Application of TH series H_2-removal catalysts in urea plants & TX-1 Oil-Removal Agent

Kong Yuhua, Wang Xianhou, Hu Dianming, Lei Jun

Gas Purification of Hubei Research Institute of Chemistry

National Key Industrial Base for Gas Purification Catalyst

Wuhan, 430074, P R China

Introduction

At present, there are more than two hundred urea plants in China based on different raw materials such as residuum, natural gas and coal. Every urea plant has a potential risk for explosions due to the presence of hydrogen in the feed and oxygen added for passivation purposes.

Different raw materials need different H_2-removal processes.

For example with residuum or coal as raw material, because different sulfides are present in the CO_2 feed gas, one needs an Ambient Temperature Fine Sulfur-Removal (ATFSR) process before the dehydrogenation step.

If oil is present in the CO_2 gas, an oil-removal agent is also necessary. Reciprocating compressors have the disadvantage that always some oil will enter the process stream. In case a catalyst is applied downstream these compressors oil will deactivate the catalyst causing an expensive shut down and cleaning procedure.

China with their numerous small fertilizer complexes have built up extensive experience with this kind of problem and found also effective and cost efficient solutions. This paper describes the solutions to handle dehydrogenation process even with difficult feedstock like residuum and coal and describes the solutions to solve oil fouling in gas streams caused by reciprocating compressors.

1. TX-1 Oil-Removal Agent

Shandong Lunan Chemical Plant in Shandong province in the People's Republic of China was founded in 1967, it uses coal as raw material to produce ammonia, methanol and urea. At present, ammonia capacity is 250,000 t per year, methanol capacity is 150,000 t per year, urea capacity is 350,000 t per year.

Before March 1998, the plant applied in the ammonia plant a high temperature shift process however from April 1998 the plant applied the sulfur-tolerant full low temperature shift process to save energy consumption. However the pressure drop of the shift reactor increased to 0.25 MPa from the initial 0.08 MPa during only19 days. The whole plant was forced to shut down and when the shift reactor was opened, we found a thick layer of oil and grease on the surface of the shift catalyst which resulted in a significant pressure drop increase.

Hubei Research Institute of Chemistry developed TX-1 oil removing agent to solve this problem. Before using TX-1 to protect the shift catalyst, TX-1 was first tested in the urea plant in order to compare TX-1 efficiency with coke.

The test condition were as below:
98 vol% CO_2 feedstock, flow rate 3000 m^3/ h, pressure 1.0 MPa, temperature 110-130 degree C, desulfurization reactor Φ1200×2000mm, loaded 1.5 t ferric oxide desulfurizer, H_2S content approx. 45 ppm.

500 ml TX-1 and coke were loaded by means of a stainless steel wire net and were filled symmetrically in the 1.5 t ferric oxide desulfurizer respectively, they were taken out 45 days later for plant overhaul.

The test result were as below:

Oil content in spent TX-1:	27.72%
Oil content in spent coke:	14.70%

TX-1 filled with oil became brown compared to initial light gray, however the extrudate remained intact, no powder formation and the crushing strength remained good.
From the test results we can conclude that TX-1 is the most efficient oil removal agent.

So from Feb. 2001, TX-1 Oil-Removal Agent was applied in the ammonia plant to protect the shift catalyst. The applied conditions are as below:

Syngas, temperature 55-60 degree C, pressure 2.10-2.15 MPa, filter Φ1400×3000mm.

After four years operating at full capacity, the pressure drop of the shift reactor was still 0.085 MPa compared to initial 0.08 MPa and the economic benefit is very obvious.

