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Contrast Analysis of Recycling and Utilization Approaches of Yellow Phosphorus Tail Gas

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Large amounts of CO (carbon monoxide) exhaust are generated in electric furnace yellow phosphorus production processes. The key issue of achieving energy saving and emission reduction of yellow phosphorus production lies in the efficient and economical way of reusing the tail gas. There are mainly two ways to reuse the yellow phosphorus tail gas: the first is to reuse its heat energy by direct combustion, and the second is to apply the tail gas in the synthesis of C_1 chemical products after purification. This paper analyzes and compares the technical impediment, economic benefit, environmental effect, energy recovery, prospect and sustainability of the two ways synthetically, concluding that the process route of recycling yellow phosphorus tail gas to produce C_1 chemical products is much better than that of reusing the heat energy of yellow phosphorous tail gas by combustion. This paper provides reference and basis for reusing yellow phosphorous tail gas scientifically.

1. Introduction

As a big country with rich phosphorus resources, the capacity and quantity of yellow phosphorus in China is larger than any other country. In 2011, the capacity of yellow phosphorus of China reached about 2 Mt and annual quantity reached about 0.96 Mt, covering more than 80% of the global quantity of yellow phosphorus (Hou et al., 2012). In China, the main method of yellow phosphorus production is electric furnace process which consumes high energy and generates large quantities of pollutants. 13,000 to 15,000 kWh electricity is consumed to produce 1 t of yellow phosphorus, and at the same time, lots of tail gas and slag are generated (Gong et al., 2013). The yellow phosphorus tail gas is a kind of mixed gas of CO (the ratio is from 87% to 92% approximately) and many other kinds of poisonous and harmful materials (Zhang et al., 2012). According to the statistics, for producing 1 t of yellow phosphorus about 2,500 to 3,000 m^3 (101.325 kPa, 0℃) tail gas will be generated (Hou et al., 2012). Burning and unloading is the old way for yellow phosphorus manufacturers to dispose the tail gas, which not only wastes many CO resources, but also results in the large emission of CO_2 and other poisonous and harmful gas. For example, 0.96 Mt of yellow phosphorus was produced in 2011, at least 4.06 Mt of CO_2 and different forms of poisonous and harmful hazard substances of sulphur, phosphorus, fluorine and arsenic were generated and discharged into the atmosphere, causing serious pollution. In 2009, Chinese government implemented the “access conditions of yellow phosphorus industry”, which clearly stipulates that phosphorus exhaust cannot be discharged into the air by direct combustion; rational utilization of resources must be implemented, and the comprehensive exhaust utilization rate of a newly-built system should be over 90%(Liu et al., 2012). At the same time, due to the high energy consumption, high production cost of the yellow phosphorus industry, yellow phosphorus manufacturers themselves are constantly looking for ways to reduce costs, and improve profitability. Reusing the yellow phosphorus tail gas can be a good way for the industry development. As a result, reusing yellow phosphorus tail gas has become a technological hot spot in the yellow phosphorus industry.

The electric furnace method of producing yellow phosphorus is to mix phosphate rock ($Ca_3(PO_4)_2$), silica (SiO_2) and coke (C) together in a certain proportion, heat and melt them in a temperature range of 1,300 to 1,500℃ to release the phosphorus. The reaction equation is as follows (Zhang et al., 2012):

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + P_2 + 5CO - 324.7kcal \quad (1)$$

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The production of yellow phosphorus will result in a lot of tail gas, which is mainly composed of CO. The phosphate rock contains impurities of complex composition, these impurities also react in the electric furnace and go into the tail gas. The yellow phosphorus tail gas also contains various forms of sulfur, fluorine, phosphorus, arsenic, cyanide and dust. The typical composition of the yellow phosphorus tail gas is shown in Table 1 (Zhang et al., 2012).

Table 1: Typical composition of yellow phosphorus tail gas (Zhang et al., 2012).

Composition	CO	CO_2	O_2	H_2	CH_4	N_2	H_2O	H_2S	PH_3	HF	AsH_3
Content	87 %- 92 %	1 %- 4 %	0 % - 1%	1 %- 8 %	0%- 0.3%	2 %- 5 %	0 % -5 %	800 - 1,100 mg/m^3	500 - 1,100 mg/m^3	0 -1,000 mg/m^3	70- 80 mg/m^3

There are mainly two ways to reuse the yellow phosphorus tail gas: to use the heat energy through combustion of the tail gas as a heat source or to generate electricity; or to purify the tail gas and make it to be a raw material of the C_1 chemical industry (Zhang et al. 2012). This paper intends to find an environmentally friendly and better way to use the tail gas as the raw material of C_1 chemical products by analysing and comparing the two technologies on technical risk, economic benefits, environmental effect, energy recovery, prospects and sustainability. The work in this paper is benefit in realizing the extension and sustainable development of the industry chain.

