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An analysis of current methanol to olefin development technology: DMTO and SMTO

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Abstract. The global demand for ethylene and propylene is about 200 million tons per year, which requires a very efficient and large number of separation systems. It is necessary to study the chemical packaging system, which is effective and emits fewer pollutants. Based on the existing literature and data, this paper includes two main advanced technologies from the Dalian Institute of Chemical Physics, the Chinese Academy of Sciences DMTO and SINOPEC Shanghai Petrochemical Research Institute SMTO. Specific analysis and optimization of energy loss and product loss in each process are carried out. The result shows that optimization of reaction conditions and other ways to improve the conversion rate and product selectivity is currently the main direction, as is the development of more energy-efficient new high-efficiency separation technology to achieve energy savings. At present, there is still ample room for innovation in the research of catalysts and the corresponding supporting reactor types, in addition to meeting quality requirements and further optimizing the process for technological innovation.

Keywords: MTO, Olefins Separation, DMTO, SMTO

1. Introduction

Ethylene, propylene, and other low-carbon olefins serve as the fundamental organic raw materials for the contemporary chemical industry. The significant disparity in equivalence of low-carbon olefins highlights the crucial nature of olefin production technology. In industrial production, the preparation of low-carbon olefin typically involves the pyrolysis of petroleum hydrocarbons along the petroleum route. However, this method is overly reliant on petroleum and produces mostly alkanes and other substances with long carbon chains, resulting in a small output of olefin. The raw material for methanol to olefin technology is methanol derived from coal. Developing coal chemical industries can promote cleaner and more efficient use of coal resources, reducing the reliance on long-carbon chain olefin produced primarily through thermal cracking. At the same time, the use of methanol to produce olefins reduces the need for oil fractionation, which helps to alleviate the problem of oil shortages in China. Methanol can also be stored effectively and used as a strategic material. This article combines the works of Chen Hongpai et al., Ma Chengcai, and Jiang Siyuan on methanol-to-olefin technology [1-3]. Chen Hongpai's article provides a summary of the current status of MTO technology [1]. Ma Chengcai's work focuses on the optimal utilisation of low-temperature heat in a methanol-to-olefin plant, while Jiang Siyuan's paper discusses the rational use of rapid cooling water in the same plant [2-3]. These results demonstrate that there is ample scope for advancing and refining MTO technology. The following step is to examine the process's impact on the environment and the economic market cycle continuously.

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Although this study does not provide an exhaustive account of the process, it aims to outline it concisely to facilitate an understanding of the direction of optimisation. The primary aim of researching the development of MTO is to obtain a range of olefins with different carbon chain lengths that are required in substantial quantities on a daily basis. This research intends to achieve high yields and capacities on an industrial scale, establish better materials to reduce decay over time, prevent frequent material replacements, and optimize the process to increase affordability and selectivity in the economic marketplace.

2. Processes of DMTO and SMTO

The latest development of MTO technology can be divided into two categories: Dimethyl Methanol To Olefins (DMTO) and SMTO from the Shanghai Research Institute of Petrochemicals (SRIP). In this part, the DMTO and SMTO processes are studied in terms of energy and energy efficiency, and the industrial plants that have been put into operation in China using the DMTO and SMTO processes, respectively, are taken as the objects of study to analyse the specific structure of the DMTO and SMTO processes, as well as the different applications of these two types of plants.

2.1. DMTO process

The DMTO manufacturing facility comprises three zones: a reaction and regeneration zone, an emergency cold stripping zone, and an olefin separation zone. The industrial flow chart in Figure 1 illustrates the process, where the reaction and regeneration zone transform methanol feedstock into waxes and a range of small-molecule olefins, such as ethylene and propylene, which are globally in high demand annually, along with a limited amount of methylene [4]. The rapid cooling vapour stripping zone is employed to cool the blended product gas and eliminate some acidic gas impurities from it. The olefin separation section is utilised to segregate the mixed olefins and generate the ultimate pure product. The main units in the process are: the reactor and catalyst regenerator in the reaction regeneration zone; the fast cooling tower, water washing tower, alkali washing tower, and stripping tower in the fast cooling and stripping zone; and, lastly, the multi-stage compressor, flash tanks, and a series of distillation columns in the olefin separation zone.