Conclusions

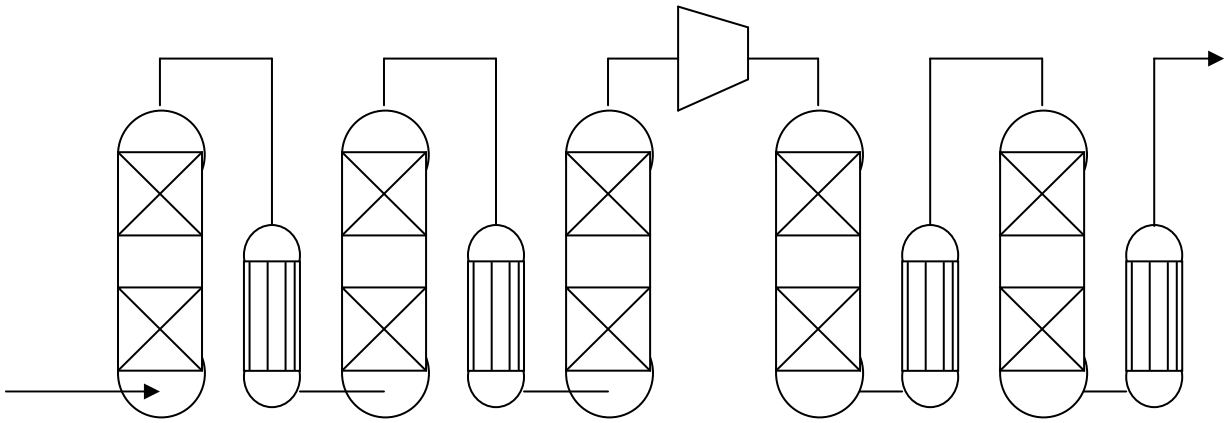
HRIC's TX-1 oil removal agent is the most efficient oil removal agent and has been successfully proven remove oil from syngas stream and CO_2 streams.

HRIC's TX-1 oil removal agent gains significant economic benefits as the lifetime of the catalysts will prolong drastically.

2. Application of TH series H_2-removal catalysts in urea plants

At present, there are approximately two hundred urea plants in China based on different raw materials such as residuum, natural gas and coal. Different raw materials need different H_2-removal processes. For example with residuum or coal as raw material, because different sulfides are present in the CO_2 feed gas, one needs an Ambient Temperature Fine Sulfur-Removal (ATFSR) process before the dehydrogenation step. If oil is present in the CO_2 gas, an oil-removal agent is also necessary.

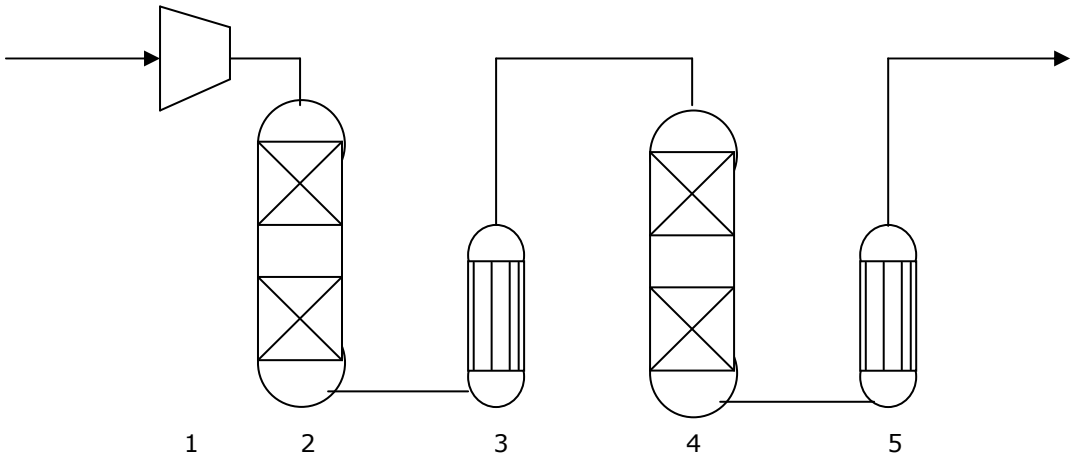
A typical flow sheet for hydrogen-removal is:



1, 2, 3, 4, 5	ATFSR unit
6	compressor
7	oil-removal tower
8	temperature adjustor
9	dehydrogenation tower
10	cooler

With residuum and coal as raw materials, TH-3 H_2-removal catalyst is always recommended because it can tolerate the low level of sulfides (less than 0.1 ppmv total sulfur) which may be present in the CO_2 feed gas after the ATFSR unit.

