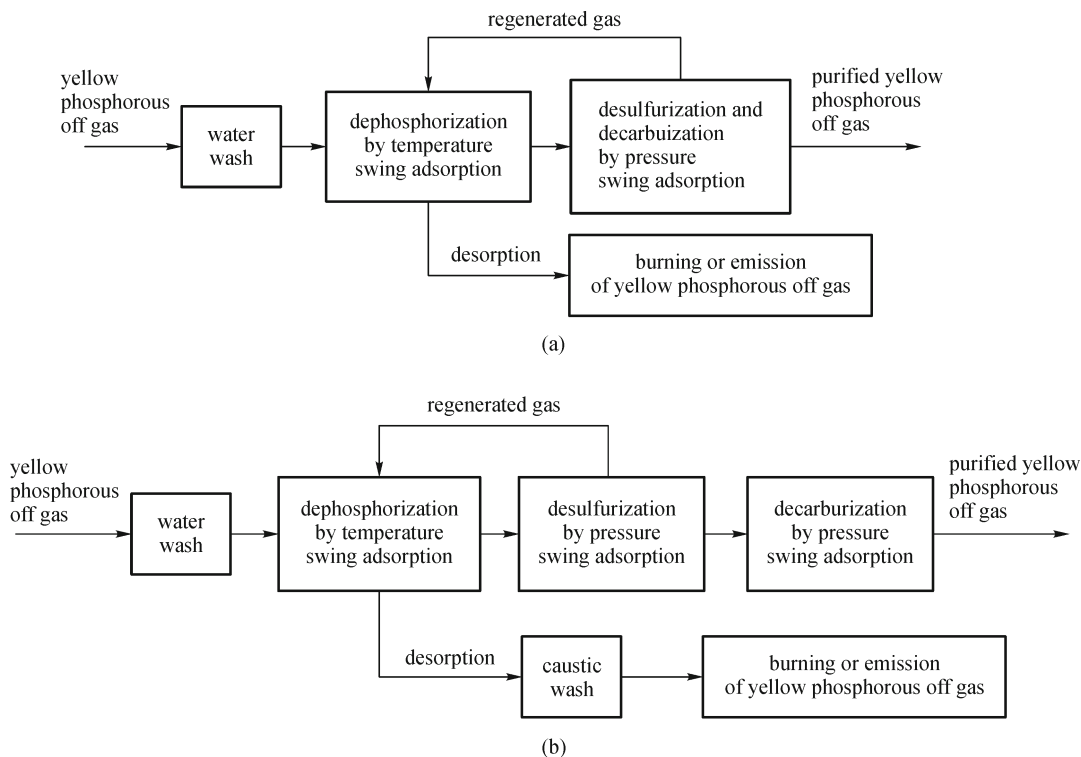


Fig. 5 Purification of yellow phosphorous off gas by temperature swing adsorption and pressure swing adsorption

low sulfur content or a small production in quantity. Flow chart shown in Fig. 5(b) can be used for purification of yellow phosphorous off gas with high content of impurities and large production in quantity. PSA is introduced for removal of carbon dioxide in yellow phosphorous off gas. About 99.8% carbon dioxide can be removed. And more than 92% carbon monoxide is recycled. Part sulfur can also be removed by PSA at low sulfur content in yellow phosphorous off gas. Desulphuration is needed after PSA. TSA and caustic washing can be carried out for removal of sulfur. Dephosphorization is conducted by TSA without catalyst. The desorbed gas can be combusted or exhausted after removal of S, P, and F with caustic washing. Phosphate impurity can be removed by adsorbent at normal or room temperature by TSA instead of using catalyst, while heat is needed for the regeneration process. The regenerated gas is flowed into adsorption tower for heating and regenerating adsorbent. Meanwhile, impurities are brought out of adsorption tower with desorbed gas. Desorbed gas can be used as fuel gas with a high caloric value [26–28].

4 Conclusions

Advanced purification and comprehensive utilization of yellow phosphorous off gas are of great importance for environmental protection, sustainable development, circular economy, and green production. Comprehensive

utilization of yellow phosphorous off gas is based on advanced purification of yellow phosphorous off gas technologies. Further studies and researches on advanced catalytic oxidation, temperature swing adsorption, and pressure swing adsorption are required for better utilization of yellow phosphorous off gas. For cleaner production and greater efficiency, advanced techniques must be conducted. Utmost effort must be carried out by yellow phosphorous manufactories for sustainable development.

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