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Study and practice of alcohol/aldehyde flexible production technology in butanol facility

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Abstract. Butanol facility of Yankuang Lunan Chemicals Co., Ltd. adopts DAVY/D0W low pressure oxo synthesis process, with design capacity of n-butanol at 135kt/a and iso-butanol at 15kt/a, and the butanol facility only sells n-butanol/iso-butanol products to foreign countries. However according to market survey, the market of the intermediate products n-butyl aldehyde/iso-butyl aldehyde produced by the butanol facility fails to be saturated, and the price of n-butanol/iso-butanol and n-butyl aldehyde/iso-butyl aldehyde fluctuates with the market situation, and the profit-creating capacity of various products differs greatly, therefore, it is of great significance to make technological reformation of the butanol facility to realize alcohol/aldehyde flexible production. Upon analysis and study, by using efficient energy-saving distillation technology, namely adding a butyl aldehyde isomer tower to the system, the butanol facility can realize alcohol/aldehyde flexible production by organizing the production mode flexibly. After reformation of the butanol facility, n-butyl aldehyde/iso-butyl aldehyde can be separated effectively, and the quality of the output products could reach relevant international quality standards and requirements; the butanol facility can organize the production mode flexibly, and put the product portfolio with high profit-creating capability into market as much as possible. Under the current production mode, many indicators of product consumption per ton of products in the butanol facility decrease effectively, and the butanol facility can create an addition annual benefit of about RMB 206.1718 million compared with that before reformation.

Keywords. butanol facility, n-butanol, iso-butanol, n-butyl aldehyde, iso-butyl aldehyde, alcohol/aldehyde flexible production, butyl aldehyde isomer tower, economic benefit.

1. Introduction

Established in May 2012, Yankuang Lunan Chemicals Co., Ltd. (hereinafter referred to as “Lunan Chemicals) is a combination of the former Lunan Chemical Fertilizer Plant, Yankuang Guotai Chemicals Co., Ltd. and Yankuang Guotai Acetyl Chemicals Co., Ltd. Over the years, based on the advanced coal gasification technology that is constantly developed and upgraded, Lunan Chemicals has formed the carbon-chemical industrial chain led by urea and methanol. For further development and expansion, in accordance with the existing production process and product configuration conditions, Lunan Chemicals has developed toward fine chemicals and high-end products gradually in recently years, and at present, its products mainly include methanol, butanol, acetic acid,methyl acetate, butyl acetate, acetic ether, acetic anhydride, urea, hydrogen peroxide, cyclohexanone, caprolactam and so on.

Butanol facility of Lunan Chemicals adopts DAVY/D0W low pressure oxo synthesis process, with design capacity of n-butanol at 135kt/a and iso-butanol at 15kt/a, and the butanol facility only sells n-butanol/iso-butanol products to foreign countries. However according to market survey, the market of the intermediate products n-butyl aldehyde/iso-butyl aldehyde produced by the butanol facility fails to be saturated, and the price of n-butanol/iso-butanol and n-butyl aldehyde/iso-butyl aldehyde fluctuates with the market situation, and the profit-creating capacity of various products differs greatly, therefore, it is of great significance to make technological reformation of the butanol facility to realize alcohol/aldehyde flexible production. Relevant conditions regarding alcohol/aldehyde flexible production of the butanol facility of Lunan Chemicals are briefly introduced below.

2. Technological process of the butanol facility and market profile of butyl aldehyde products

2.1. Brief description of technological process of the butanol facility

In oxo synthesis reactor, under the action of catalyst, the propylene and syngas whose H_2/CO is 1.02 (molar ratio) react to generate the intermediate product - mixed butyl aldehyde (n-butyl aldehyde/iso-butyl aldehyde), which is then sent to the butanol unit; in the butanol unit, under the action of special hydrogenation catalyst in butanol converter, the butyl aldehyde and hydrogen sent by the pressure swing adsorption unit react to generate mixed butanol (n-butanol/iso-butanol), which then outputs qualified n-butanol and iso-butanol products via the distillation tower and butanol isomer tower, and then the products are sent to the tank field for storage and selling.