2. Brief introduction of two process flow sheets for reusing tail gas

2.1 The process of reusing heat energy of yellow phosphorous tail gas by combustion

One of the main ways to reuse the yellow phosphorus tail gas is burning it directly and recovering its heat energy. There are two ways to reuse the heat energy: one is to directly use the flue gas as a heating source, and the other is to generate steam for power generation. The yellow phosphorus tail gas contains a lot of impurities which are highly corrosive and can generate toxic and hazardous substances at high temperatures. If the heat is to be used through burning the tail gas, the purification pretreatment has to be made to remove most of the acidic and toxic substances. After purification, the exhaust gas will be pressurized and burned to generate flue gas or steam. According to the specific needs of the user, the steam can be further used for power generation. Boiler exhaust should be purified before discharge to the air. The process flow diagram is as shown in Figure 1.

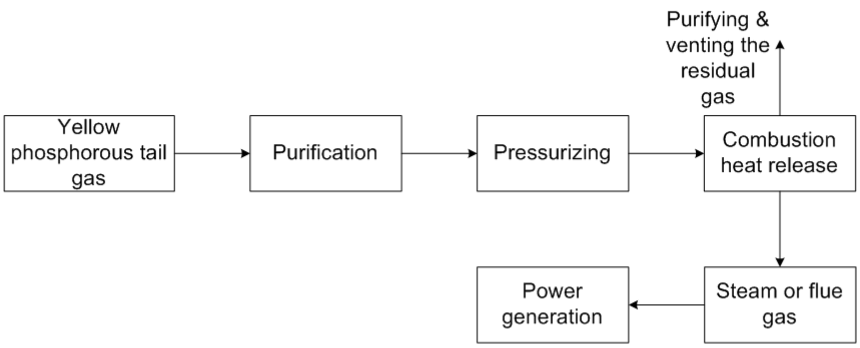

Figure 1: Process flow diagram of reusing heat energy of yellow phosphorous tail gas by combustion.

There are many mature techniques for reusing heat energy by combustion of the yellow phosphorus tail gas for industrial use. To increase the efficiency of the thermal energy and the economic benefits, the manufacturers adopt slightly different technologies and processes.

2.2 The process of using yellow phosphorus tail gas to produce C_1 chemical products

Another reusing method of the yellow phosphorus tail gas is to produce chemical products by using the tail gas as C_1 chemical raw material. Lots of chemical products can be made from CO, such as: Methyl Alcohol, Formate (sodium formate, calcium formate, potassiumformate), Methyl formate, Formic acid, Methyl-carbonate and so on. All these chemical products are widely used and have high added value. Comparing with the process of reusing heat energy by combustion, as the C_1 chemical raw material, the yellow phosphorus tail gas needs further deep purification. The deep purification methods include catalytic oxidation, temperature and pressure swing adsorption, membrane separation and so on. After being pressurized and heated, the purified tail gas will be sent to the reactor to react with other raw materials. The residual gas can be recycled again or be emitted after purification. The process flow diagram is shown in Figure. 2.

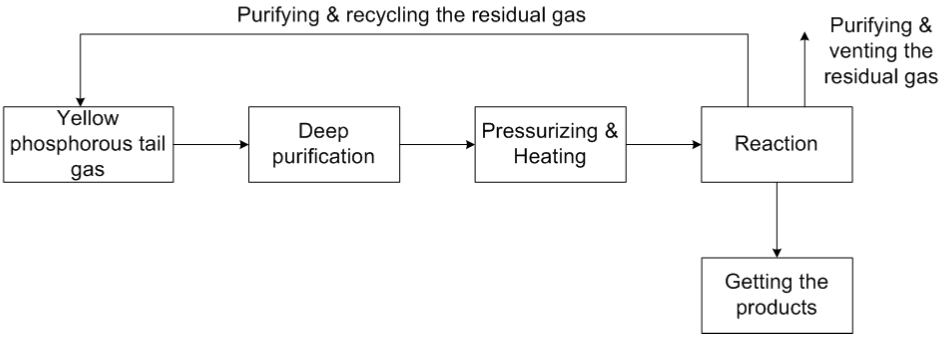

Figure 2: The process flow diagram of using yellow phosphorus tail gas to produce C_1 chemical products.

