Purification of Foodgrade CO_2

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Abstract

This paper shows the foodgrade CO_2 standard of the International Society of Beverage Technologists and points out that the total sulfur, benzene and total hydrocarbon specifications are the most difficult to achieve. The paper describes in detail a purification process for foodgrade CO_2, developed by Hubei Research Institute of Chemistry and Hangzhou Kuaikai Company, and its main industrial applications. As determined by the Atlantic Analytical Laboratory and the Chemical Gas Supervision and Test Center, the finished product CO_2 totally satisfies all 20 items of the IBST foodgrade CO_2 standard and has been approved by the Coca Cola (China) Company and by the Pepsi-Cola Company.

Introduction

Foodgrade CO_2 is used widely in the beverage industry, tobacco swelling, supercritical extraction, etc. In recent years, the demand for foodgrade CO_2 gas has increase rapidly. Feed gas for foodgrade CO_2 comes mainly from nitrogen fertilizer factories, lime kilns and fermentation plants. The foodgrade CO_2 standard of the International Society of Beverage Technologists (ISBT) [1] is shown in Table 1; there are 20 items specified, which is very stringent. Of these 20 items, the most severe are :

1] Total sulfur ≤0.1 ppm
2] Benzene content ≤20 ppb
3] Total hydrocarbon content (as CH_4) ≤50ppm (of which CH_4 ≤30 ppm)

Since 1991 we have developed various ambient temperature fine sulfur-removal catalysts and, using them, the JTL-1, JTL-4 and JTL-5 ambient temperature fine sulfur-removal processes. These have been successfully applied in the fields of ammonia synthesis, the fine chemical industry, the electrical industry, environmental protection etc. with clear benefits [2, 3, 4, 5, 6]. By combining much research work on sulfur-removal from CO_2 gas, we have improved our JTL-1 process to remove sulfides from CO_2 gas and have obtained beneficial effects [7]. At the same time, we have developed THC-1 Hydrocarbon-Removal Catalyst (noble metal), which can remove benzene and various hydrocarbons from CO_2 feed gas, so as to meet the ISBT standard for foodgrade CO_2. Thus we and Hangzhou Kuaikai Company successfully developed a purification process for foodgrade CO_2 which has been applied in six foodgrade CO_2 plants and underwent expert examinations by the Zhejiang Province Science and Technology Office in December 2005. This paper will introduce its principles, characteristics and industrial applications.

Table 1- Foodgrade CO_2 Standard of ISBT

Items	Requirement
CO_2 Purity	≥ 99.9% (v/v)
Odor	No foreign odor
Odor and Taste in Water	No foreign odor and taste
Water	≤ 20 ppmv
Total Sulfur	≤ 0.1 ppmv
Total Hydrocarbon Content (as CH_4)	≤ 50 ppmv (CH_4 ≤30 ppmv)
Oxygen	≤ 30 ppmv
Ammonia	≤ 2.5 ppmv
Nitrogen oxides (NO/NO_2)	≤ 2.5 ppmv
Carbon Monoxide	≤ 10 ppmv
Carboxyl Sulfide	≤ 0.1 ppmv
Hydrogen sulfide	≤ 0.1 ppmv
Sulfur Dioxide	≤ 0.1 ppmv
Acidity	Acceptable
Phosphine	≤ 0.3 ppmv
Total Non-Volatile Residue	≤ 10 ppmv
Total Non-Volatile Organic Residue	≤ 5 ppmv
Acetaldehyde	≤ 0.2 ppmv
Aromatic Hydrocarbons, Benzene	≤ 0.2 ppmv
Appearance in Water	No color or turbidity

Purification process of foodgrade CO_2

To meet the requirements of foodgrade CO_2 standard of ISBT, we developed the purification process of foodgrade CO_2 shown in Figure 1:

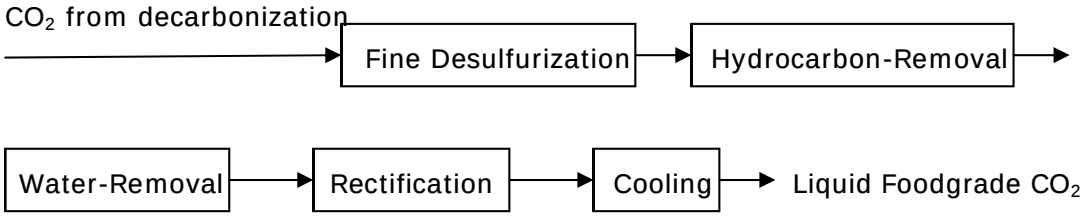


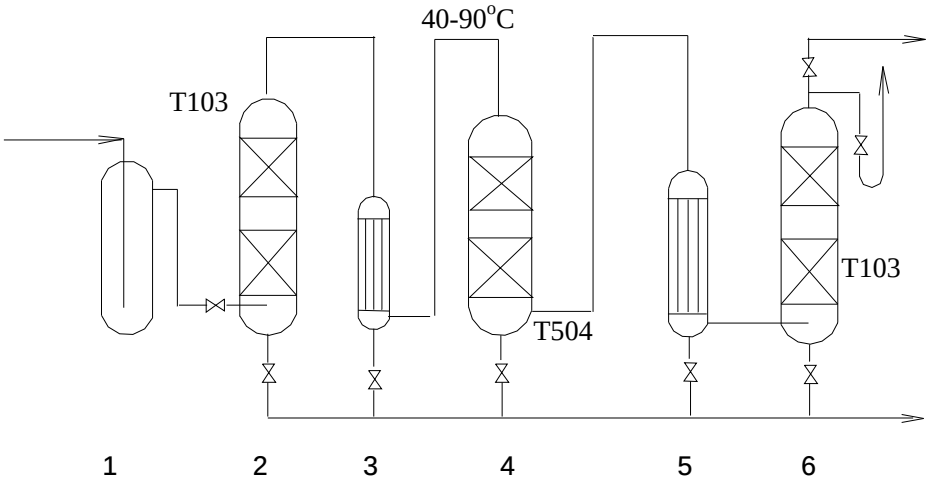
Figure 1- Flow Sheet of Purification Process of Foodgrade CO_2

1. Introduction to JTL-1 process

CO_2 gas always comes from the CO_2- removal systems of ammonia plants. Its temperature is low (about 10 - 50^oC) so high-temperature sulfur-removal catalysts are not suitable. The traditional method uses ordinary activated carbon or ferric oxide. For reasons of competitive adsorption, the sulfur-removal effect of these absorbents is very restricted

when they are applied to remove sulfides (such as H_2S, COS, SO_2) from CO_2 gas, their precision is limited (> 1 ppm), and sulfur capacity is low. So it is difficult to remove sulfides satisfactorily in the manufacture of foodgrade CO_2. The JTL-1 ambient temperature fine sulfur-removal process has been used to solve this problem.

Figure 2 shows a typical JTL-1 process for foodgrade CO_2. The first sulfur-removal tower is to remove H_2S from the CO_2 feedgas to prevent sulfiding of the hydrolysis catalyst, which converts COS to H_2S (COS + H_2O => H_2S + CO_2). H_2S is then removed in the second sulfur-removal tower.



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

Figure 2- Flow Sheet of JTL-1 Process

2. Introduction to THC-1 Hydrocarbon-Removal Catalyst

We have developed various noble metal catalysts. To date the TH series H_2-removal catalysts, TO series O_2- removal catalysts and THC-1 Hydrocarbon -removal catalyst have been applied successfully. Since first application of TH-2 and TH-3 Urea H_2-removal catalysts in the fertilizer plant of the Zhenhai Oil Refinery in 1999 [8], they have been applied in large, medium and small ammonia plants with natural gas, coal or residual oil as raw material. Their share of the Chinese market has reached 70%; TO-2 O_2- removal catalyst has been applied to purify N_2 in air separation plants and THC-1 Hydrocarbon-removal catalyst has been applied in six foodgrade CO_2 plants since 2003.