2.2. Market profile of butyl aldehyde products

2.2.1. Purpose of n-butyl aldehyde/iso-butyl aldehyde

During production process of the butanol facility, the intermediate products involved are n-butyl aldehyde/iso-butyl aldehyde, n-butyl aldehyde/iso-butyl aldehyde, which have a broad range of application, and the details are as follows:

(1) N-butyl aldehyde: n-butyl aldehyde is an important intermediate product, and can produce 2-ethyl hexanol with addition of hydrogen after condensation and dehydration; it can produce trimethylolpropane (TMP) upon condensation

with formaldehyde, where, TMP is the raw material for synthesis of alkyd resin plasticizer; it can produce oil-soluble resin (OSR) upon condensation with phenol, and can produce alcohol-soluble resin (ASR) upon condensation with urea; it is a solvent for rubber and medical products; it is used for making "miltown" in medical industry; it is used for preparation of flavors and spices; it is used as an intermediate product of resin and plastic plasticizer, vulcanization accelerator and insecticide, etc.

(2) Iso-butyl aldehyde: iso-butyl aldehyde and formaldehyde could generate hydroxy trimethyl acetaldehyde upon addition reaction, and then generate neopentyl glyco with addition of hydrogen, to be used as the raw material for varnish, resin, fiber and lubricant; it can produce fertilizer upon reaction with urea, and the fertilizer can release nitrogen slowly; it is used as the intermediate product for amino acid, vitamin and other drugs; a huge amount of iso-butyl aldehyde can be utilized as fuel; it is used for synthesis of cellulose ester, fragrance and spice, etc., to be commonly used in baked food, meat products and icing sugar; it is used for making rubber and vulcanization accelerators and antioxidant, isobutyric acid and so on.

2.2.2. Market demand and price of iso-butyl aldehyde

Production of chemical products needs to take market capacity into consideration [1], so the author collected the monthly import volumes of iso-butyl aldehyde in China from January 2018 to February 2019, which were respectively as follows: 1,826.4t, 662.4t, 2,620.7t, 1,310.8t, 3,080.8t, 2,826.9t, 1,859.0t, 2,569.0t, 1,501.1t, 2,418.1t, 1,112.9t, 2,091.2t, 3,978.3t, 1,865.9t; and during this period, the monthly import prices of iso-butyl aldehyde were respectively as follows: USD 2,274.6/t, USD 3,060.6/t, USD 2,183.5/t, USD 3,167.8/t, USD 2.033.1/t, USD 2,250.3/t, USD 2,471.4/t, USD 1,777.4/t, USD 2,974.0/t, USD 2,078.2/t, USD 3.079.5/t, USD 2,025.1/t, USD 1,701.8/t, USD 1,846.8/t. It can be seen that: iso-butyl aldehyde was imported every month in China, and there was still a relatively big market capacity in China; average import price of iso-butyl aldehyde was USD 2,351/t, which was about RMB 15,000/t. At present, full production cost of iso-butyl aldehyde in Lunan Chemicals is about RMB 5,100/t, and the profit of iso-butyl aldehyde is about RMB 10,000/t; however, at present, sales price of iso-butanol in China is RMB 9,800/t, while full production cost of iso- butanol in Lunan Chemicals is about RMB 5,400/t, therefore, its profit from iso-butanol is about RMB 4,400/t.

3. Application of distillation and energy-saving technology

In view of that in recent years, profit-creating capacity of iso-butyl aldehyde is far greater than that of iso-butanol, therefore, it is necessary to use reasonable separation technology to optimize and reform the butanol facility in Lunan Chemicals, to realize efficient separation of n-butyl aldehyde/iso-butyl aldehyde, and organize the production mode flexibly according to the market situation, so as to realize alcohol/aldehyde flexible production of the butanol facility, thus maximizing the enterprise benefit.

