Application of TH series H_2-removal catalysts in urea plants

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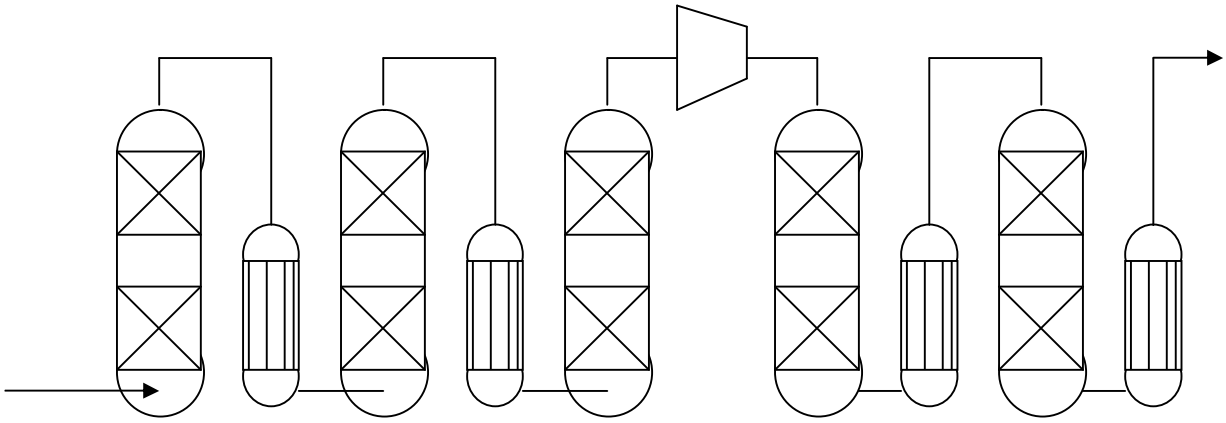
At present, there are approximately two hundred urea plants in China based on different raw materials such as residuum, natural gas and coal. Different raw materials need different H_2-removal processes. For example with residuum or coal as raw material, because different sulfides are present in the 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:

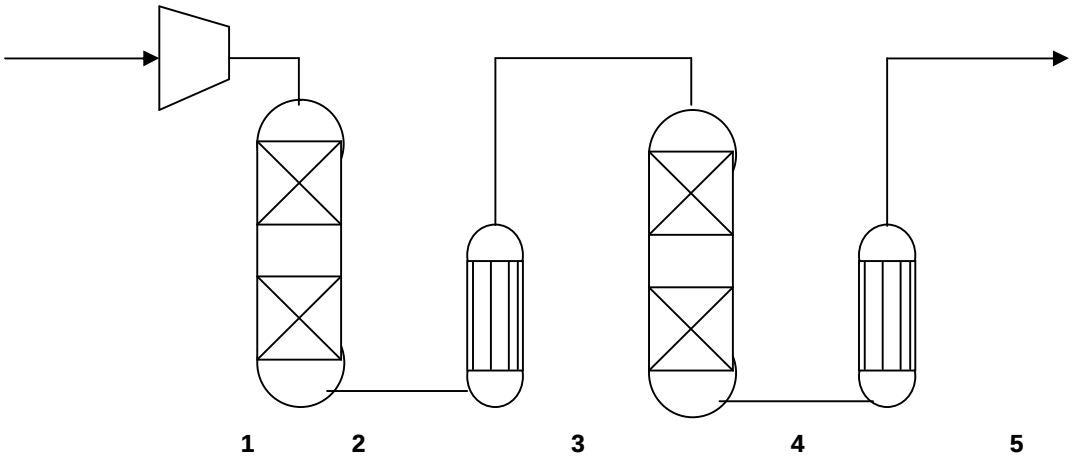


1 2 3 4 5 6 7 8 9 10

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.

