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JTL SERIES OF NEW, AMBIENT TEMPERATURE, FINE SULFUR-REMOVAL PROCESSES AND THEIR INDUSTRIAL APPLICATIONS

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ABSTRACT

The paper introduces the composition, principles and characters of JTL--1, JTL--4, JTL--5 series of new, ambient temperature, fine sulfur-removal processes. The different models are composed of T504 COS hydrolysis catalyst, T102 (or T103) special active carbon or EF-2 special ferric oxide fine desulfurizer and EZX fine desulfurizer. JTL-1, JTL-4, and JTL-5 new processes can remove H_2S+COS, H_2S+lower content COS and CS_2, H_2S+higher content COS and CS_2 in feed gas with less than 0.1×10^{-6} total sulfur at ambient temperature respectively. These are used to protect many high efficient catalysts, adsorbents , improve the quality of food CO_2 or other fine chemical products, prevent equipment corrosion and environment pollution. They supplemented each other and can entirely solve the fine sulfur-removal problem under various conditions in the plants that use coal or heavy oil as raw materials. Currently, they have been applied in more than 180 plants in the fields of ammonia synthesis, fine chemical industry (TDI, DMF, MDI, methanoic acid, etc), food CO_2, natural gas chemical industry, electrical industry, environmental protection, etc..

Chinese chemical plants usually use coal or heavy oil as raw materials. Besides H_2S, COS and CS_2 are the main sulfide impurities in the feed gas. The trace sulfides can deactivate many highly effective catalysts (such as methanol, methanation, ammonia catalysts) or adsorbents, affect the quality of products, corrode equipment and the pollute environment. The maximum limit of sulfur content of some important catalysts are listed in Table 1. We can see that the total sulfur (H_2S+COS+CS_2) must be less than 0.1×10^{-6}.

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Table 1 Poisoning of Trace Sulfur to Catalysts

Catalyst	Cu-Zn Conversion Catalyst	Ni Methanation Catalyst	Ammonia synthesis Catalyst	Methanol Synthesis Catalyst
Poisoning Description of Trace Sulfur	Adsorbed sulfur 0.2%,activity decrease 35%.	Adsorbed sulfur 0.2~0.4%, activity basically has been lost.	Adsorbed sulfur 0.1%, activity decreased se obviously.	Adsorbed sulfur 2.4%, Activity decreased 75%.
Maximum Limit of Total Sulfur Content in Purified Gas ($\times 10^{-6}$)	<0.1	<0.1	<0.1	<0.1

Traditional high temperature fine sulfur removal process is composed of Co-Mo hydrogenation catalyst and ZnO desulfurizer. Co-Mo hydrogenation catalyst can convert COS, CS_2, RSH to H_2S, then H_2S is removed to less than 0.1×10^{-6} by ZnO desulfurizer. The disadvantages are: its energy consumption is high, time required for starting operation is long, etc. Sometimes high-temperature ZnO is adopted alone, but experimental data show that its ability of H_2S removal is strong, but COS removal is poor. So it is necessary to develop ambient temperature fine sulfur-removal process.

Ambient temperature fine sulfur-removal was developed by a foreign corporation in the late 1980s. The process is composed by a hydrolysis catalyst and ambient temperature ZnO, and it can remove the total sulfur (H_2S+COS) to less than 0.1×10^{-6} in the feed gas.