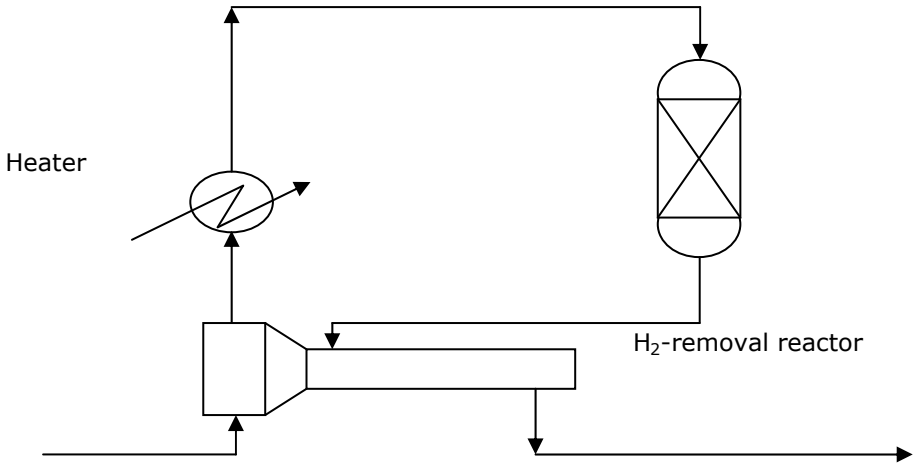
With natural gas as raw material, the sulfide in the CO_2 feed gas has already been removed to a very low level so, after removing oil, the feed gas can enter directly the H_2-removal reactor. A typical flow sheet of hydrogen-removal is then:



1 compressor
2 oil-removal tower
3 temperature adjustor
4 dehydrogenation tower
5 cooler

With natural gas as raw material, TH-2 H_2-removal catalyst is preferred.

We also have experience with an energy-saving flow scheme, which uses energy from the H_2-removal reactor to heat the inlet CO_2 feed gas. In this case the typical flow sheet is:



We have more than 30 references for hydrogen removal processes in China, all successfully in operation.

We would now like to present four different urea plant references based on residuum, natural gas (2) and coal respectively:

3.1 Application of TH-3 in the Fertilizer plant of Zhenhai Refinery, Zhejiang province

This urea plant, capacity 520,000 t/y, uses high-sulfide residuum as raw material. There is no desulfurization system, so the CO_2 feed contains approximately 1 vol-ppm total sulfur, the TH-3 H_2-removal catalyst was used since 2002.

Before adding air, the components of the carbon dioxide feed gas are:

Component	CH_3OH, ppm	CH_4	CO	CO_2	H_2	N_2	Ts, ppm
V %	100~360	0.11~0.26	0.06~0.19	98.5~98.7	0.8~1.02	0.05~0.1	≤3

The gas flow is approx 30,000 Nm^3/h, pressure 14.3 MPa, and TH-3 catalyst load 1.0 m^3. The lifetime of the first charge of TH-3 catalyst was 10451 hours. Subsequent charges have each lasted 1 – 1.5 years.

The operating data are:

Operating Data of TH-3 Hydrogen-Removal Catalyst

Date	CO_2 flow (Nm^3/h)	Inlet O_2 vol.%	Inlet Ts ppm	Inlet temp. °C	Outlet temp. °C	Residual H_2 ppm	Pressure drop MPa
2002-04-25	28825	1.20	1.89	158	202	27.7	0.032
2002-05-15	28542	1.24	0.79	153	197	2	0.030
2002-06-14	29115	1.28	0.67	153	197	22.3	0.030
2002-07-15	29126	1.22	0.73	153	196	2	0.029
2002-08-15	27071	1.25	0.64	153	195	47.8	0.027
2002-09-15	24191	1.28	0.96	156	197	187	0.023
2002-11-15	23553	1.27	0.74	166	209	187	0.023
2002-12-15	27436	1.27	0.53	167	211	149	0.028
2003-01-15	25032	1.27	0.48	178	222	10	0.026
2003-02-15	23192	1.23	0.56	180	223	51	0.023

At the outlet of the TH-3 H_2 removal catalyst bed the residual H_2 content was less than 200 vol-ppm versus the specified maximum of 500 vol-ppm.

3.2 Application of TH-3 in No.2 chemical plant of Chuanhua Group, Sichuan province

This urea plant, capacity 600,000 t/y, uses natural gas as raw material. TH-3 H_2-removal catalyst has been used since 2004.

Before adding air, the components of the carbon dioxide feed gas are:

Component	O_2	CO_2	H_2	N_2	Ts, ppm
V %	0.91	94.32	0.9	3.87	≤0.1

Gas flow is approx 38,000 Nm^3/h, pressure 8 MPa, and TH-3 catalyst volume 2.0 m^3. The lifetime of the first charge of TH-3 catalyst was more than three years.