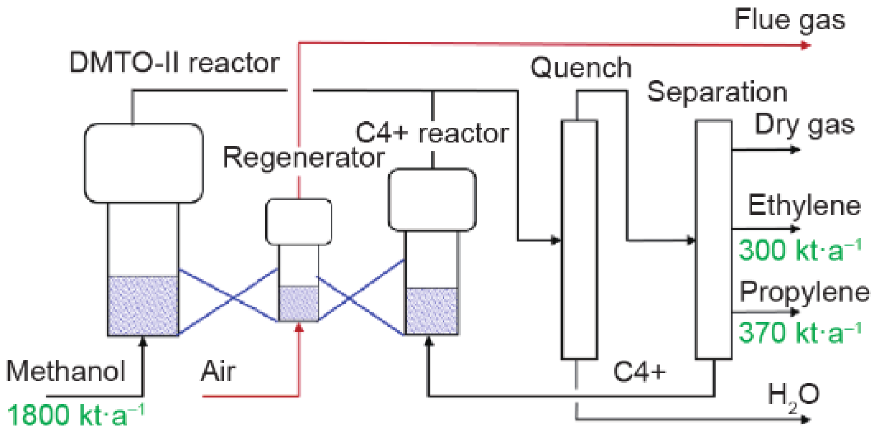

Figure 1. DMTO process [5]

2.2. SMTO process

The distinctions between the SMTO method and the DMTO approach are as follows: In the SMTO approach, an olefin cracking (OCC) unit is included, while in the DMTO process, recent research has integrated the cracking phase with the MTO reaction phase in the reaction regeneration area. In the area where acute cooling vapour extraction takes place, the olefinic gas from the SMTO reactor is directed to the vapour generating equipment. Energy is recovered by producing high- and medium-pressure vapour [4]. In the DMTO process, the product gas is used directly to heat low-temperature methanol

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feedstock. Separation of mixed olefins in the DMTO process is carried out using pre-propane technology, whereas the SMTO process uses pre-deethanation technology. The DMTO employs the product gas as a direct heating source for the low-temperature methanol feedstock.

2.3. Comparing of two processes in energy saving potential

In Ai Xiaobing's simulation and optimization of MTO olefin separation process, they utilized the SRK equation(Soave RK equation) of state as the chosen thermodynamic method [6]. The Lee-Kesler equation was utilized to correct the liquid phase density. The results demonstrated that the simulated values were consistent with the design values, confirming the established model's accuracy. Comparison of the data demonstrates that the simulated values align well with the design values, confirming the dependability of the selected thermodynamic approach and model computation.

Both the SMTO and DMTO processes require significant amounts of energy. The preheating of the feedstock methanol and distillation column feed, as well as the energy consumed by the reboiler, are the main energy-consuming components. In addition to treating and utilising cooling water, further optimisations are required to lessen feedstock consumption and achieve a more environmentally friendly chemistry and chemical industry. These optimisations must focus on achieving higher capacities and yields. The significant energy-consuming components include the preheating of raw methanol, the preheating of the feed for the distillation tower, and Reboiler energy use.

The minimum required cooling loads for both processes are similar due to several factors. Firstly, the boiling points of the main products have a low threshold in both processes. Additionally, the distillation tower's top temperature in the olefin separation zone of the third part is also low. Finally, the condenser in the rapid cooling vapor stripping zone of the second part cannot be cooled by the cold streams or cooling water present in the system. It is necessary to use a specific coolant, which significantly increases demand and consumption costs. Additionally, since the yields and production rates of the primary products (ethylene, propylene) are similar, the required amount of cooling load is also comparable.

