Application of Methanol Synthesis Reactor to Large-Scale Plants

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Abstract: The developing status of world large-scale methanol production technology is analyzed and Linda's JW low-pressure methanol synthesis reactor with uniform temperature is described. JW serial reactors have been successfully introduced in and applied in Harbin Gasification Plant and the productivity has been increased by 50% and now six sets of equipments are successfully running in Harbin Gasification Plant, Jiangsu Xinya, Shandong Kenli, Henan Zhongyuan and Handan Xinyangguang, Now it has manufacturing the reactors of 200,000 to 300,000T/Y for Shanxi Weihua, Inner Mongolia Tianye and Liaoning Dahua. Some solutions for the structure problems of 1000-5000T/D methanol synthesis rectors are put forward.

Key words: methanol, synthesis, reactor, large-scale

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0 Preface

Whether being the raw chemical material (for producing formaldehyde, propene or ethene) or being the energy source (methanol gasoline fuel), the application and size of the latter-day methanol are increasing consistently. The size of the foreign equipments has reached million-ton grade, and China has listed the methanol synthetic technology as it essential project in its "9^{th} 5-year Plan and 10^{th} 5-year Plan". The leaders of the State Council gave many important instructions on the production of methanol. In April 2004, the State Development and Reform Council held a session about "On the Development of Methanol Fuel", and now the Methanol & Aether and Methanol & Aether Clean Automobile Association of Sinopetrol have been established. The methanol gasoline is promoted in four trial provinces such as Shanxi. Under the situation that the size of the methanol production is increasing consistently and toward the large-scale development, it is possible for China to develop its own modern methanol production technology. For decades, China has imported over 20 large ammonia synthesizing reactors during constructing large fertilizer plants. But now, we can build large methanol production facilities with our own intellectual property.

1 The status quo of the large methanol synthesizing technology in foreign countries

The low pressure approach is the major one in the modern methanol synthesizing production technology due to the energy-saving. It is said that the technologies of British ICI Company and the German Lurgi Company occupies 70% min of the foreign production facilities, and which represents the technology level of the foreign methanol synthesizing production. Now the single reactor that has the largest productivity is the united one – Lurgi united reactor- which is composed by 3 reactors and with productivity of 5000T/D, and started production in Atlas, Trinidad in June, 2004. The structure of the ICI methanol reactor is simple, has a large coefficient for filling the catalyzer and easy to be enlarged.

At present, it has the facilities that can product 3000T/D with single set, but the temperature difference at the layer of the catalyzer bed is huge, the return and mixing of the gas are heavy and the efficiency of synthesizing is poor.

For the Lurgi Tube and Shell methanol reactor, the temperature difference at the layer of the catalyzer bed is small. It is easy to be operated and the efficiency of synthesizing is good. But the catalyzer bed of the reactor has strong cool tube effect, which will impact the increasing of the time and space productivity. It has a small coefficient for filling the catalyzer, its structure is complicated, and the single reactor is not productive and hard to be enlarged.

There are also TOPSΦE radial flow reactors, where the heat is exchanged between the towers, the global KBR reactors, the horizontal CASALE multiple bed reactor, where the heat is exchange between the sections. This kind of reactor is composed or stringed by multiple units or multiple beds and the exterior heat exchanger configured between the towers or sections can remove heat from reaction. The pressure on the bed layer of this kind of reactor is lowered and it is easy to be enlarged, but the cost on the equipments is huge, the process for manufacturing the reactor is complicated and the distribution of the catalyzer bed is not good enough.

In the above three kinds of methanol reactors, the production strength of the successive heat exchanging and constant temperature catalyzer are the best: 0.9—1.0kg (L.h); while the cold treating type is the worst: 0.35—0.40kg (L.h); the indirect heat exchanging and heat insulation type is between them: 0.55—0.6kg (L.h).

2 The methanol synthesizing technology with China own intellectual property

2.1 In recent years, the technology of low pressure methanol synthesizing has been developed greatly and the Productivity Promotion Center of Sinopetrol Association and others have done a great deal of works. Hangzhou Linda Company, East China University of Science and Technology and some Design Institutes have undertaken a series of methanol project jointly. Hangzhou Linda Company has a series of successful innovated technologies about the methanol and ammonia synthesizing reactors, and it has applied for the international patents, European patents, Russian patents, the USA patents and domestic patents including PTC.

