Developing And Engineering Of Integration of Large Methanol, DME, Gasoline Synthesis and IGCC

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Abstract: The paper analyzed major technical and technological difficulties of Methanol , DME and gasoline Synthesis from syngas and its large-scale production, introduced Linda horizontal water-cooled reactor's application in methanol production, as well as the development of low cycle ratio fixed-bed technology used in large-scale methanol synthesis process, one-step DME procuction, one-step syngas to gasoline and chemical-IGCC Joint Production technology-which saving 10% power comparing with those isolated chemical industry. A single reactor with an annual output capacity of 1,000,000 tons is developed.Its net contents of methanol is 20%.

Keywords: methanol, reactor, Linda, DME, IGCC

Coal-based methanol system at the core of the energy chemical industry in China as the 21st century chemical industry developing direction, are understood and accepted by more and more people, which will gradually become a reality. In recent years, China Coal Chemical Industry is developing rapidly, our country is building around a large number of LP methanol synthesis plants, and their scales are becoming larger and larger. Recently, there is an upsurge of building more dimethyl ether plant being rasied. At the same time, olefins (MTP, MTO), hydrogen MTH, oil MTG from methanol and the projects of Integrated Gasification Combined Cycle power generation (IGCC) with methanol or dimethyl ether synthesis plant, are concerned by more people.

In these technologies of large-scale methanol, dimethyl ether, syngas to gasoline process and chemical-IGCC Joint Production, the reactor technology as one of the core is particularly significant. Linda company has developed a low-cycle or non-cycle water-cooled fixed-bed reactor, one-step dimethyl ether and one-step syngas to gasoline process and IGCC with dimethyl ether, methanol and synthesis gasoline plant, and so on a number of new technology. So we have applied for a number of Chinese and PCT patents.

1 The technology bottleneck of large-scale syngas to methanol, DME, gasoline and IGCC joint production.

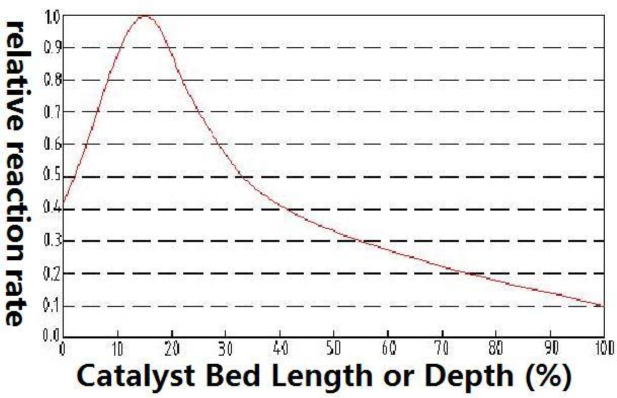
1.1 Synthesis equipment amplification is limited by transport conditions. At present, foreign large-scale methanol synthesis technology in the context of the measures taken are: First, amplification of reactors' size, and the other is to increase the number of reactor, to set a number of (in series or parallel) reactor, etc. It will increase investment and Running costs with a number of reactors in series or parallel. Enlarging equipment will increase manufacturing difficulties. And Chinese coal resources are mostly landlocked, with the manufacture factory of large-scale processing equipment are far apart, the current roads, bridges and culverts can only provide max 4.5 meters passing capacity. E.g. there is A methanol synthesis reactor device of annual output of 600,000 tons in CNOOC Kingboard which diameter is more than 5M. So how to transport it in the inland of China becomes a serious problem.

1.2 Low-cycle is the key to lower running costs and solving the problems of large-scale synthesis system. In the existing methanol synthesis technology, the mole flowrate ratio of cycle gas to the raw gas (the cycle mole ratio) is more than 5 times. In the synthesis system of syngas to dimethyl ether or Fischer-Tropsch reaction to gasoline, the gas flow rate is also several times more than fresh gas. Methanol contents in the outgas of the reactor is only 5% upper and lower, much lower than the equilibrium concentration of reaction product. As far as possible to reduce the cycle mole ratio means the system handling less gas can effectively reduce the specifications of the equipment and pipelines, investment, then enable large-scale, fully recover reaction heat, reduce compressor energy consumption, save the cost of production,etc.