Properties and technical parameters of THC-1 catalyst

These are shown in Table 2,

Table 2- Properties and Technical Parameters of THC-1 Catalyst

Item	Properties	Item	Technical parameter
Components	Pt-Pd/Al_2O_3+additive	Space velocity	1000-2000 h^{-1}
Appearance	Grey spheres	Inlet temperature	320-470 ^oC
Diameter	2-3.5 mm	Pressure	≤ 16.0 MPa
Bulk density	0.5-0.7 kg/l	Inlet total sulfur	≤ 0.1ppmv
Crushing strength	≥20N/point	Outlet total hydrocarbon (as CH_4)	≤ 5-30 ppm
		Outlet benzene	≤ 20 ppb
		life	2-5 years

Principles of THC-1 catalyst

THC-1 catalyst can remove hydrocarbons, CO, H_2, VOx and VOC by catalytic oxidation.

$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$

$C_6H_6 + {}^{15}/_2\ O_2 \longrightarrow 6\ CO_2 + 3\ H_2O$

$C_xH_y + (x + {}^y/_4)\ O_2 \longrightarrow x\ CO_2 + {}^y/_2\ H_2O$

$C_xH_yO_2 + (x + {}^y/_4 - 1)\ O_2 \longrightarrow x\ CO_2 + {}^y/_2\ H_2O$

$2\ CO + O_2 \longrightarrow 2\ CO_2$

$2\ H_2 + O_2 \longrightarrow 2\ H_2O$

Main laboratory data for THC-1 catalyst

2.3.1 Effect of temperature on removal of benzene and methane

The data in Table 3 show that the outlet CH_4 and benzene content satisfy the ISBT standard for foodgrade CO_2 when the process temperature is above 350 ^oC.

Table 3 - Effect of Temperature on Removal of Benzene and Methane (original size)

Temperature, ^oC	THC-1 hydrocarbon-Removal Catalyst	
	Outlet CH_4 content, ppmv	Outlet C_6H_6 content, ppmv
450	≤ 0.01	≤ 0.01
400	≤ 0.01	≤ 0.01
375	≤ 0.01	≤ 0.01
350	10.1	≤ 0.01
325	348	0.172
300	1311	0.8
275	1508	0.94
250	2076	1.35

Note: inlet CH_4 content, 2500ppm; inlet benzene content, 35ppm; SV, 500 h^{-1}.

CH_4 standard gas content, 9.0ppm, comes from Tianhong Chemical Co.Ltd. of Wuxi city, Jiangsu province. Benzene standard gas content, 1.0ppm, was supplied by BOC

Canada.

2.3.2 Effect of Space Velocity on removal of benzene and methane

The data in Table 4 show that outlet CH_4 and benzene content satisfy the ISBT standard for foodgrade CO_2 when the space velocity (SV) is $1000h^{-1}$.We believe that the outlet benzene content will satisfy the ISBT at SV $2000\text{-}3000h^{-1}$ when the benzene content is less than 10ppm or the temperature is above 400 ^oC.

Table 4- Effect of Space Velocity on removal of Benzene and Methane (original size)

Space velocity, h^{-1}	THC-1 Hydrocarbon-removal catalyst	
	Outlet CH_4content, ppmv	Outlet C_6H_6 content, ppmv
500	≤ 0.01	≤ 0.01
1000	1.8	0.010
2000	14	0.04
3000	323	0.13

Note: inlet CH_4 content, 2500ppm; inlet benzene content, 35ppm; temperature, 400^oC.

Industrial applications of Foodgrade CO_2 purification process

1. Industrial application in Henan Datong Chemical Ltd.

Henan Datong Chemical Ltd. uses coal as raw material to produce ammonia [80,000 t/a] and methanol [30,000 t/a]. Formerly CO_2 desorbed from the decarbonization section was directly emitted to air, which polluted the environment. In recent years, the demand for foodgrade CO_2 gas increased rapidly so the plant decided to build a 15,000 tons/year foodgrade CO_2 unit in 2004.