Comparing with reusing heat energy by combustion, using the tail gas as the C_1 chemical raw material is more complicated, because it requires more stringent standards for gas purification, and also needs pressurizing and heating operation.

3. The comprehensive contrast analysis of two reusing approaches

3.1 Technical difficulty and feasibility

The approach of reusing heat energy by combustion is simpler than the approach of using the tail gas to produce C_1 chemical products. The yellow phosphorus tail gas just needs water washing or alkaline washing before sent to the boiler. The technology of getting flue gas or steam by combustion and the technology of using steam to generate electricity are mature techniques. This technology has some disadvantages, like strong corrosiveness to the boiler, short service life of the boiler and some other problems. But this technology is very mature, which has little development space.

When the yellow phosphorus tail gas is used as C_1 chemical raw material, it needs deep purification and fully removing the impurities. At the same time, it still needs pressurizing, heating, reaction and other operations to prepare the C_1 chemical products. This approach is much more complicated than that of reusing heat energy by combustion. In recent years, with the yellow phosphorus tail gas recycling value and attention increases, many researchers have concentrated on the development of the technology of yellow phosphorus tail gas purification, and they have made significant progress in the lab (Ning et al., 2011), pilot (Wang et al., 2011) and industrial scale (Deng et al., 2013). The technology of deep purification for yellow phosphorus tail gas can realize industrialization. The technological process of using the yellow phosphorus tail gas to produce the C_1 chemical products are complicated, not mature enough, high investment, and more difficult to connect with the original devices. Such technologies are still at the stage of industrialized promotion and development.

3.2 Economic Benefits

Considering the industrial device, the easiest way of reusing heat energy from the yellow phosphorus tail gas by combustion is to directly make use of flue gas or steam as the heating source, to dry the rock phosphate and coke, or boil hot water for the yellow phosphorus production process. But the economic benefit of such process is poor. Another way is to reuse the heat source from the tail gas boiler for power generation. According to the research results from Yang and He (2014), a set of yellow phosphorus tail gas power generating device with handling capacity 9,000 m^3/h (101.325kPa, 0℃), will generate 37,440,000 kWh electricity power per year if the annual operating time is 7,200 h.If1 t yellow phosphorus can generate 3,000 m^3 (101.325 kPa, 0℃) tail gas which contains 87% CO, 1,733 kWh electricity power can be generated by reusing the tail gas from producing each ton of yellow phosphorus. If the industrial electricity cost is 0.5 RMB/kWh, 867 RMB economic benefit will be made from reusing the tail gas from producing each ton of yellow phosphorus, much more than reusing the flue gas or steam as heating source. Reusing the tail gas for power generation requires investment for the new power generation station and subsidiary facilities, which will be higher than directly reusing the flue gas or steam as the heating source, its overall economic benefits are still better. This is the reason the majority of the enterprises would like to choose to burn the yellow phosphorus tail gas for power generation.

Comparing with the approach of reusing heat energy from the yellow phosphorus tail gas by combustion, the economic benefits of the approach of using yellow phosphorus tail gas to produce the C_1 chemical products are hard to estimate. Because the price and technical conditions of different target products are different, and the production cost, investments and added value of each product have a significant difference. But using the yellow phosphorus tail gas to produce the C_1 chemical products will help to get good added value. According to the research from Zhang et al. (2012), the cost of per ton of the methyl alcohol produced by the yellow phosphorus tail gas are 1,000 RMB lower than the methyl alcohol produced by the natural gas. The added value of the byproduct sodium formate is 1.2 times more than that of the main product yellow phosphorus. Ma et al. (2016) have made a study for the feed grade calcium formate produced by the yellow phosphorus tail gas, and through estimating the pilot plant testing data, at least the profit of per ton calcium formate is 2,000 RMB. Assuming that 3,000 m^3 (101.325kPa, 0℃) tail gas which contains 87 % CO can be produced from producing each ton of yellow phosphorus, about 6.7 t of calcium formate can be produced by the tail gas and it will obtain 13,400 RMB profits. The economic benefit is substantial. The added value of the C_1 chemical products produced by the yellow phosphorus tail gas is higher than the added value of the yellow phosphorus, there is a viewpoint in the yellow phosphorus industry that the C_1 chemical products should be considered as the main products of this process, and the yellow phosphorus is just a byproduct. From the investment perspective, for producing the C_1 chemical products, the yellow phosphorus tail gas should be deep purification, pressurizing, heating and reaction, and so the investment amount is much larger than the approach of reusing heat energy from the yellow phosphorus tail gas by combustion. Taking the technological process invented by the author that using the yellow phosphorus tail gas to produce the feed grade calcium formate as an example, since the feed grade calcium formate standard requires the impurity content of the product to be strictly limited to a low level, this process has a stringent standard for the purification of the yellow phosphorus tail gas. One set of tail gas purification device with handling capacity 9,000 m^3 (101.325 kPa, 0℃) per hour is about 30 M to 40 M RMB, which is much higher than that of purification device for reusing heat energy by combustion. If the gas pressurizing device, heating device, the reactor, post-purification device and some other devices are also taken into consideration, the difference of the investment of these two processes will be even much greater. A large amount of working capital should also be invested in producing the C_1 chemical products, although this process could generate great benefits, it also takes risks.