Till now, it has gotten 13 domestic or international patents. It has developed successfully the large-scale, low pressure and even temperature type methanol synthesizing technology after having developed successfully intermediate pressure integrated methanol reactor applying for the integrated methanol production in the synthesized ammonia plant, and the reactor has become the most applicable one in the integrated methanol production units in China. The effect of this technology has been proven when it was used in multiple plants and was honored the National Innovation Award 2004.

The methanol synthesizing is a strong heat reaction. The synthesized raw material gas that should go into the catalyzer layer should not react before being heated to the reaction temperature (＞210℃), while the low pressure methanol synthesized catalyzer (copper base accelerant) is easy to be overheated and lost activity (＞280℃) and the reaction heat from the methanol synthesizing should be removed timely. As this synthesizing reactor has combined the heating of the raw material gas and the heat removing during the reaction, the reactor and the heat exchanger are combined and remove heat successfully, and it can also reduce the size of the equipments and the temperature difference at the catalyzer layer so as to reach the goal of "even temperature, high efficiency and easy to be enlarged".

This low pressure and even temperature type methanol reactor is a completely new reactor structure which is different from the existing foreign methanol reactor and is the first one internationally and domestically. After the initial inspection and testing by PCT, as well as the real reviewing by the state, it was honored a patent and has many unique creative technologies. Its key part is that the double U shape tube cooling tube pot structure with 2 innovative and unique elbows, big and small, as the heat exchanging component. The U-shape tube with small elbow is in the U-shape tube with big elbow to form a pair of U-shape tube. The U-shape tube with the big and small elbows in the double U-shape tubes is jointed in a counter-direction array, and the feedgas flows up and down in each 2 cooling tubes that are neighbor to each other and the directions are refluence, so as to achieve the goal of even and equal temperature reaction at the accelerant layer and the temperature difference can be as low as 10℃. As the completely free extensive and compound seal structure has been developed, the ring tube is in the free space above the catalyzer and the double U-shape tube is in the catalyzer layer. As there is no welding point on the cooling tube, the structure is reliable. Another one is the low temperature and even temperature type methanol reactor with double ring tubes at the upper and lower parts. The cooling tube pot has an upper ring tube and lower ring tube. The upper ring tube connects the gas inlet tube and the downward cooling tube, while the lower ring tube connects the downward cooling tube and the upward cooling tube.

The creative development has been applied successfully in the Reactor Designer – reactor analog computing software of methanol synthesizing. After corrected by quantity of real production data, the math model is more near to the real effect. The integrated reactor that applies in the even temperature single (integrated) methanol reactor, the Tube and Shell type reactor, ICI Quench type reactor and the large methanol equipments includes various of dynamics data of the methanol catalyzer, so the design of the reactor can be easily optimized and which can provide a powerful backing to developing and optimizing the high-performance methanol synthesizing reactor.

2.2 The operation effect and main technical parameters of the Linda Methanol Synthesizing Reactor

6 sets of new synthesizing reactor have been operated. Comparing with the above said foreign equipments, they present the features of small reactor, low temperature difference at the accelerant layer, high CO conversion rate, high output and less gas consumption.

After Harbin Gasification Plant has change its Φ2000 Quench reactor into the JW even temperature type methanol tower, the temperature difference at the accelerant has lowered from the former 30-70℃ to the ＜ 5℃ at the same level and ＜ 10℃ radially. Under the condition that there is no increasing in raw gas, the inlet gas or the accelerant for methanol synthesizing, the output of the methanol has been increased by 50%. The raw material consumption for each ton of methanol has decreased by 129Nm^3 and the power consumption has decreased by 120kWh. Under the effective synthesizing pressure of 5MPa, the production strength of the methanol catalyzer can reach 0.69t/(m^3.h), comparing with the 0.382t/(m^3.h) from the Quench tower, it has been increased by over 50%, and also higher than the imported and foreign Luigi Tube and Shell type (0.58t/(/(m^3.h))) and 0.65t/(/(m^3.h)). For the comparison of the main technical indexes between the JW Tower, the Quench Reactor and the Tube and Shell Type Methanol Tower, see table 1:

Table 1：Comparison of JW reactor, Quench Type Reactor and Tube-Shell Type Reactor