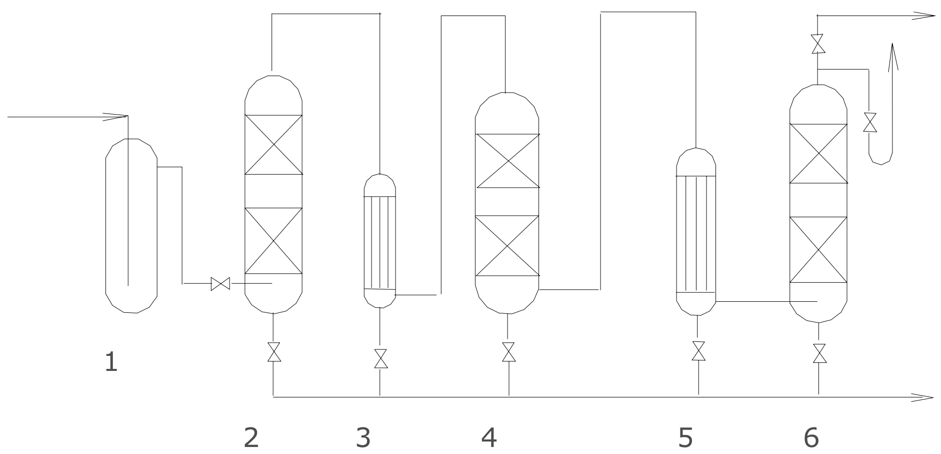
According to the situation of Chinese ammonia plant, we developed a novel JTL-1 ambient temperature fine sulfur-removal new process, composed by T504 COS hydrolysis catalyst and T102 (or T103) special active carbon or EF-2 special ferric oxide. It was first used in a ammonia plant in June 1991 and was patented in China. On this basis, we have also developed the JTL-4 new process composed by T102 or EF-2 and EZX COS, CS_2 multi-function fine desulfurizer and JTL-5, new process composed by JTL-1 process and EZX desulfurizer. These were first used in two ammonia plants in 1994 and 1995 respectively. The new processes mentioned above have been used successfully in more than 180 plants. This paper will introduce the principles, characters and industrial applications of the three ambient temperature fine sulfur-removal new processes.

1. JTL-1 NEW, AMBIENT TEMPERATURE FINE SULFUR-REMOVAL PROCESS

As mentioned above, other corporation successfully developed COS hydrolysis catalyst and ambient temperature ZnO fine desulfurizer , but ZnO has some disadvantages: its capacity of H_2S is low (about 2 ~ 3%) and the price is too high.

After many years of hard work, we successfully developed the T504 COS hydrolysis catalyst, (1) T102, T103 fine desulfurizers(special active carbon)(2) or EF-2 fine desulfurizers(special ferric oxide), JTL-1 ambient temperature fine sulfur-removal new process, which have been applied in ammonia plants since June 1991. Figure 1 shows the typical process applied in methanol plants. The first sulfur-removal tower is to remove H_2S in process gas and prevent sulfation of the hydrolysis catalyst, which convert COS to H_2S ($COS+H_2O=H_2S+CO_2$), then the H_2S is removed by the second sulfur-removal tower.

Fig. 1 JTL-1 New Process Chart



1. Gas-Water Separator
2. First Sulfur-Removal Tower
3. Heater
4. Hydrolysis Tower
5. Cooler
6. Second Sulfur-Removal Tower

In methanol plant, JTL-1 new process is always placed behind CO_2-Removal tower, the working conditions are :

Temperature: 40 ~ 80 °C (hydrolysis catalyst)

Pressure: ≤15.0Mpa

Space Velocity: T102, T103, EF-2 800 ~ 1500 h^{-1} (according to H_2S content)
T504 1500 ~ 2500 h^{-1} (according to COS content)

Inlet gas: H_2S≤20mgS/Nm^3 (14×10^{-6})
COS≤10mgS/Nm^3 (7×10^{-6})
(If COS≥10mgS/Nm^3, double grade hydrolysis can be used.)

Exit gas: H_2S≤0.05 mgS/Nm^3 (0.03×10^{-6})
COS≤0.05mgS/Nm^3 (0.03×10^{-6})

Six years of operation shows the advantage of JTL-1 new process :

(1) Activity of T504 hydrolysis catalyst is better than the same kind product at ambient temperature, it can be used in some severe conditions, such as high COS-high O_2, high CO-high O_2 and high CO_2 contents.

(2) Usually in feed gas there it is saturated with vapor, which causes capillary condensation and decreases the catalyst activity severely. So we install a small heater

to raise the catalyst temperature about 20 ~ 30ºC, it can avoid the capillary condensation and increase reaction velocity when the catalyst age.