3.1. Analysis of physical and chemical parameters

For separation of substances in chemical production, it needs to understand relevant physical and chemical parameters of the substances, so as to separate the mixture effectively using reasonable and mature separation technology. Relevant physical and chemical parameters of n-butyl aldehyde/iso-butyl aldehyde are as follows in details.

(1) N-butyl aldehyde: molar mass: 72.11 g/mol, density: 800 kg/m^3, flash point: -22℃, boiling point: 75.7℃, slightly soluble in water; upper explosive limit: 12.5%, lower explosive limit: 1.9%.

(2) Iso-butyl aldehyde: molar mass: 72.1057 g/mol, density: 790 kg/m^3, flash point: -10.6℃ (OC) / - 40℃ (CC), boiling point: 64℃, slightly soluble in water; upper explosive limit: 10.6%, lower explosive limit: 1.6%.

According to preliminary analysis based on the above data, for n-butyl aldehyde and iso-butyl aldehyde, their physical and chemical properties did not differ greatly, and the boiling point had a difference of 11.7℃. N-butyl aldehyde and iso-butyl aldehyde could be separated effectively by making use of distillation technology and efficient tower inner parts.

3.2. Distillation technology

Distillation technology is generally used in distillation tower [2-3], where the gas phase and liquid phase make inter-phase mass and heat transfer via counter-current contact - the volatile components in the liquid phase transfer into the gas phase, and the non-volatile components in the gas phase transfer into the liquid phase, thus nearly pure volatile components could be obtained on the top of the tower, while nearly pure non-volatile components could be obtained at the bottom of the tower.

The feed liquid is fed from the middle part of the distillation tower, and the tower section above the feed inlet would further increase concentration of the volatile components in the uprising steam, and this section is referred to as distillation section; the tower section below the feed inlet would strip the volatile components from the falling liquid, and this section is referred to as the stripping section. For the gas-phase material from the top of the tower, upon condensation, a part of the distillate would return to the distillation tower as re-flux liquid, while another part of the distillate would be withdrawn as overhead product. For the liquid gas from the bottom of the tower, upon vaporization via the re-boiler, the gas-phase material from the vaporization would rise along with the tower, while the remaining liquid would be withdrawn as bottom product. The ratio between the amount of liquid flowing back into the tower at the top and the amount of product at the

top of the tower is called the re-flux ratio, the size of which influences the separation effect and energy consumption of the distillation operation, thus, it is an important link for product quality control.

3.3. Optimization, reformation and production mode

According to analog computation, n-butyl aldehyde and iso-butyl aldehyde can be effectively separated by the distillation tower. After reformation, the technological process of the butanol facility is: a butyl aldehyde isomer tower is added after the oxo synthesis reactor and before the gas-phase hydrogenation evaporator, and the mixed butyl aldehyde is withdrawn to the butyl aldehyde isomer tower by an increased path, and then re-boiler in the butyl aldehyde isomer tower would heat up with 0.5 MPa steam, thus using the butyl aldehyde isomer tower to realize effective separation of n-butyl aldehyde and iso-butyl aldehyde, and the bottom liquid phase (n-butyl aldehyde is sent to the butyl aldehyde hydrogenation system as an intermediate product or is set to the n-butyl aldehyde storage tank upon cooling) and the overhead gas phase (iso-butyl aldehyde is sent to the iso-butyl aldehyde storage tank as the final product upon cooling) would be sold to foreign countries.

In November 2020, making use of the short stop of the butanol facility, a T-junction was added to corresponding part of the process pipeline of the system, and valves of good air-tightness were also equipped, and then the facility was restarted and came into normal operation upon completion of overhauling of the butanol facility; construction continued after this technological reformation, and upon completion of the whole project, the butyl aldehyde isomer tower system was incorporated into the butanol facility for operation. After reformation, butanol facility of Lunan Chemicals could switch flexibly among the 3 production modes as follows, thus realizing alcohol/aldehyde flexible production.