1.1 Flow sheet and operating conditions

The flow sheet is shown in Figure 3:

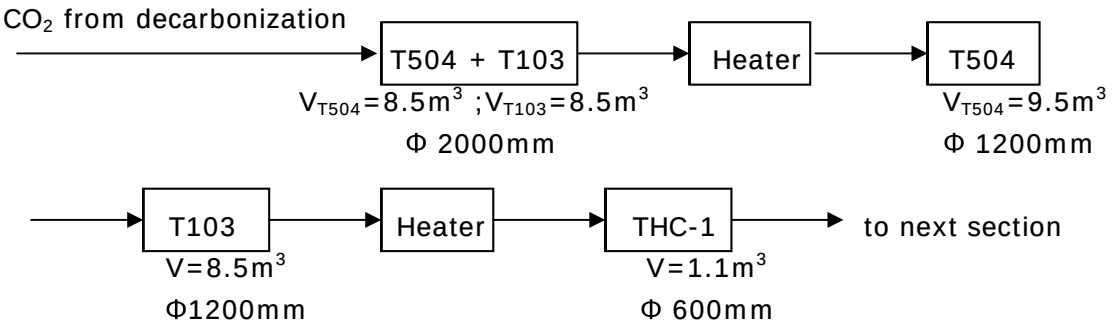


Figure 3- Flow Sheet of Purification in Henan Datong Chemical Ltd.

The components of the CO_2 feed gas are shown in Table 5

Table 5 - Components of CO_2 Feed Gas in Henan Datong Chemical Ltd.

Components	CO_2	CO	O_2	H_2	Total hydro-carbon	Benzene	H_2S	COS
vol %	98	0.2	0.2	0.6	0.18	12.4 ppm	< 0.1 ppm	7-21 ppm

Operating conditions: gas flow 1,500 Nm^3/h; pressure 0.3-1.8 MPa; sulfur-removal temperature 30-100^oC; hydrocarbon-removal temperature 400-450^oC.

1.2 Operating experience

In the plant, the maximum content of COS reaches 21 ppmv, so we use two stages of sulfur-removal [as in Figure 3, if COS content is less than 10 ppmv, one stage of sulfur-removal is enough]. The operating data of the sulfur-removal section are shown in Table 6.

Table 6 - Operating Data of Sulfur-Removal Section

Time	Inlet of sulfur-removal, ppmv		Outlet of sulfur-removal, ppmv	
	H_2S	COS	H_2S	COS
2005-06-01	0.08	7	<0.03	<0.03
2005-06-02	0.10	21	<0.03	<0.03
2005-06-03	0.07	18	<0.03	<0.03

Note: above data are analyzed by HC-2 Trace Sulfides Analyzer developed by Hubei Research Institute of Chemistry.

The data of Table 6 show that outlet H_2S and COS content of sulfur-removal section are both below 0.03 ppmv which satisfies the requirement of the ISBT standard. For CH_4, benzene and total hydrocarbon content, please see the data in Table 7:

Table 7- the Operating Data of Hydrocarbon-Removal Section

	THC-1 working Temp.	Outlet O_2 content of THC-1	C_6H_6, ppm	CH_4, ppm	Total hydrocarbon (as CH_4), ppm	Testing company
Inlet CO_2			12.4		1800	CGSTC*
			0.42	1078		HRIC*
Outlet CO_2 of THC-1	430°C	0.25%	<0.02		7.8	CGSTC
					4.21	THAO*
			<0.01	5.8		HRIC
	445°C	0.25%			2.98	THAO
			<0.01	0.3		HRIC

Note: CGSTC = Chemical Gas Supervision and Test Center
HRIC = Hubei Research Institute of Chemistry
THAO = Total Hydrocarbon Apparatus Online

From the data of Table 7, we can see the data tested by different companies were basically consistent except the data for benzene in the inlet CO_2 for which the testing times were different. These data also show that the outlet CH_4, benzene and total hydrocarbon contents of hydrocarbon-removal section all met the ISBT standard. As determined by the Chemical Gas Supervision and Test Center [the authoritative company appointed by the Chinese government], finished product CO_2 totally satisfied the 20 items of the ISBT standard for foodgrade CO_2. This equipment has run very well for about one year, bringing large economic benefits to the plant.