(3) Main breakthrough of JTL-1 process is the application of special active carbon (T102, T103 fine desulfurizer) or special ferric oxide (EF-2 fine desulfurizer), their sulfur capacities are high and prices are low. One always considers the sulfur-removal precision of ZnO as the best, but we prove the equilibrium constant of active carbon's sulfur-removal reaction is greatly larger than that of ZnO through our thermodynamic calculation and some results from relevant dynamic experiments also support the conclusion. The fine sulfur-removal capacities of T102, T103 and EF-2 are four times more than that of ZnO, but their prices are only one-fifth of ZnO. So JTL-1 new process is adopted rapidly, while experts of the Chemical Industry Ministry authorized it as a new invention. Its investment and operating expense are only half to one-third that of the process composed by COS hydrolysis and ZnO. It has been applied in more than one hundred plants including methanol, methanation, food CO_2 gas, DMF, TDI, MDI that are located in more than twenty provinces of China by now.

2. JTL-4, NEW, AMBIENT TEMPERATURE FINE SULFUR-REMOVAL PROCESS:

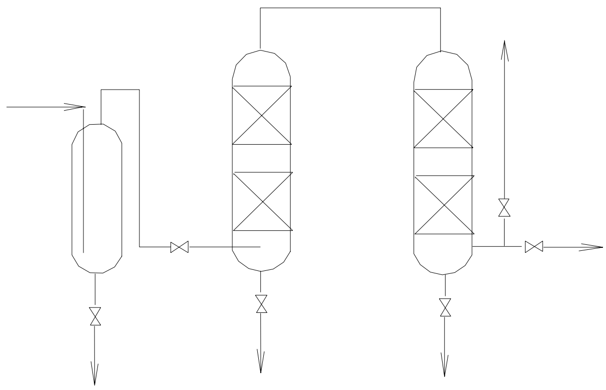
Although the JTL-1 new process has been applied successfully, it has some limitations:

(1) The COS hydrolysis catalyst must be operated at a temperature above dew point 20ºC,it must install equipment to heat the hydrolysis catalyst and a second sulfur-removal tower to remove H_2S converted by the hydrolysis catalyst .

(2) COS hydrolysis catalyst cannot remove CS_2 below 100ºC.

These two difficulties have not been solved in the world. The JTL-4 ambient temperature fine sulfur-removal new process can remove H_2S, COS, CS_2 to less than 0.1×10^{-6} at the temperature of 10 ~ 60ºC[(3).] This process is consisted of T102, EF-2 fine desulfurizer and EZX multi-function fine desulfurizer. The sulfur capacity of T102 or EF-2 desulfurizer is more than 15% (original size, SV $1000h^{-1}$, outlet gas H_2S $<0.03\times10^{-6}$), its main function is to remove H_2S. EZX can remove H_2S, COS, CS_2 at ambient temperature. COS and CS_2 sulfur capacities of EZX are about 3%, its life can be longer than two years, if COS and CS_2 contents are less than 1 mgS/m^3 in feed gas. Another advantages of EZX fine desulfurizer are that it can be operated at 10 ~ 60ºC and does not need to raise or lower temperature and install second sulfur-removal tower.[(4)] Because its sulfur capacity is less, JTL-4 new process can only remove low content organic sulfides in feed gas.

Fig. 2 JTL-4 New Process Chart



1. Gas-Water Separator
2. First Sulfur-Removal Tower
3. Second Sulfur-Removal Tower

In methanol plant, the new process is also put behind CO_2-Removal tower, its main working conditions are as following:

Temperature: 10 ~ 60ºC

Pressure: ≤15.0Mpa

Space Velocity: T102, EF-2 800 ~ 2000 h-1 (According to H2S content)
EZX 800 ~ 1500 h-1 (According to COS, CS2 content)

Inlet Gas: H2S≤20 mgS/Nm3 (14×10-6)
COS≤2 mgS/Nm3 (1.4×10-6)
CS2≤2 mgS/Nm3 (0.7×10-6)

Exit Gas: H2S≤0.05 mgS/Nm3 (0.03×10-6)
COS≤0.05 mgS/Nm3 (0.03×10-6)
CS2≤0.05 mgS/Nm3 (0.018×10-6)

JTL-4 new process has been used in more than twenty plants since 1994. In fourth section of the article, we will introduce its industrial application.