1.3 The key of reducing cycle ratio and increasing methanol content at reactor outlet is to raise the heat exchanging capacity of reactor. Different from those natural gas-based methanol plant abroad, China methanol plants are mostly coal-based. Texco and Shell coal gasification technology can use pure oxygen to product synthesis gas which H2, CO content of the total is as high as 95% ,inert gas is little. The methanol equilibrium content is more than 50% under 8MPa and 230℃. However, it will produce a large number of heat during methanol synthesis reaction . If the reaction heat can not be removed in time, it will cause the temperature of the catalyst bed exceed the permissible limits,and this will seriously affect the efficiency of the reaction. So it takes a large number of cycle-gas to take the reaction heat away and dilute CO content from about 30% in synthesis gas down to 5-10%, to avoid catalyst deactivation over heat-resistant temperature.It makes the methanol content in the outlet gas decreases to about 5%. If we need to reduce cycle ratio sharply, even to one-through operation (for example, for methanol, dimethyl ether and IGCC), the existing fixed-bed reactor technology can not meet the requirements in the heat transfer capacity.

1.4 The limitations of slurry bed to resolve heat transfer problem. Slurry bed can be used to strengthen the heat transfer capacity, reduce the cycle ratio, raise the content. of product in reaction gas. However, slurry bed (three-phase bed) increases the mass transfer resistance in the reaction process between gas, liquid (conducting oil) and solid (catalyst), reduces the efficiency of reaction, causes the larger equipment diameter, higher bed and handles the catalyst more complex, so large-scale engineering applications is restricted. A foreign 260t/d slurry methanol plant and 100 t/d (60 t/d actually) dimethyl ether slurry reactor has been stopped for many years.

1.5 The optimized design of fixed bed to resolve heat transfer problem at low cycle ratio.



The key of large-scale synthesis technology is lowering the cycle ratio, and that reducing the cycle ratio of fixed-bed synthesis system whose breakthrough is to resolve the heat transfer problem, the heat exchange area per unit catalyst of reactor whose catalyst is outside the cold tube is usually 20 ~ 30m^2/m^3, Linde spiral tube reactor is 50 m^2/m^3, the kind of double cannula reactor-no matter domestic or abroad- is usually lower than 20 m^2/m^3。They are much lower than the tube-shell reactor. In order to strengthen the heat transfer, they had no choice but to move to reduce the boiler water vaporization pressure and temperature, even existing double cannula reactor’s inside and outside heat transfer temperature difference is up to 140 ℃, but under this condition of low cycle ratio and high methanol net of one-way synthesis will cause some problems.

As the methanol synthesis reaction heat is deal to the gas reaction rate in the catalyst, and the reaction rate keeps changing during the syngas's flowing across the catalyst bed. Whether radial or axial reactor, their reaction rate is increasing at the beginning, it will reaches a peak of reaction rate, and then gradually decreases (Fig 1). If we simply lower the steam pressure to control the temperature, the temperature of the later bed will be too low . If we take some appropriate measures such as increase the heat exchange area in the front part of the bed to move the strong reaction heat,we can make the better reaction condition and higher efficiency. However,we can't solve this problem use the most kind of reactor but this kind of horizontal reactor.

2 Linda large-scale horizontal water-cooled reactor structure and characteristics

Basing on the analysis of domestic and foreign large-scale methanol synthesis technology, Linda has developed one kind of methanol synthesis technology successfully, which can be applied to the condition of large-scale and low cycle ratio, includes vertical and horizontal water-cooled Under-pressure steam methanol synthesis reactor joint producing medium-pressure steam, have been successfully used for more than 100kt/a methanol plant, especially the horizontal water-cooled methanol reactor (patent "horizontal tube heat exchanger", Chinese patent number: ZL200420116978.6), nearly develops the non-cycle horizontal synthesis reactor technology further.

Horizontal water-cooled reactor structure shows in following Figure 2. Horizontal water-cooled reactor is formed from shell and water-cooled tube units, filled with catalyst outside the tube, the syngas through the head is imported into the bow-shaped channel of the top, dispersed by a gas distribution plate into the catalyst bed, formed 90 ° cross-flow inside the bed with water pipe, exports syngas from the other side of the head, cooling water goes into water tubes via inlet pipe and tube box and absorb heat to control the reaction temperature.