2. Industrial application in Jinan Fertilizer Plant

Jinan Fertilizer Plant uses coal as raw material to produce ammonia [120,000 t/a] and methanol [40,000 t/a]. Like Henan Datong Chemical Ltd., the plant used to release CO_2 desorbed from the decarbonization section to atmosphere. When the demand for foodgrade CO_2 gas increased rapidly in 2004, the plant decided to build a 20,000 tons/year foodgrade CO_2 unit.

2.1 Flow sheet and operating conditions

The flow sheet is shown in Figure 4:

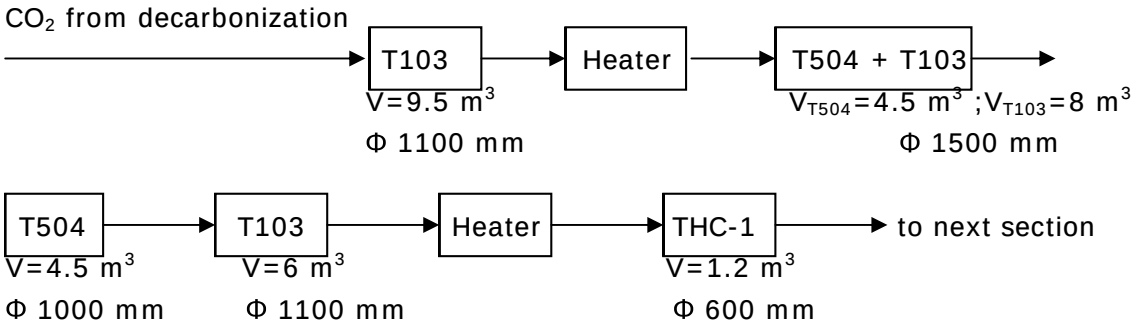


Figure 4- CO_2 Purification Flowsheet in Jinan Fertilizer Plant

The components of the CO_2 feed gas are shown in Table 8

Table 8 - Components of CO_2 Feed Gas in Jinan Fertilizer Plant

Components	CO_2	CO	O_2	H_2	Total hydrocarbon	Benzene	H_2S	COS
vol %	98	0.26	0.2	1.0	0.2	2.7 ppm	< 60 ppm	< 60 ppm

Operating conditions: gas flow 1,920 Nm^3/h; pressure 0.3-1.8 MPa; sulfur-removal temperature 30-100^oC; hydrocarbon-removal temperature 400-450^oC.

2.2 Operating experience

The data of Table 8 show that the maximum design COS content was 60 ppm, so we adopted two stages of sulfur-removal [as in Figure 4]. The operating data for the sulfur-removal and hydrocarbon-removal sections are shown in Table 9 and Table 10 respectively.

Table 9 - Operating Data for Sulfur-Removal Section

Time	Inlet of sulfur-removal, ppmv		Outlet of sulfur-removal, ppmv	
	H_2S	COS	H_2S	COS
2005-06-06	1.5	40	<0.03	<0.03
2005-06-07	3.8	47	<0.03	<0.03
2005-06-08	1.2	44	<0.03	<0.03
2005-06-09	0.65	30	<0.03	<0.03
2005-06-10	0.55	36	<0.03	<0.03
2005-06-11	0.65	45	<0.03	<0.03
2005-06-12	1.25	36	<0.03	<0.03

Note: above data are analyzed by HC-2 Trace Sulfides Analyzer developed by Hubei Research Institute of China.

