

Product Quality Control in Crude Methanol Distillation Operation

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Abstract: in the rectification process of crude methanol, the quality control of finished products requires not only the separation of two key components “methanol water”, but also the reduction of the content of organic impurities in refined methanol, which is the key control point of Methanol Quality in rectification operation.

1. Introduction

As one of the important basic organic chemical raw materials, methanol plays a very important role in the world economy. With the increasing shortage of energy in the world, methanol has gradually developed into an important energy substitute. Chemical industries such as dimethyl ether and olefin synthesis from methanol have also developed rapidly. At present, China's methanol production capacity has accounted for 1 / 4 of the world's total capacity, with a total capacity of more than 15 million T / A. Moreover, with the rapid development of methanol derivatives and their downstream products and the application of methanol fuel, the demand for methanol will be increasing. Therefore, people pay more and more attention to improving the quality of methanol products and reducing production consumption. Methanol distillation is the last process of methanol production unit, and its energy consumption accounts for about 20% of the total energy consumption of methanol production. The quality of methanol distillation technology is directly related to the quality of refined methanol. Therefore, it is an important measure to select the distillation technology suitable for the production needs of enterprises to reduce costs, save energy and reduce consumption, and improve the economic benefits and market competitiveness of enterprises.

2. Composition of Crude Methanol

The methanol synthesis unit of our company adopts the patented equipment of Chengdu general engineering company - “spiral tube - straight pipe compound series external cooling methanol synthesis tower”, and the catalyst uses megamax NJ-1 catalyst produced by Nanjing Shide. Due to the influence of pressure, temperature and gas composition of methanol synthesis system, there are a series of side reactions during the reaction. Therefore, the crude methanol obtained from flash tank is mainly composed of methanol, water and organic impurities.

3. Control of Main Process Indexes in Distillation Process

In many years, the quality of methanol depends on the process design and operation.

3.1 Main Equipment and Its Functions

The distillation unit mainly includes pre distillation tower, pressure tower, atmospheric tower and recovery tower. The main function of the pre rectification column is to remove the dissolved gas in crude methanol and the substances lower than the boiling point of methanol such as dimethyl ether and methyl formate. The main function of the pressurized tower and atmospheric tower is to remove water, ethanol and other substances higher than the boiling point of methanol, so as to obtain high-quality methanol with short boiling range, high purity and good stability. It can meet the requirements of Methanol Quality in industrial production. In addition, the heavy fraction mainly composed of ethanol accumulates in the 6-10 layers of the atmospheric tower, so the side line outlets are set at the 5, 7 and 9 layers of the tower plates to extract the methanol aqueous solution rich in ethanol and other fusels[1].

3.2 Control of Main Process Parameters

3.2.1 The Vent Temperature of Pre Tower Should Be Controlled At 30 ~ 55 °C

This is because the crude methanol contains more ethers, the boiling point is low, the chemical properties are not active, and the impurities can not be fully vented when the vent temperature is lower than 30 °C, which affects the distillation effect. However, when the vent temperature is higher than 55 °C, the methanol content in the gas increases greatly, resulting in the waste of raw material methanol.

3.2.2 The Proportion of Methanol Remained between 0.84 and 0.87

Crude methanol contains some c5-c10 alkane impurities, which is easy to form azeotrope with methanol. Its boiling point is lower than or close to the boiling point of methanol, which is insoluble in water. However, methanol and water can be mixed in any proportion. The boiling point can be increased by adding extraction water into the extraction tank, which is conducive to the separation of the substances.

3.2.3 The Ph Value of Methanol Should Be Controlled within 7-9

In the process of methanol rectification, dilute lye with concentration of 5% is added, the amount of which is about 0.05-0.1% of the feed amount, which is used to decompose organic amines and remove them in the pre tower. At the same time, it can neutralize formaldehyde, formic acid and other reducing impurities to prevent equipment and pipeline corrosion. However, if the amount of alkali liquor is too much, it will not only increase the consumption, but also cause saponification reaction, and the generated lipids will hydrolyze in the pressurized tower and atmospheric tower, which will cause the acidity of the product to exceed the standard and affect the product quality.

3.2.4 The Reflux Ratio of Atmospheric Tower Should Be Controlled At about 2.0

In the process of crude methanol rectification, a small amount of methanol will be discharged from the residual liquid. In order to reduce the loss of methanol, the temperature of atmospheric tower bottom should be stabilized between 105 °C and 115 °C. Such impurities with high boiling

point will move up to the top of the tower. Therefore, increasing the reflux is a necessary condition to solve this problem. However, if the return flow is too large, it will not only affect the production capacity of the system, but also increase the energy consumption[2]. Therefore, it is necessary to control the appropriate reflux ratio.