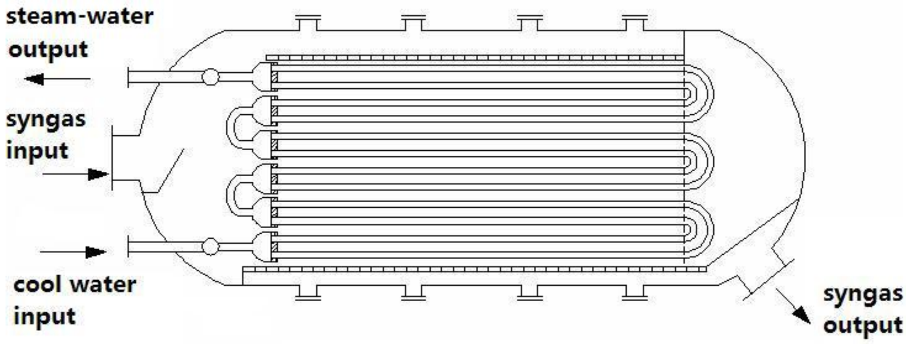


Fig 2 The Structure Of Horizontal Water-cooled Reactor

We can see horizontal reactor overcome the disadvantage of tube-shell reactor which can't regulate heat transfer rate along the reaction process. Its horizontal water-cooled tube can be arranged in accordance with the needs of different density from top to bottom along the flow direction of gas, that is in the upper part of the catalyst bed which is the site of largest reaction rate we can arrange more tubes, less tubes in the part of lower reaction rate and less reaction heat. Through the optimized design of cooled water tubes and the continuous heat exchanger, we can realize that the catalyst is not over-temperature, under the harsh condition of the lower cycle ratio(which can be even lower than 1) and high CO concentration synthetic gas (up to 20%).

Linda horizontal water-cooled reactor creates favorable conditions from the following aspects in order for the large-scale methanol of coal-based raw syngas:

1. The higher volume utilization ratio. The catalyst is loaded outside the cooled water tubes, so the

volume utilization ratio is two times than tube-shell reactor.

2. To strengthen reactor heat transfer in many ways:

(1) The cooled water tube is arranged compactly, large heat transfer surface, high cold area ratio which is the highest in the type of catalyst loaded outside the tubes, more than double cannula water reactor several times.

(2) The high heat transfer coefficient for syngas and water in the horizontal tubes flow like 90 ℃ cross-flow, is higher than vertical reactor one time. The cross-flow can reduce the wall effect of which can cause the temperature and concentration of non-uniformity.

(3) The horizontal arranged cooled water tube, the reaction syngas flow from the top to bottom; we can arrange more tubes, less tubes in the part of lower reaction rate and less reaction heat. Through the optimized design of cooled water tubes and the continuous heat exchanger make heat removal system, strengthen heat transfer, solve the bottleneck.

3. The lower cycle ratio, high methanol outlet concentration. As a result of these strong measures heat transfer can be lower than the cycle (<2) or one-throught, the concentration of methanol tower from the present 5% to 10% or even 20%. It significantly reduce the size and the investment of the pipeline and device of methanol synthesis loop,decrease the cooling water and power consumtion,and increase the by-product steam.

4. Low pressure drop. Reaction gas flows catalyst bed from top to bottom, the catalyst bed is thin and short distance, so the reactor pressure drop is only 0.03 ~ 0.05Mpa.

5. The diameter of reactor is small, production capacity of reactor can be improved by increasing the length of catalyst bed, so this reduces manufacturing costs and solves transportation problems.

6. Breaking up the whole reactor into parts and minimizing the large equipment are some ways to solve large-scale problems. First, separating shell and internal, so the internal can be replaced to improve the life of equipment shell; second, the internal is divided to manufacture and then to facilitate the manufacturing process and overhaul. Especially the large-scale reactor, its shell, internal and other pieces of parts can be sent to the scene firstly, with only a small space can be assembled, and do not need large-scale lifting equipment like the vertical reactor.

7. Internal and shell is connected on the one side, and free can be extendable on the other side, which resolves the shortcomings of other synthetic reactor’s heat transfer fixed tube expanded by the thermal stress.

3 Engineering applications and performance of Linda horizontal water-cooled reactor

The horizontal water-cooled reactor is the Linda's latest technology.It can be applied to large methanol plant, can achieve a single set of 400kt/a to 1800kt/a, Ningxia pagoda 600kt/a methanol project has decided to adopt the technology and signed a contract which is included in the national scientific and technological supporting projects. Inner Mongolia Sulige Natural Gas Chemical Co., Ltd. 180,000 tons per year methanol synthetic reactor reconstruction project has used horizontal water-cooled reactor which joint produces 2.0~4.0MPa pressure steam to instead Japanese Mitsubishi-synthetic methanol quench converter. The device has been successfully put into operation in the past 5 months, mainly as follows:

The reactor TPR operated since June 3, 2008 to June 6, 2008, totally 78 hours. Finally, the temperature rose to 231 ℃ constant temperature, before the end of TPR restored the water: ≤ 25 Kg, the water accumulated 8015 Kg at last. The catalyst layer temperature difference ≤ 3 ℃ in TPR process, the water out of the total volume is 94.8% when the temperature is under 190℃, so that more water could restore under low temperatures. June 8 operation data in the early cases as follows:

Table 1 Data Sheet

	Natural Gas		Fresh Syngas	Cycle Syngas
Flowrate (Nm^3/hr)	14031		54546	141175
	Reactor Inlet	Reactor Pressure Drop	Drum Steam	Separator outlet
Pressure (MPa)	8.1	0.03	2.4	7.8

Table 2 Temperature (℃): catalyst layer (point No.1 to 12):

231.1	229.1	232.9	232.7	229.3	234.1
224.9	225.0	227.2	225.5	225.6	227.2

Full capacity: the reactor after a short time of light load, since June 16 started running fully, refined methanol yield reached 624 tons per day continuously many days, more than the original design value 600 tons per day.

The reactor in the operation made small temperature difference, smoothed uniform temperature, changed former high-temperature and bed temperature fluctuations. Horizontal water-cooled reactor in the TPR and production process, facilitated temperature regulation, operated easily, and bed temperature difference dropped.

This is the first large-scale horizontal water-cooled reactor of the methanol synthesis plant in the world, which breaks through a number of limitations of the traditional synthesis technology, and shows many advantages after put into operation:

1. The bed resistance of reactor is low, and the pressure drop is only 0.02 ~ 0.03MPa, as one-tenth of the general reactor.
2. There is a high pressure difference between internal and external cooled water tube, which is 7MPa currently, affordable up to 9MPa according to the design pressure. So this is rarely at home and abroad for the water-cooled reactors. The high-pressure difference reactor can get smaller size, increase the production capacity.
3. The low cycle ratio and high methanol outlet concentration. The design cycle ratio of horizontal water-cooling reactor is 2.5, actually about 2.1, 50% lower than usual. According to the accounting of actual production of methanol, methanol outlet concentration is as high as 9%, twice for general synthesis methanol reactor.

4 The application and promotion prospects of Linda horizontal water-cooled reactor

4.1 An annual output million tons reactor scheme

Linda had provided the 2000 to 7500 tons per day scheme of methanol horizontal water-cooled reactor for many users, according to China Petrochemical Association of Productivity Promotion Center of Chemical requirements reported a optional integrated innovation scheme of 1,800,000 tons per year methanol large-scale demonstration project to the Chinese Ministry of Science and Technology, which adopt a joint reactor process, synthetic devices see diagram 3.Its reactor used one Linda horizontal water-cooled reactor and one gas-cooled reactor, the main equipment and technical parameters in Table 3, Table 4.