Types of the reactor	Quench	Tube-Shell	JW even Temp. Inner cooling in whole bed
Temperature difference at the catalyzer layer/℃	30-70	10-30	5-20
Reference time and space productivity/t/(m^3.h)	0.3-0.4	0.5-0.65	0.6-0.73
The filling coefficient of the reactor accelerant	＞70	35	＞70
Power consumption/%	130	100	100
The catalyzer consumption for the same output/%	150-200	100	＜100
The size of the equipment with the same productivity/%	100	100	50
The investment /%	70	100	＜50

The result of real use shows that the JW low pressure and even temperature type reactor has combined the advantages of the quench methanol reactor – simple structure, large catalyzer filling coefficient; and the advantages of the Tube-Shell type methanol reactor—lower temperature difference at the methanol reactor bed layer and effective synthesizing. With the same productivity, its size is smaller than the 2 types of reactor above said (see table 2):

Table 2: Size comparison of JW Reactor and Tube-Shell reactor

Productivity 1000T/D	100	200	300
Lurgi Tube-Shell Reactor/m	3.2	4.0	Hard to
JW even temperature reactor/m	2	3.0	produce 3.8

2.3 The information about the application and promotion of the Linda methanol synthesizing reactor:

6 sets of equipments with this technology have been operated successfully and the total productivity has been over 300,000t/a. The enterprise has gotten good economical and social benefits. Before 2000, the output of the Harbin Gasification Plant was only 40,000t/a. But since it enlarged its productivity with the JW low pressure methanol reactor, its productivity has reached 150,000t/a. Till now, total 12 contracts for transferring this technology have been signed—respectively for producing integrated methanol with gas and with the materials converted from natural gas, coal or various other materials. For details, see table 3.

Table 3: Projects with the JW reactors

No.	Clients	Diameter	Productivity	Delivery and running starting time
1	Harbin Gasification Plant	2000	60	2000
2	Harbin Gasification Plant	2000	80	2001
3	Jiangsu Wujin Chemical Plant	1400	20	2001
4	Henan Zhongyuan Gasification Plant	2000	70	2003
5	Shandong Kenli Fertilizer Plant	1600	30	2003
6	Hebei Hendan Xinyangguang	1400	20	2004
7	Yunnan Qujing Jiaohua	2000	80	2004
8	Henan Junma Group	2000	80	2004
9	Fujian Zhangzhou Changtai	1600	30	2005
10	Shanxi Weihua Group	3000	200	2005
11	Inner Mongolia Tianye Group	3000	200	2005
12	Dalian Dahua Group	3200	300	2006

The successful development and application have stopped the long-term importing of the modernized reactor technology. In three large plants—Weihua, Tianye and Dahua—which ammonia reactor has adopted foreign technologies, our technology has won over the foreign ones and saved plenty of foreign exchanges that should be cost for importing them. After the completion and starting operation of the equipments with this technology, the total productivity will be over 1 million t/a. In addition, several coal-gases made and cookery made methanol projects plan using this technology, such as that the 600,000t/a methanol project in Jiaocheng Shan-xi has adopted this technology and has passed the appraisal by the experts. Except for the above JW low pressure methanol reactor, Linda Company has also water cooling type methanol synthesizing reactor with the by-product intermediate pressure steam(water goes in tubes), as well as the water-cooling & gas cooling combined methanol synthesizing process and the PCT international patent has been applied for it. Several imported ICI Quench Reactor with 4m-up diameter in Inner Mongolia and Sichuan asked for technical renovation with this technology so as to improve their productivity. This technology is very competitive internationally and many foreign companies have discussed it with us.