(1) Production Mode I: when the iso-butyl aldehyde products have a higher profit than iso-butanol products and the n-butanol products have a higher profit than n-butyl aldehyde products, iso-butyl aldehyde shall be separated by butyl aldehyde isomer tower for foreign sales, and n-butyl aldehyde shall be hydrogenated to produce n-butanol, and the post-process butanol isomer tower shall stop operation.

(2) Production Mode II: when the iso-butyl aldehyde products have a higher profit than iso-butanol products and the n-butyl aldehyde products have a higher profit than n-butanol products, both n-butyl aldehyde and iso-butyl aldehyde shall be used for foreign sales, and the post-process butanol converter shall stop operation.

(3) Production Mode III: when n-butanol/iso-butanol products have a higher profit than n-butyl aldehyde/iso-butyl aldehyde products, the newly-added butyl aldehyde isomer tower shall stop operation, and n-butanol/ iso-butanol shall be produced by the original production process.

Under the current market condition, iso-butyl aldehyde has a far better profit-creating capacity than iso-butanol, and n-butanol has a far better profit-creating capacity than n-butyl aldehyde, therefore, the butanol facility adopts the Production Mode I to organize the production.

4. Operation condition

4.1. Product output and consumption analysis under Production Mode I

Before reformation, butanol facility of Lunan Chemicals adopted Production Mode III to organize the production, and the products produced were n-butanol/iso-butanol; after reformation, butanol facility of Lunan Chemicals adopted Production Mode I to organize the production, and the products produced were n-butanol and iso-butyl aldehyde. Comparison of the data on product output and consumption per ton of products (the data was the daily mean value of 3d) before reformation (October 24, 2020, 00:00 — October 26, 2020, 24:00) and after reformation (April 24, 2021, 00:00 - April 26, 2021, 24:00) is as shown in Table 1. It could be seen that: after reformation, output of n-butanol had an increase of about 33 t/d, and output of iso-butyl aldehyde was up to 59.50 t/d; there was a consumption of propylene at 602.7 kg, syngas at 604.0m^3, steam at 950.6 kg and hydrogen at 301.81m^3 per ton of the products, which compared with that before reformation, consumption of all materials decreased except slightly increase in consumption of syngas.

Table 1. Comparison of product output and consumption per ton of products before and after reformation

Item	Daily output of n-butyl aldehyde/t	Daily output of iso-butyl aldehyde/t	Daily output of iso-butanol/t	Total daily output	Consumption per ton of products			
					Propylene/ kg	Syngas/ m^3	Steam/kg	Hydrogen/m^3
Before reformation	406.63	0	46.73	453.37	605.9	603.9	1,887.6	305.4
After reformation	439.63	59.50	0	499.63	602.7	604.0	950.6	301.8

4.2. Product quality analysis

(1) Under Production Mode I of the butanol facility, quality of iso-butyl aldehyde products would be analyzed 4 times a day, and the analysis data of iso-butyl aldehyde products on the 3 days from April 24 to April 26, 2021 (the sampling

time was the 08:10, 14:10, 18:10 and 20:10 of the current day, with 4 groups of data recorded per day) was as follows: purity of iso-butyl aldehyde was 99.65% ~ 99.92%, with the mean value of 99.86%; content of n-butyl aldehyde was 0.03% ~ 0.06%, with the mean value of 0.05%; water content was 0.02% ~ 0.06%, with the mean value of 0.04%. It could be seen that, purify of the iso-butyl aldehyde products (mean value) after reformation was 99.86%, which reached relevant international quality standards and requirements, therefore, the products were equipped with the conditions for foreign sales.