3. Special devices in the process

3.1. Low temperature heat

The mechanism of the methanol reaction, producing low carbon olefins, is intricate. The accepted reaction mechanism is the carbon pool reaction, in which polytoluene, as an active element in the carbon pool, reacts distinctively with methanol. This reaction results in the development of side-chain alkyl groups, which are subsequently peeled off to produce low carbon olefins, including ethylene and propylene. Thermodynamic research has demonstrated that the reaction is highly exothermic. Sometimes the low temperature also is produced by products. During the process of cooling products, they emit a mount of heat energy, which is called low temperature [3].

However, the use of low-temperature heat has numerous shortcomings, not only in terms of capacity yield and utilisation efficiency, but also regarding economic market placement and costing. The heat exchanger's acute cold water side and other devices are factors in the operation cycle that can lead to poor heat transfer and the need for frequent cleaning, causing an increase in overhaul costs [3]. In approximately a month's time, the heat exchange efficiency may decrease, necessitating cleaning once more. During the cleaning process, a significant amount of equipment is used, and the consumption of low-pressure steam increases during operation. After cleaning the heating device, the heat exchange efficiency worsens, which may cause the ethylene tower's feed temperature to drop, resulting in downstream operation implications and significant losses. During the heat exchange and cleaning stages, increased losses of ethylene could occur if the system is not functioning effectively due to specific energy consumption and temperature profiles. Also, various factors impact the production of different products in the distinct distillation columns. Therefore, it is economically and technically challenging to replace the unit to enhance the yield.

To resolve the cost of device replacement, two measures can be taken. Firstly, the quality of pipeline welding must be ensured to minimize the effect of external factors on the low-temperature heat within the pipeline. Welders should analyze the situation of oil and gas pipelines and choose an appropriate welding process. Secondly, to ensure welding efficiency for long-distance pipelines, the electrode arc welding method can be chosen. Different welding methods offer varying conditions and advantages. When selecting the appropriate method for a specific application, one must consider the actual situation. The welding process must be analyzed with respect to the quality of welding materials, material strength, and toughness to ensure the technology's and material's adaptability in achieving optimal welding results.

3.2. Rapid colling water

Methanol is reacted by the reactor catalyst at high temperatures to produce olefin-containing gas, and the temperature of olefin gas is still close to 300°C after heat exchange with methanol gas. In the rapid cooling tower, the olefin gas is washed by rapid cooling water for heat exchange, the temperature of the olefin gas is reduced to 110°C, and the olefin gas is further cooled and separated in the downstream equipment [2]. In the rapid cooling tower, the rapid cooling water is from 75°C to 105 °C, but the rapid cooling water contains catalyst particles with a higher solid content (volume fraction) of 0.01%~0.05% [2]. The equipment in the normal operation of the process is often caused by the downstream rapid cooling water heat exchanger clogging, resulting in a reduction of the rapid cooling water heat exchanger heat transfer capacity, and the temperature of the rapid cooling water increases.

The main function of the emergency cooling water in the emergency cooling tower is to cool the olefin gas from the reactor and to wash the catalyst fines carried in the olefin gas. Due to more catalyst fines in the emergency cooling water, the emergency cooling water heat exchanger needs to be taken out and cleaned once in about 3 months, which has a certain impact on the stable operation of the unit [2]. In order to make the equipment can be stable long cycle operation, the olefin separation heat exchanger heat source is changed to water washing water, water washing water instead of emergency cold water; the water washing water temperature is about 90°C. Due to the absence of catalyst fines in the water washing water, its heat transfer effect is better and is not easy to scale. Olefin separation heat exchanger of the rapid cooling water to water washing water, heat exchanger did not occur again scaling, the device has been extended the operating cycle, heat exchanger water washing water by the amount of larger heat exchanger heat exchanger capacity did not change much, basically to meet the original function of the heat exchanger. Of course, there are some shortcomings in this improvement method: the higher temperature at the top of the emergency cooling tower increases the heat transfer load and may produce more dirt; the emergency cooling water itself is not well used; and after the replacement, the emergency cooling water needs to find a better use.