3. JTL-5, NEW AMBIENT TEMPERATURE FINE SULFUR-REMOVAL PROCESS:

Because JTL-1, JTL-4 new process have some limitations, on the basis of them we have developed JTL-5, a new ambient temperature fine sulfur-removal process composed by JTL-1 and EZX. It not only adopts JTL-1 to remove higher content H_2S and COS, but also adopts EZX to remove higher content CS_2 on ambient temperature.(5)

In JTL-5 new process, the feed gas passes JTL-1 at first (sulfur-removal principle is the same as above) to remove H_2S and COS, then passes EZX fine dusulfurizer to remove the CS_2, so it can ensure H_2S, COS, CS_2 content to less than 0.03×10^{-6} respectively in outlet gas.

Working conditions of JTL-5 new process are as following:

Temperature: 10 ~ 100ºC(hydrolysis catalyst)

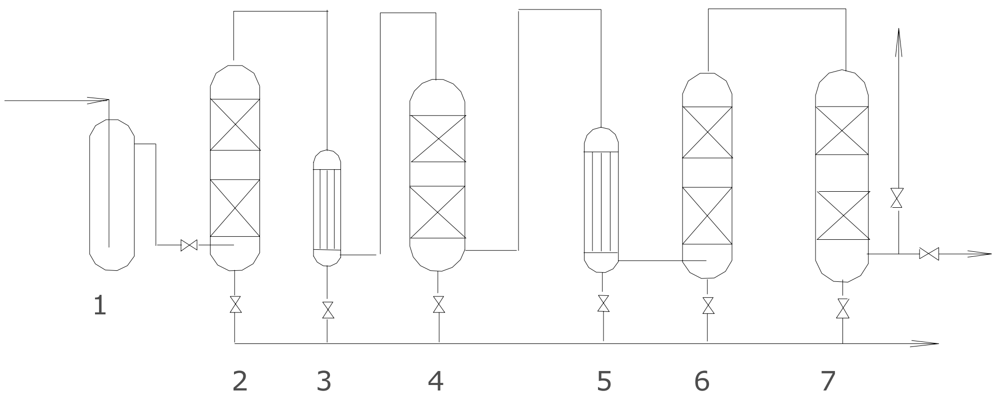
Pressure: $\le$15.0 Mpa

Space Velocity: T102, T103, EF-2: 800~1500 h^{-1}(According to H_2S content)
T504: 1500 ~ 2500 h^{-1}(According to COS content)
EZX: 800 ~ 1500 h^{-1}(According to CS_2 content)

Inlet Gas: $H_2S \le 20$mgS/Nm^3(14×10^{-6})
COS$\le$10mgS/Nm^3 (7×10^{-6})
$CS_2 \le 4$ mgS/Nm^3 (0.7×10^{-6})
(If COS$\ge$10mgS/Nm^3, $CS_2 \ge 4$ mgS/Nm^3 , double grade hydrolysis and EZX can be used.)

Outlet Gas: $H_2S \le 0.05$mgS/Nm^3 (0.03×10^{-6})
COS$\le$0.05mgS/Nm^3(0.03×10^{-6})
$CS_2 \le 0.05$mgS/Nm^3 (0.018×10^{-6})

Fig. 3 JTL-5 New Process Chart



1. Gas-Water Separator
2. First Sulfur-Removal Tower
3. Heater
4. Hydrolysis Tower
5. Cooler
6. & 7. Second Sulfur-Removal Tower

Note: EZX installed in Tower 7 may be put into under layer of Tower 6, then the process will be simplified.

The comparison of JTL-1, JTL-4, JTL-5 new process is shown in Table 2.