(2) Under Production Mode I of the butanol facility, quality of n-butanol products would be analyzed 2 times a day, and the analysis data of n-butanol products on the 3 days from April 24 to April 26, 2021 (the sampling time was the 08:10 and 20:10 of the current day, with 2 groups of data recorded per day): purity of n-butanol was 99.85% ~ 99.88% ,with the mean value of 99.86%; content of iso-butanol was 0.07% ~ 0.09%, with the mean value of 0.08%; content of ethyl acetic acid was 0.02% ~ 0.03%, with the mean value of about 0.02%; content of triphenylphosphine (TPP) was 0.006% (TPP in n-butanol products was of trace amount, and only the sampling analysis data on April 25 20:10 was recorded); water content was 0.01% ~ 0.03%, with the mean value of 0.02%. It could be seen that, purity of n-butanol products (mean value) after reformation was 99.86%, which reached relevant international quality standards and requirements, therefore, the products were equipped with the conditions for foreign sales.

4.3. Economic benefit analysis

Before reformation, Lunan Chemicals adopted Production Mode III to organize production, and with the output of n-butanol before reformation as the benchmark, n-butanol showed no increased output, and created profit of RMB 0; iso-butanol output was 15 kt/a, market sales price of iso-butanol was about RMB 10,100/t, and full production cost of iso-butyl aldehyde was about RMB 5,342.56/t, with creation of profit per ton of iso-butanol products being about RMB 4,757.44, and annual creation of profit being about (10,100 - 5,342.56) x 15,000 + 10,000 = RMB 71.3616 million. It can be seen that, if not giving consideration to profit amount of n-butanol, the butanol facility created a profit at about 7,136.16 +0=RMB 71.3616 million.

After reformation, Lunan Chemicals adopted Production Mode I to organize the production, where, n-butanol had an increased output of about 33t/d, market sales price of n-butanol was about RMB 5,300/t, and if calculating by annual operation of 330d, the annually increased sales revenue was about RMB 57.717 million, full production cost of n-butanol products was about RMB 5,042.56/t, with creation of profit per ton of n-butanol products being about RMB 257.44, and the annually increased profit of the increased output of n-butanol was about 257.44 x 33 x 330 + 10,000 = RMB 2.8035 million; output of iso-butyl aldehyde was about 59.5t/d, market sales price of iso-butyl aldehyde was about RMB 15,500/t, and if calculating by annual operation of 330d, the annually increased sales revenue was about RMB 304.3425 million, full production cost of iso-butyl aldehyde was about RMB 5,142.56/t, with creation of profit per ton of iso-butyl aldehyde products being about RMB 10,357.44, and the annually increased profit of the increased output of iso-butyl aldehyde was about 10,357.44 x 59.5 x 330 + 10,000 = RMB 203.3683 million. It could be seen that, under Production Mode I, if giving consideration to profit amount of the products with increased output, the butanol facility of Lunan Chemicals could create an addition profit of about 280.35 +20,336.83 = RMB 206.1718 million all year round.

5. Conclusion

(1) By adding a butyl aldehyde isomer tower, butanol facility of Lunan Chemicals could separate n-butyl aldehyde and iso-butyl aldehyde effectively, and the quality of the output products reached relevant international quality standards and requirements.

(2) After reformation, butanol facility of Lunan Chemicals could organize the production mode flexibly according to the market condition, thus realizing alcohol/aldehyde flexible production, and put the product portfolio with high profit into market - under Production Mode I, butanol facility of Lunan Chemicals took iso-butyl aldehyde and n-butanol as the main products (no iso-butonal products were withdrawn), where, n-butanol had an increased output of about 33t/d, and iso-butyl aldehyde had an increased output of about 59.5t/d, therefore, compared with that before reformation, the butanol facility could have an additional annual profit of about RMB 206.1718 million.

(3) After reformation, many consumption indicators of the butanol facility per ton of products decreased effectively, especially the consumption of steam and hydrogen - steam consumption per ton of products decreased from 1,887.6kg to 950.6kg, which could reduce fuel coal consumption of the boiler greatly; hydrogen consumption per ton of products decreased from 305.4m^3 to 301.8m^3, and the surplus hydrogen was used to improve load of other production facilities and increase output of other products.

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