3.3 Environmental and social effects

From the prospective of environmental protection, compare with directly combusting and venting the tail gas to the air in the past, both these two approaches can effectively reduce the emission of poisonous and hazardous waste gas for both these two technologies purify the tail gas in different degrees, eliminate the hazardous substances and play a very important and positive role in environmental protection.

The emission of CO_2, one of the major greenhouse gases, has raised great concerns about the relationship between anthropogenic CO_2 and global warming (Puccini et al., 2016).Many studies dealt with carbon capture and storage to mitigate climate change by capturing CO_2 into geological sequestration, biological fixation or utilization (Nawi et al., 2016).Combusting and reusing the yellow phosphorus tail gas will not directly reduce the emission of CO_2, because the recovery of heat energy can replace the original coal-fired boiler for heat supply in factories or reduce purchased electricity of factories, the technology still possesses favorable effect of CO_2 emission reduction. According to the research results from Yang and He (2014), for an electricity generation set with the processing capacity of 9,000 m^3/h (101.325 kPa, 0℃) of yellow phosphorus tail gas, 13,100 t of standard coal can be saved every year, which is the equivalent of reducing emissions of 30,130 t of CO_2 and 196.5 t of SO_2 every year. For recycling the yellow phosphorus tail gas to produce C_1 chemical products, CO can be completely converted to C_1 chemical products theoretically, and the emission of CO_2 is significantly reduced. Taking the example of a set of yellow phosphorus device with the tail gas amount of 9,000m^3/h (101.325kPa, 0 ℃), assuming that the content of CO is 87 %, and it runs 7,200 h/y, the emission of 109,708 t of CO_2 can be reduced every year, and so the emission reduction effect is remarkable.

Recycling the yellow phosphorus tail gas to produce C_1 chemical products reduces the emission of poisonous and harmful substances as well as CO_2, which realizes favorable environmental protection effect. Although the method of combusting the yellow phosphorus tail gas to reuse the heat energy can reduce the emissions of poisonous and harmful gas as well as CO_2, the effect is far inferior to the approach of recycling the yellow phosphorus tail gas to produce C_1 chemical products. It is more difficult to remove CO_2 from the atmosphere, focusing on emissions reduction is always a natural choice (Pritchard et al., 2015). From the perspective of environmental protection, recycling the yellow phosphorus tail gas to produce C_1 chemical products is a better choice.

Both the two methods of reusing the yellow phosphorus tail gas can alter the situations that enterprises directly combust and discharge the tail gas and seriously pollute the environment, and change the public’s preconceptions, thereby obtaining favorable social effect.

3.4 Energy recovery and energy-saving efficiency

The calorific value of combusting the yellow phosphorus tail gas is 10.5-11.0 MJ/m^3 (101.325 kPa, 0℃), and it has the reusing value from the perspective of energy recovery. According to the research results from Yang and He (2014), for an electricity generation set with the processing capacity of 9,000m^3/h(101.325kPa, 0℃) of the yellow phosphorus tail gas, 1,733 kWh of electricity can be generated for producing per ton yellow phosphorus. Assuming that 13,000 kWh of electricity is consumed for producing per ton yellow phosphorus, 13.3 % of power consumption for yellow phosphorus production can be reduced by combusting the yellow phosphorus tail gas for generating electricity, with the energy-saving efficiency is 86.7 %.