Table 2 The Comparison of JTL-1, JTL-4, JTL-5 New processes

Type of process		JTL-1	JTL-4	JTL-5
Combination of New process		T504 hydrolysis and T102, T103 Fine Desulfurizer	T102 and EZX Fine Desulfurizer	JTL-1 and EZX fine Desulfurizer
Working Conditions	Temperature , ºC	40 ～ 80	10 ～ 60	10 ～ 100
	Pressure , MPa	≤15.0	≤15.0	≤15.0
	Sulfide content in Inlet Gas, mgS/m^3	H_2S≤20 COS≤10	H_2S≤20 COS≤2 CS_2≤2	H_2S≤20 COS≤10 CS_2≤4
	Sulfide content in Outlet Gas, mgS/m^3	H_2S+COS≤0.1 (0.06×10^{-6})	$H_2S+COS+CS_2$ ≤0.15(0.10×10^{-6})	$H_2S+COS+CS_2$ ≤0.15(0.10×10^{-6})

4. APPLICATIONS OF NEW AMBIENT TEMPERATURE FINE SULFUR-REMOVAL PROCESSES:

Protection of Methanol Synthesis Catalyst:

Chinese chemical plants usually use coal or heavy oil as raw materials where total sulfur content (including organic sulfur) is high, so the life of methanol catalyst is short. Anyang Methanol Plant of Henan Province adopts JTL-1 new process to protect the NC501 methanol catalyst, one of the most advantageous catalysts in China. The process can ensure the total sulfur content of less than 0.1×10^{-6} in the outlet gas. The life span of NC501 is 549 days, while methanol output reaches 5116 tons per cubic meter of catalyst. In Tanchen Ammonia Plant of Shandong Province , methanol is produced under ammonia production. By adopting the JTL-4 new process, the total sulfur ($H_2S+COS+CS_2$) is less than 0.1 mgS/Nm^3 in the purified gas, while the methanol catalyst has been in operation for three years and eight months, and the methanol output reaches 4281 tons per cubic meter catalyst. Harbin Gasification Plant also adopts the JTL-4 process and by putting behind the system of low temperature methanol washing, it prolongs the life of methanol catalyst significantly. (6)

Application in Ammonia Synthesis Process:

New ambient temperature fine sulfur-removal processes have also been used to protect CO_2-removal system (such as PC,NHD),methanation catalyst, H_2-removal catalyst, ammonia synthesis catalyst. JTL-5 new process initially was successfully applied in Jiexiu Ammonia Plant of Shanxi Province to protect ammonia synthesis catalyst. Because the life of catalyst was only five months, it was necessary to resolve the problem. Through the determination of sulfide content with HC-1 Trace Sulfide Analyzer developed by us, we found H_2S ~25mgS/Nm^3□, COS ~2.5mgS/Nm^3, CS_2 ~2.5mgS/Nm^3 in the feed gas, the high sulfides contents were the main reason that made catalyst deactivated. According to the result, the plant decided to use JTL-5 new process. After the process was applied, the contents of H_2S, COS, CS_2 were less than 0.03 mgS/m^3 respectively, the total sulfur was less than 0.1 mgS/m^3, the life of ammonia catalyst was prolonged to more than two years. JTL-4 process also has good effect in protection of ammonia synthesis catalyst. Shouguan Ammonia Plant of

Shandong Province adopted the new JTL-1, JTL-4 processes in Jun. 1996, and the sulfur-removal very effective. The life of ammonia catalyst is more than three years. Some other plants have successfully adopted the new processes to prolong the life of ammonia catalyst to 5~8 years. Heilongjiang Chemical Plant has also adopted JTL-1 process to protect H_2-removal catalyst.(7)

Application in Food CO_2 Gas:

Food CO_2 gas requires the total sulfur to be less than 0.5×10^{-6}, and due to competitive adsorption, it is a difficult task to remove sulfides in the manufacture of food CO_2. Shanghai Jinfu Gas Company adopts JTL-1 process to remove minute amounts of sulfur. Through the fine sulfur-removal system, the total sulfur in CO_2 gas can reach food-class standard (total sulfur $<0.5\times10^{-6}$) and quality of product is fully guaranteed. The catalysts can be used for more than one year and as the CO_2 production also increases, its economic benefit is obvious. The company noted that some foreign chemical corporations, adopting their technology would spend USD 300,000, while the total costs of our catalysts and equipment was only RMB 300,000, approximately one-eighth the investment costs and hence the economic benefit is obvious.(8)