3 How to solve the structural problems of the large methanol synthesizing reactor

As the single series enlarged methanol production equipments can decrease the investment and the production cost, it has become the essential development direction for the methanol production technology. About this issue, as the Tube-shell reactor is actually an undividable large tube array heat exchanger that integrates tube plate and shell body, it is hard to be enlarged. For example, under the 5MPa pressure, the diameter of the single 200,000t/a Tube-Shell reactor has reached 4m, and this has been the width limitation of the highway transportation in China. If it is over 4m, it would be hard to be transported. Therefore, the equipments over 200,000t/a should be paralleled with multiple Tube-Shell reactor, while this would bring some problems such as more investment to the equipments. One way for decreasing the diameter is increasing the ratio between the height and the diameter. Some ratio between the height and the diameter for the quench reactor in China has reached 10. Such a large ratio between the height and diameter not only adopts the axes reactor but also has large resistance. Even though the radial reactor is adopted, it is not sure if the methanol catalyzer that is shaped by pressing and with low strength will be grinded or powdered if a successive catalyzer bed is used. Although increasing the synthesizing pressure can improve some productivity on the reactors with certain diameter, it may increase the pressure difference between the inside and outside of the reacting tube, as well as between the reaction gas at upper and lower part of the tube plate and the vapor of the shell distance. It also increases the investment in equipments and makes it more difficult for the manufacturing technology. JW even temperature reactor has many advantages for enlarging it.

(1) First, the JW reactor has a large coefficient for the accelerant filling. With the same productivity and the filled catalyzer, the size of the reactor is minimized (see table 2), therefore the productivity of the single 5MPa synthesizing reactor with 4m diameter can reach 300,000t/a.

(2) When the JW reactor increases its synthesizing pressure, the pressure difference between the inside and outside of the tube of the inner parts. Therefore only the designed pressure of the shell is increased and no more difficulties are added on the technologies for manufacturing the inner parts, and the productivity under certain diameter can be improved easily by improving the synthesizing pressure. The productivity of the single reactor with about 9MPa synthesizing pressure can reach 600,000t/a.

(3) The separated cooling pot and the multiple coaxial packages are adopted as the inner parts of the JW reactor. Therefore, even if the diameter is over 4m, the inner parts can be separated and transported to the assembly site. The shell can be welded heat treated on site. Linda Company has bought several synthesizing reactor which diameter is over 4m, 4.3m, 4.5m and 4.8m, and has rebuilt them. The productivity of such single reactor can reach 1million t/a.

(4) With combination of multiple reactors. In the foreign plans on enlarging reactor of the methanol synthesizing equipment, ICI is the single reactor with the enlarged reactor diameter; TopΦe strings three radial heat insulation reactors; in the past, Lurgi advised two paralleled Tube-Shell type reactor co-using one bubble, but nowadays, it advocates using the reactor combining the water-coolinggas-cooling , that is, they are combined with a cooling tube synthesizing reactor by gas cooling and the water cooling reactor by the outside cooling by-product vapor. The raw material gas goes in the gas cooling reactor first. This combination needs one gas cooling reactor with over 4m diameter and a water cooling reactor with over 6m diameter. If the diameter of the water cooling reactor is same as the one of the gas cooling reactor and the gas goes through the reaction tube, the section for gas flowing is half of the gas cooling reactor, its resistance is huge. As it is difficult to manufacture the Tube-Shell type reactor with 6m diameter, Lurgi parallels two water cooling reactors and combines one gas cooling reactor. While for the reactor combining the water cooling and the gas cooling developed by Linda Company, the vapor produced by the water goes through the tube and the catalyzer is filled outside the tube. As the gas flow section is the same size as the gas cooling reactor, only one water-cooling reactor and one gas-cooling reactor is required. Comparing with Lurgi's method, one water-cooling reactor is lessened; therefore its configuration is more reasonable and more cost effective. For the super-large reactors with over 5000t/d productivity, this type can be adopted. An international PCT patent has been applied for it.

Except for applying for synthesizing methanol, Linda's JW low pressure synthesizing reactor is very applicable for the reaction of producing dimethyl ether by dehydrating methanol. Calculated as the design, the diameter of the 600,00t/a dimethyl ether reactor is 3.6m, much smaller than the 4.6m of the Tube-shell type reactor and the 4.4m of the heat insulation reactor.

4. Conclusion

China is rich in the coal and natural gas resource and that are the very profitable conditions for producing methanol (dimethyl ether). At the same time, methanol has a great future in the market, either as the chemical material or as the clean fuel. Enlarging methanol production and decreasing the cost have been the inevitable requirement for being the fuel replacer and replacing the oil tube to producing the main chemical products such as ethene and propene.

Multiple foreign companies have made great progress in enlarging the production of methanol. Represented by Linda Company, some domestic enterprises have also developed some new technologies with our own intellectual property in enlarging the production of methanol. It is a must that the breakthrough on the domestic technology of enlarging the production of methanol promotes the quick development of the methanol production in China.