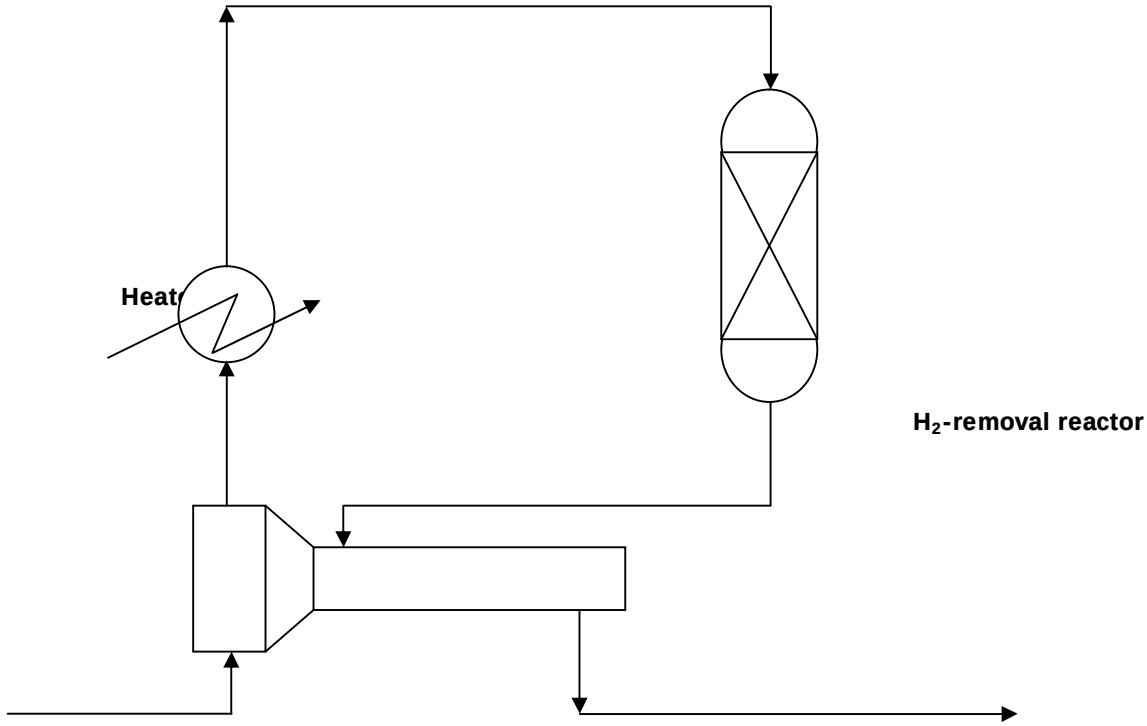
With natural gas as raw material, the sulfide in the CO_2 feed gas has already been removed to a very low level so, after removing oil, the feed gas can enter directly the H_2-removal reactor. A typical flow sheet of hydrogen-removal is then:



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

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
2002-10-15	27822	1.25	0.67	160	206	339	0.028
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
2002-12-25	28590	1.23	0.67	175	218	229	0.031
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
2003-03-05	24008	1.19	0.54	182	226	235	0.024
2003-03-17	28496	1.25	0.55	193	236	234	0.032
2003-03-19	28926	1.27	0.60	200	242	405	0.033
2003-04-15	25836	1.2	0.51	200	242	305	0.028
2003-05-15	24823	1.21	0.64	198	239	289	0.025
2003-06-15	23342	1.23	0.58	210	251	391	0.024
2003-07-15	23667	1.21	0.45	210	251	674	0.023

Notice: Hydrogen was leaked out through bypass valve when red figures in table above.

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.

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 100ppm. During the 3 years′ application of TH-3 Catalyst, the residual H_2 was always less than 70ppm.

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

(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°C. However, during several process start-ups and shut-downs, we found that, even when the inlet temperature of the catalyst bed only was 115°C, the catalyst still had excellent activity and the residual H_2 was still below 70ppm.

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 9,000Nm^3/h, pressure 14.5MPa, and TH-2 catalyst load 0.502m^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 analyze through XRF, we found that sulfur content is approx 10%(wt), we calculated average inlet feed gas sulfur content according above applied condition, calculated result is that average inlet total sulfur content is 0.05ppm. From the result, we can know that sulfur poison still is a key reason of catalyst deactivation, in NG based ammonia plant of China, inlet total sulfur content of reforming catalyst is controlled below 0.5ppm, not 0.1ppm, so there are higher sulfur content in CO_2 feed gas of urea plant than that of western plant. We consider that

sulfur content of CO_2 feed gas is decreased to 0.01-0.02ppm, lifetime of catalyst will be prolonged to 10-15 years.

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

Conclusion

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.