Protection of High Efficient Adsorbent in PSA:

Chemical Plant always uses PSA to extract CO from water-gas, which often contains high total sulfur content (H_2S about $1000\sim3000\times10^{-6}$, $COS+CS_2$ about $100\sim200\times10^{-6}$). If the total sulfur is too high, it will affect the applied effect and the life of adsorbent. So it is necessary to adopt fine sulfur-removal process to remove total organic sulfur to be less than 20×10^{-6} before PSA. However, it is very difficult to remove high content organic sulfur at ambient temperature. Jiangshan Chemical Plant of Zhejiang Province adopts JTL-1 process to remove high content COS (about 70×10^{-6}) to be less than 20×10^{-6}. The performance has been good in the past four years. Ambient temperature fine sulfur-removal new processes have also been applied in the manufacture of TDI, DMF, MDI, methanoic acid.

Sulfur-Removal in Coke Oven Gas:

Because the range of sulfides present in coke oven gas is complicated, its contents are also high, such plants always use high temperature sulfur-removal catalysts to remove sulfides, while ambient sulfur-removal catalysts have not been adopted worldwide. Shijiazhuang Glass Screen Plant uses coke oven gas to produce glass screen of color TV which demands the total sulfur to be less than 7 mgS/M^3. After studying for two years, we successfully solved the problem. JTL-1 and JTL-4 new processes have been used to remove COS $100\sim200mgS/M^3$, CS_2 $50\sim100mgS/M^3$ to less than 0.5×10^{-6} for three years very effectively.

Protection of Noble Metal Catalyst:

Noble metal catalysts require the total sulfur in feed gas to be less than 0.1×10^{-6}. COS content in feed gas of a acetic acid synthesis plant in China reaches 1000×10^{-6}.

Through sulfur-removal with NHD wet process plus JTL-1 process, total sulfur in feed gas is reduced to less than 0.1×10^{-6},effectively protecting the precious Rh catalyst. The process has been in operation in the plant for the past 2 years, with obvious effect.

Sulfur-Removal in Natural Gas:

Tianjin Dagang Oil Field adopts EF-2 ambient temperature fine sulfur-removal catalyst to remove H_2S to be less than 0.01×10^{-6} from $15\sim20\times10^{-6}$ to prevent equipment corrosion. The sulfur-removal system has been operated smoothly for two years, the problem of corrosion has been solved entirely, with satisfactory results.

5. SUMMARY

(1) The new JTL-1 ambient temperature fine sulfur-removal process composed of T504 COS hydrolysis catalyst and T102 (or T103) special active carbon or EF-2 special ferric oxide fine desulfurizer can remove H_2S, COS and achieve targets of $H_2S+COS<0.06\times10^{-6}$, its investment is only half of the process consisting of hydrolysis and ZnO, its operating fee is only one-third of that.

(2) New JTL-4 ambient temperature fine sulfur-removal process consisting of T102 (or EF-2) and EZX fine desulfurizer can remove not only H_2S and COS, but also CS_2 ($H_2S+COS+CS_2<0.1\times10^{-6}$) and realizing this fine sulfur-removal at ambient temperature. In this way, it solves the two difficulties in the field of ambient temperature fine sulfur-removal. However, it can only remove low content organic sulfides in feed gas.

(3) New JTL-5 ambient temperature fine sulfur-removal process is composed of JTL-1 and EZX fine desulfurizer, which can remove H_2S, COS, CS_2 ($H_2S+COS+CS_2<0.1\times10^{-6}$) simultaneously while removing higher content organic sulfides in feed gas.

(4) Similar JTL-1, JTL-4, JTL-5 new processes have not been reported at home and abroad; they are supplemented each other and can entirely solve the fine sulfur-removal problem under various conditions in ammonia or chemical plant using coal or heavy oil as raw materias.

(5) New JTL-1, JTL-4, JTL-5 processes have been used in more than 180 plants in the fields of ammonia synthesis, fine chemical industry(TDI, DMF, MDI, methanoic acid, etc.), food CO_2, natural gas chemical industry, electrical industry, environment protection, etc.. The economic benefit is very obvious.

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