4. Discussion

In the process of using catalysts, it is mentioned in Yemao's DMTO: A Sustainable Methanol-to-Olefins Technology that the synthesis of a funny and stable catalyst can increase the conversion of methanol, and DICP scientists have found that silicoaluminophosphate (SAPO)-34 molecular performs well in the conversion of methanol due to its shape selectivity. Research on this topic is still necessary and of interest today [7].

Undoubtedly, a crucial aspect that must not be overlooked in technological advancements is the hazards and safety concerns associated with its manufacturing. Most of the main safety threats faced by companies constructing ethylene production plants come from the chemical properties of the chemicals themselves. Methanol is a flammable substance. It is a flammable liquid, and its vapor can form a combustible mixture with air, posing a significant risk of fire and explosion [8]. For example, on February 23, 2002, an explosion occurred during the polyethylene plant renovation and expansion process at Liaoyang Petrochemical in Liaoning Province. The accident resulted in 8 deaths, 1 serious injury, 18 minor injuries, and direct economic losses of 4.5278 million yuan [9]. This incident proves the importance of proper storage, transportation, and handling of methanol. Meanwhile, it is crucial for the plant to ensure the integrity of equipment and pipelines by implementing appropriate fire and explosion protection measures such as installing firewalls, spark detectors, explosion pressure relief devices, etc. In addition to being flammable, methanol is also toxic. Excessive inhalation or ingestion of methanol can lead to poisoning. Therefore, the plant needs to take measures to minimize the risk of employees' exposure to methanol. This includes providing adequate ventilation systems and requiring the use of appropriate protective equipment such as respirators, goggles, protective clothing, etc. [10]. The methanol to olefins process is typically conducted under high temperature and high pressure conditions. The plant needs to ensure that the equipment meets safety standards and can withstand high temperatures and pressures. Regular equipment inspections, maintenance, and repairs are necessary.

5. Conclusion

To summarize, when comparing the energy efficiency of SMTO and DMTO processes, the minimum cooling load is similar due to the lower boiling points of the main products. However, SMTO requires a higher minimum heating load than DMTO. After conducting simulations using Aspen Plus software and optimizing operating conditions such as the reflux ratio, tower pressure, and heat transfer medium, it is possible to enhance the efficiency of the DE propane, DE ethane, ethylene distillation, and debutante towers in the DMTO plant, as well as the efficiency of the DE propane, ethylene distillation, and DE ethane towers in the MTO plant. Certain hazards in production necessitate that the factory provide workers with appropriate protective equipment, including goggles and protective clothing. Additionally, the optimization of catalysts must be explored in order to develop new products. Regarding the present domestic and international methanol-to-olefin MTO process technology, there is still significant scope for innovation related to the effective exploitation and enhancement of low-temperature waste heat and cooling water, refining and refining catalysts, and catalytic bed configuration for better distillation tower performance. The ultimate goal of this innovation is to promote olefin selectivity and decrease feedstock consumption. Therefore, there are opportunities for the development of future catalysts and the corresponding supporting reactor cooling towers that could potentially lessen the number of required catalysts and cooling towers. Improved Version: The effective use of waste materials, such as unused substances from temperature reactions, can improve the use of raw materials. In olefin separation process technology, a trend towards simpler processes with reduced energy consumption and longer operating cycles is observed when compared to earlier deep-cooling separation processes. Therefore, it is recommended to reduce investment in equipment and operating costs while ensuring that product quality requirements are met. The present dissertation represents a literature review based on available data. In the future, the focus will be on resolving the issues related to material selection and cost reduction through process optimisation and technological innovation.

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