The operating data are:

Operating Data of TH-3 Hydrogen-Removal Catalyst

Date	Inlet temp. °C	Outlet temp. °C	Inlet O_2 %	Inlet H_2 %	Residual H_2 ppm
2004-02-27	137	156	0.51	1.00	<70
2004-05-17	135	158	0.51	1.00	<70
2004-06-02	144	160	0.52	1.00	<70
2004-08-26	151	177	0.50	0.98	<70
2004-10-13	139	150	0.55	0.99	<70
2004-10-28	141	160	0.54	1.10	<70
2005-02-06	147	164	0.49	0.95	<70
2005-03-07	144	172	0.55	1.00	<70
2005-04-05	147	176	0.50	1.10	<70
2005-04-06	146	173	0.49	0.92	<70
2006-02-14	148	178	0.49	1.00	<70
2006-03-10	147	170	0.52	0.96	<70

2006-04-05	148	173	0.50	1.09	<70
2006-10-09	143	172	0.49	0.92	<70

Conclusions:

(1) The target residual H_2 is 100 ppm. During the 3 years' application of TH-3 Catalyst, the residual H_2 was always less than 70 ppm.

(2) The strength of TH-3 catalyst is good. The pressure drop of catalyst layer was 0.02 MPa.

(3) The activity of the TH-3 catalyst is excellent. According to the design, there is no heater before the H_2-removal reactor. The temperature of the raw CO_2 gas from the compressor was normally about 141 ^oC. However, during several process start-ups and shut-downs, we found that, even when the inlet temperature of the catalyst bed only was 115 ^oC, the catalyst still had excellent activity and the residual H_2 was still below 70ppm.

3.3 Application of TH-2 in Sichuan Meifeng Ammonia Plant

This urea plant, capacity 180,000 t/y, also uses natural gas as raw material. There is a high temperature fine sulfur-removal process (Co-Mo hydrogenation catalyst plus ZnO), so the total sulfur in carbon dioxide feed gas is about 0.1ppm. TH-2 catalyst has been used since August 2000.

Before adding air, the components of the carbon dioxide feed gas are:

Component	CH_3OH	CH_4	CO	CO_2	H_2
V, %	Trace	200ppm	~0.15	~99	~1.0

After adding air, the oxygen content is about 1.2%. Gas flow is approx 9,000 Nm^3/h, pressure 14.5 MPa, and TH-2 catalyst load 0.502 m^3. There is no ZnO sulfur-removal protective layer. Lifetime of TH-2 catalyst was more than six years.

The operating data are:

Operating Data of TH-2 Hydrogen-Removal Catalyst

Date	Inlet temp. °C	Outlet temp. °C	Inlet H_2 ppm	Residual H_2 ppm	Pressure drop MPa
2000-08-20	150	183	6751	85	0.029
2000-09-15	150	181	6458	90	0.031
2000-10-21	150	184	7143	145	0.029
2000-11-25	148	182	6925	97	0.030
2000-12-18	150	180	6270	75	0.031
2001-01-16	150	183	6896	125	0.030
2001-02-19	151	181	6104	113	0.030
2001-03-20	151	182	6562	123	0.029
2001-04-21	150	182	6560	108	0.030
2001-05-22	146	171	5591	112	0.031
2001-06-20	148	173	5713	109	0.029
2001-07-20	150	176	5235	107	0.030

Total sulfur in carbon dioxide feed gas is about 0.1ppm, so the catalyst operates at the low inlet temperature 150~160 °C. This reduces ammonia consumption by one kg per tonne of urea produced, increasing annual profit by about 250 thousand Yuan (= US$ 37,000). The temperature rise through the reactor is 25~35 °C, residual $H_2 \leq 150$ppm, which makes the equipment run safely.

Above spent sample after 6 years has been analyzed through XRF; we found that sulfur content is approximately 10 %(wt). We calculated the average sulfur content according above applied conditions of the inlet gas feed and concluded that the average inlet total sulfur content is 0.05 ppm. From this result, we can conclude that sulfur poison still is a key reason of the catalyst deactivation in Natural Gas based ammonia plants in China. The inlet total sulfur content of reforming catalysts is controlled below 0.5 ppm, and not 0.1 ppm. This means there are higher sulfur content in CO_2 feed gas of urea plants in China than that in urea plants outside China. We consider that in case the sulfur content of CO_2 feed gas is decreased to 0.01-0.02 ppm, the lifetime of catalyst will be prolonged to 10-15 years.

3.4 Application of TH-3 in Jiangsu Huachang Chemical plant

This urea plant, capacity 150,000 t/y, uses coal as raw material. There are some traces of CO, H_2, CH_4, N_2 and sulfides in the CO_2 feed gas so, before dehydrogenation, an ATFSR process is necessary. TH-3 H_2-removal catalyst has been used since 2005.