Table 10 - Operating Data for Hydrocarbon-Removal Section

	THC-1 working Temp.	Outlet O_2 content of THC-1	C_6H_6, ppmv	CH_4, ppmv	Total hydrocarbon (as CH_4) ppmv	Testing company
Inlet CO_2			2.7		2000	CGSTC
			4.3	1960		HRIC
Outlet	445	0.25%	<0.02		<2	CGSTC
CO_2 of			<0.01	0.6		HRIC
THC-1	425	0.25%	<0.01	0.87		HRIC

The data in Table 9 show that the outlet H_2S and COS contents from the sulfur-removal section are both less than 0.03 ppmv.

From the data in Table 10, we can see the data tested by different companies are basically consistent, and that the outlet CH_4, benzene and total hydrocarbon content from the hydrocarbon-removal section all meet the ISBT standard. As determined by the Chemical Gas Supervision and Test Center, the finished product CO_2 totally satisfied the 20 items specified in the ISBT standard. The equipment has run very well for about one year bringing large economic benefits to the plant.

3. Industrial Application in Liuzhou Fertilizer Plant

Liuzhou Fertilizer Plant uses coal as raw material to produce ammonia and methanol. The plant decided to build a 10,000 tons/year foodgrade CO_2 plant in 2003.

3.1 Flow sheet and operating conditions

The flow sheet is shown in Figure 5:

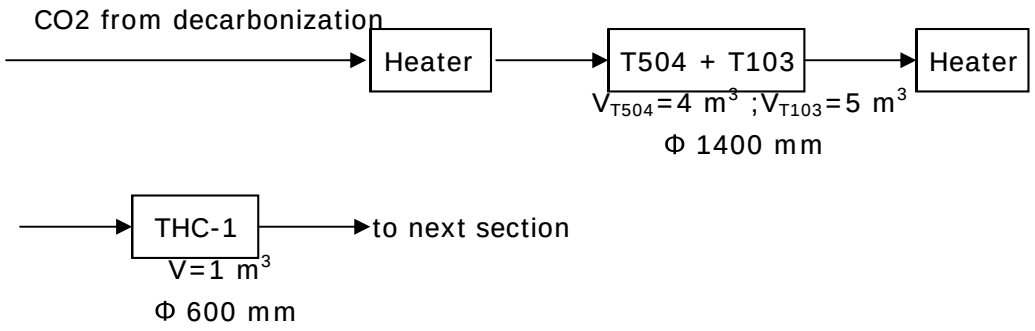


Figure 5- CO_2 Purification Flow Sheet in Liuzhou Fertilizer Plant

Operating conditions: gas flow 1,200 Nm^3/h; pressure 0.3-1.8 MPa; sulfur-removal temperature 30-100^oC; hydrocarbon-removal temperature 400-450 ^oC;
Inlet H_2S is less than 2 ppmv, COS is less than 2 ppmv.

3.2 Operating experience

Inlet H_2S and COS contents are low so fine sulfur-removal is correspondingly easy; outlet H_2S and COS contents are consistently less than 0.03 ppmv.

The operating data for the hydrocarbon-removal section are shown in Table 11.

Table 11- Operating Data of Hydrocarbon-Removal Section

	THC-1 working Temp.	Outlet O_2 content of THC-1	C_6H_6, ppm	CH_4, ppm	Total hydrocarbon (as CH_4) ppm	Testing company
Inlet CO_2			17.3	104	245	CNSSRC*
Outlet CO_2 of THC-1	425^oC	0.25%	< 0.02		< 5	CGSTC
	425^oC	0.25%	< 0.002	< 0.5	< 0.5	AAL*

Note: CNSSRC = China National Standard Substance Research Center
AAL = Atlantic Analytical Laboratory

From the data of Table 11, we can see that the outlet CH_4, benzene and total hydrocarbon contents of hydrocarbon-removal section all satisfy the requirements of the ISBT standard for foodgrade CO_2. As determined by AAL, the finished product CO_2 totally satisfies all 20 items of the ISBT standard and the product has been approved by Coca Cola (China) Company and the Pepsi-Cola Company. This equipment has run very well for more than two years bringing large economic benefits to the plant.

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