For the approach of recycling the yellow phosphorus tail gas to produce C_1 chemical products, from the perspective of direct energy recovery, the energy consumption is increased rather than decreased due to additional processes of purifying tail gas, pressurizing, heating and reaction. As new products are added, the average energy consumption of per unit product is reduced. For example, according to the research from Zhang et al. (2012), the tail gas generated by producing 1 t yellow phosphorus can be used to produce 6 t sodium formate, the total quantity of products increases to 7 t, and the average energy consumption for per unit product is significantly decreased, and energy conservation is realized indirectly.

3.5 Prospect and sustainability

In China and all over the world, environmental protection as well as energy conservation is becoming stricter. The development prospect of the approach of combusting the yellow phosphorus tail gas is limited, and the energy-saving efficiency of the method is also limited no matter how the technology is improved. A large amount of CO_2 is still discharged after combusting the tail gas, and the requirements of environmental protection and sustainable development still cannot be met. On the other hand, the technology of recycling the yellow phosphorus tail gas to produce C_1 chemical products will not discharge CO_2, gain higher profits of per unit product, and reduce the average energy consumption of per unit product by extending the industrial chain and enriching product structure. With the continuous development of technology, more new products will be developed in the technical field, and the industrial chain will be extended to change and develop the yellow phosphorus industry fundamentally, to realize real sustainable development. From the prospect of technological development and sustainability, the approach of recycling the yellow phosphorus tail gas to produce C_1 chemical products is much better than that of combusting the yellow phosphorus tail gas to recover the heat energy.

4. Discussions

The advantages and disadvantages of the two approaches are listed in Table 2.

Table 2: Advantages and disadvantages of two approaches of reusing yellow phosphorus tail gas.

	Recover the heat energy of yellow phosphorous tail gas by combustion	Recycle yellow phosphorus tail gas to produce C_1 chemical products
Technical impediment and feasibility	Low technical difficulty and high feasibility	High technical difficulty and moderate feasibility
Economic benefits	Not good enough	Remarkable
Environmental and social effects	Rather good environmental effect, low emission reduction of CO_2 and favourable social effect	Remarkable environmental effect, high emission reductions of CO_2 and favourable social effect
Energy recovery and energy-saving efficiency	Heat energy can be directly recovered, and energy consumption in production can be lowered slightly; the energy-saving effect is general.	Average energy consumption per unit product can be lowered; the energy-saving effect is remarkable.
Prospect and sustainability	Development prospect is limited; the status of the industry cannot be changed fundamentally; poor sustainability	Favourable development prospect; the status of industry can be changed fundamentally; favourable sustainability

From Table 2, the approach of recycling the yellow phosphorus tail gas to produce C_1 chemical products is superior to that of combusting the yellow phosphorus tail gas to recover the heat energy in more aspects, such as the economic benefits, environmental effects, social effects, energy-saving efficiency and sustainable development. Although the technology of recycling the yellow phosphorus tail gas to produce C_1 chemical products is not as mature as the other one, it is believed that with the need of industrial development, more enterprises and researchers will focus on corresponding new technologies, the technology will eventually be mature and reliable.

5. Conclusions

The Chinese yellow phosphorus industry is struggling with the development being disrupted by high energy consumption, high pollution and low benefits. Efficient and comprehensive utilization of the yellow phosphorus tail gas is the key issue for the Chinese enterprises to get out of the dilemma and find new development directions. There are two reusing approaches of the yellow phosphorus tail gas, reusing the heat energy of the tail gas by combustion, and recycling the tail gas to produce C_1 chemical products. In this paper, the advantages and disadvantages of the two methods in the aspects of technical difficulty and feasibility, economic benefits, environmental and social effects, energy recovery and energy-saving efficiency, prospect and sustainability are compared and analysed. It is concluded that recycling the yellow phosphorus tail gas to produce C_1 chemical products is the future development direction of comprehensive utilization of the yellow phosphorus tail gas in the whole yellow phosphorus industry. The energy consumption and costs in the yellow phosphorus industry can be really shared and lowered only with the way that high value-added products are produced with the yellow phosphorus tail gas as the raw material of C_1 chemical products, and favourable economic benefits can be gained, to realize the extension and sustainable development of the industry chain. The future main direction of developing this technology is to develop a low-cost purification technology, and the other way is to develop a series of mature and reliable synthetic technology.

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