The components of the carbon dioxide feed gas are:

Component	N_2	CO	CO_2	H_2	Ts, ppm
V %	0.3	0.07-.01	98.5	0.5-0.6	3-40

Gas flow is approx 10,000Nm^3/h, pressure 15.5MPa, and the TH-3 catalyst load 0.4m^3. The lifetime of the first charge of TH-3 catalyst was about 3.5 years.

The operating data are:

Operating Data of ATFSR before H_2-Removal

Date	Before ATFSR(ppm)		After ATFSR(ppm)	
	H_2S	COS	H_2S	COS
2005-07-02	1.55	0.23	<0.03	<0.03
2005-10-22	2.85	0.38	<0.03	<0.03
2006-04-24	1.62	0.25	<0.03	<0.03
2006-10-25	3.85	0.27	<0.03	<0.03
2007-04-26	9.60	0.39	<0.03	<0.03
2007-10-26	7.63	0.46	<0.03	<0.03
2008-05-26	6.53	0.51	<0.03	<0.03
2008-10-26	6.35	0.42	<0.03	<0.03

Operating Data of TH-3 Hydrogen-Removal Catalyst

Date	Inlet temp. °C	Outlet temp. °C	Inlet H_2 ppm	Residual H_2 ppm	Pressure drop MPa
2005-07-02	162	181	5300	<30	0.027
2005-10-22	160	178	5200	<30	0.028
2006-01-27	162	176	5000	<30	0.030
2006-04-24	172	180	5100	<30	0.031
2006-07-10	185	186	5450	35	0.031
2006-10-25	162	182	5700	38	0.033
2007-01-26	168	183	4950	45	0.032
2007-04-26	169	175	4800	53	0.031
2007-07-26	175	178	4470	65	0.035
2007-10-26	185	186	4120	83	0.035
2008-01-26	162	181	5020	<30	0.034
2008-03-26	165	180	4830	<30	0.035
2008-05-26	170	182	4580	<30	0.036
2008-07-26	175	183	5220	<30	0.036
2008-09-26	178	185	5200	<30	0.037

The target residual H_2 is 100 ppm. During the four years application of TH-3 catalyst, it has always been below this level.

4 Conclusions

The application of new H_2-removal technology provides safety in urea production and is essential in any type of urea plants.

Ambient Temperature Fine Sulfur-Removal (ATFSR) new processes effectively protect the H_2-removal catalyst from sulfur poisoning thereby extending the catalyst life. In fact we have abundant experience to apply H_2-removal catalysts in difficult circumstances such as residuum or coal as raw materials and/or with reciprocating compressors which always lose some amount of oil.

Our TH-3 and TH-2 H_2–removal catalysts are very reliable and cost effective catalysts for the dehydrogenation of the CO_2 feed to a urea plant.

HRIC's TX-1 oil removal agent is the most efficient oil removal agent and has been successfully proven remove oil from syngas stream and CO_2 streams.

HRIC's TX-1 oil removal agent gains significant economic benefits as the lifetime of the catalysts will prolong drastically.

湖北省化学研究所
HUBEI RESEARCH INSTITUTE OF CHEMISTRY

An Introduction to Gas Purification Center of Hubei Research Institute of Chemistry (HRIC)

HRIC is a National Key Industrial Base for CO water gas shift and gas purification catalysts. The research and development activities of the center are led by three professors, six associate professors, one nationally authorized expert and two provincially authorized experts.
Through 20 years hard work, our center has developed H_2-removal, O_2-removal, hydrocarbon-removal, sulfur-removal, Cl^- removal gas purification technologies plus a whole set of ambient temperature fine sulfur-removal (ATFSR) new technologies. Above technologies have been applied in methanol, ammonia, urea, food CO_2, fine chemical industry (DMF, HAC, TDI, MDI), petrochemical industry, natural gas chemical industry, electronics and environment protection industries.

HRIC is the largest hydrogen converter catalyst supplier in China (market share is 60%) and has achieved great experience with the purification of gases in ammonia plants based on coal or heavy oil gasification technologies and of course with the purification of gases in ammonia plants based on natural gas.

In case of interest please contact for more details Mr. Lei Jun
T +86 (27) 874 083 82
F +86 (27) 874 135 14
E juniyun2003@yahoo.com.cn
I www.haiso.com.cn