4. Finished Product Quality Control - Water Solubility

Water solubility: when the refined methanol contains organic impurities which are insoluble or insoluble in water, these impurities will precipitate out in the form of colloidal particles after adding water, resulting in turbidity.

4.1 Types of Impurities

According to the research, there are two kinds of impurities that affect the turbidity of refined methanol with water

Type I impurities are in the gas-liquid separator at the top of the pre tower. After sampling, the liquid is precipitated and the liquid is stratified. The oil on its upper layer is analyzed. Most of these impurities have higher boiling points than methanol. Because of the azeotrope formed with methanol, the boiling point of the azeotrope is lower than that of methanol, so it is carried to the top of the pre distillation column. Class II impurities are concentrated in the distillation section of atmospheric tower, which are collectively referred to as fusel oil

4.2 Removal Method

4.2.1 Removal of Class I Impurities

The stability of methanol can be improved by increasing the amount of extraction water in the pre column. However, the amount of water added should not be too large, otherwise the production capacity of the pre distillation column will be reduced and the consumption of heat and power will be increased. If the water solubility of the product is not improved obviously, the pre tower condensation temperature should be increased appropriately. If the tower top temperature is controlled within a certain range, once the tower top temperature decreases, there may be class I substances.

4.2.2 Removal of Class II Impurities

First of all, it is necessary to strictly control the operating conditions in the column, especially the temperature of the sensitive plate in the distillation section, so as to avoid the rise of heavy components and the rise of heavy components, which may bring the second type impurities into the refined methanol. Secondly, continuous and effective lateral extraction can reduce the accumulation of this kind of material. If the heavy components are not recovered in a short time, it seems that the water solubility of refined methanol will not be affected. However, with the accumulation of heavy components in the tower, it will move up plate by plate. At normal tower temperature, the water solubility of refined methanol will also be reduced[3].

5. Analysis and Summary of Excessive Acidity in the Actual Production Process of Our Factory

From March 18, 2016 to March 20, 2016, the acidity of products exceeded the standard for three consecutive days. In view of this abnormal phenomenon, the following aspects were analyzed and

summarized to solve such problems.

(1) firstly, the methanol produced from the pressure tower and the atmospheric tower was analyzed. The results showed that the acidity of the pressure tower was qualified, and the output of the atmospheric tower exceeded the standard. According to the post prognosis pH control, the pH control is normal, and the actual alkali addition is mainly to neutralize the organic acid in crude methanol to prevent corrosion of tower bottom and pipeline. Too much alkali liquor will promote the hydrolysis of esters, which will also cause the product acidity to exceed the standard. Therefore, timely adjust the alkali dosage according to the prognosis pH and control it between 8-8.5.

(2) control of pre tower condensation temperature. The high efficiency cooling control temperature of the pre tower is generally above 40 °C, which avoids excessive condensation of light components (methyl formate, methyl acetate and other light components are not completely removed and are hydrolyzed to corresponding formic acid in the pressure tower or atmospheric tower, and the acidity of the products caused by acetic acid is over standard). In addition, due to the influence of product recovery and fusel temperature, the control temperature of secondary condensation (five in one) of pre tower is lower (23 °C), but the secondary condensate is not returned to the pre tower, so this factor can be eliminated.

(3) add extraction water into the pre column (too little extraction water will cause some light components in the crude methanol to form azeotrope with methanol, which is difficult to separate, and it will be brought into the pressurized tower and atmospheric tower products, resulting in excessive acidity). In general, the amount of extraction water is adjusted according to the proportion of prognosis, and the proportion of prognosis is about 0.86-0.87[4].

(4) control of Fusel recovery. Some time ago, due to the high inventory of Fusel tank in the finished product tank farm, a part of the fusel mixture extracted from the atmospheric tower measuring line and secondary condensation of the pre tower was discharged to the underground tank, and this part of the mixed liquid re entered the system. In this regard, the post is required to pour all the mixture into the fusel tank. Through sampling analysis, the acidity of atmospheric tower products decreased.

The pressure of methanol synthesis was reduced by 0.054 MPa in flash tank. (from the original set value of 0.35MPa to 0.3MPa, the pressure decreases, which is conducive to the flash evaporation of light components in crude methanol[5].

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