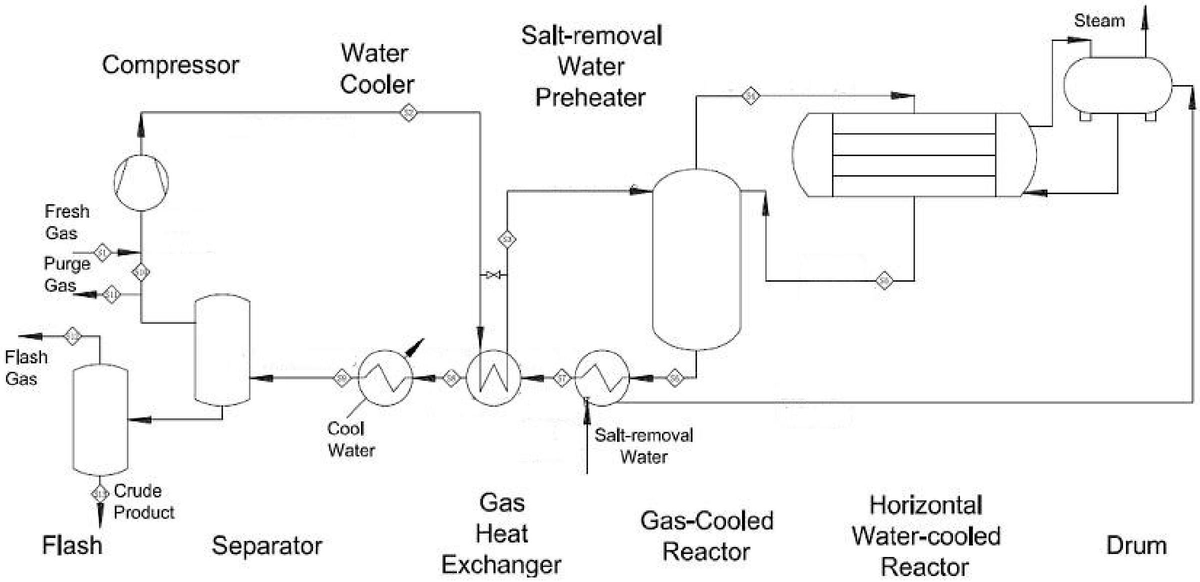


Fig 3 United Methanol Synthesis Reaction Process

Table 3 Technical Specifications

	Unit	Value	Remarks
Synthesis Pressure	MPa	8.3	
Refined Methanol Yield	t/d	5525	does not include distillation loss
Crude Methanol Concentration	wt%	95.24	
Fresh Gas Flowrate	m^3/h	528000	
Gas consumption	m^3/t	～2350	refined methanol
Cycle Ratio		2.0	
Cycle Compressor Power	kw	5500	adiabatic efficiency 0.75
Pressure Drop of Synthesis System	MPa	0.6	
Total CO conversion rate	%	98.69	
Catalyst Loading Volume	M^3	210	based on the domestic catalyst
Reactor Outlet Concentration of Methanol	mol%	13.15	
Public Works			
Cycled water consumption	t/t	43	refined methanol
By-product steam			
Pressure	MPag	2.5～4.0	
Yield	t/t	1.03	refined methanol

Table 4 Main Equipment Parameters

Name	Specifications	Number	Remarks
Gas-cooled reactor	Φ4000×7000（T-T）,Vcat=$80m^3$	1	

Horizontal water-cooled reactor	Φ4000×17000（T-T）, Vcat=130m^3	1

At present, the methanol plant equipment generally is large and has high energy consumption problems, the main reason for this is: the strong exothermic of methanol synthesis reaction, low heat resistance of copper-based catalyst, as well as the current methanol reactor's heat transfer capacity constraints, so it needs to increase the cycle rate of synthesis loop, dilute the concentration of CO to ease the exothermic reaction and take heat away, in the synthesis loop in the handling gas flowrate is more 6 times than the feedstock gas. The content of methanol of Linda horizontal reactor could be up to 20% even 30% with low cycle ratio or no circulation, which is fit to simulated result. The throughput will be extremely increased compared above with the same gas flowrate. For example, the methanol yield is 300,000 tons per year with flowrate of 560000 Nm^3/h and cycle ratio of 5 while it can be up to 1,800,000 tons per year without circulation. This enlarges scale easy, but also decreases the investment and energy consumption sharply. Table 5 lists the yield comparison with different cycle ratio when gas flowrate is 560000 Nm^3/h.

Table 5 Different productivity under different cycle ratio

Cycle Ratio	5	2	1	0
Fresh Gas Flowrate（Nm^3/h）	93333	186667	280000	560000
Reactor Inlet Flowrate（Nm^3/h）	560000	560000	560000	560000
Productivity（kt/a）	300	600	900	1800

4.2 One-step syngas to DME process

One-step synthesis of dimethyl ether from syngas,have low energy consumption and investment. In order to effectively separated the products, it is necessary to improve the content of CO in the syngas, which makes synthetic reaction in greater heat. Slurry bed can be used to take the reaction heat away, but easy to cause the active components separated from the catalyst. The reaction through a gas - liquid - solid mass transfer in the slurry bed, reduces the efficiency of the reactor with low utilization, high investment. The tube-shell fixed Bed reactor in the conditions of low cycle and high content of CO is more difficult than the slurry bed with lower water temperature to take heat away, because this will cause the lower part of the bed temperature was too low adverse reaction.

Linda horizontal water-cooled reactor can be as a result of optimized designing the water tubes and connected steam generating system, control the heat transfer speed of different parts of the reactor, it can be successfully solved the problem. Linda layered one-step synthesis system of dimethyl ether is horizontal water-cooled methanol to link up the dehydration reactor, the methanol synthesis catalyst and dehydration catalyst fill separately. The layered one-step synthesis Dimethyl ether with two towers, methanol synthesis and dehydration are two independent catalytic reactions, so their temperatures can be adjusted separately, such as methanol synthesis temperature 220 ~ 280 ℃, methanol dehydration temperature 260 ~ 360 ℃. Second, separating the two catalysts can avoid the active centers interfering each other, susceptible to dehydration catalyst for methanol steam produced by oxidation of inactivation, the methanol synthesis catalyst and methanol dehydration catalyst for industrial applications are very mature, there is no technical risk.

On the basis of the current success solution to one-step dimethyl ether bifunctional catalyst each match, it can use non-layered one-step synthesis dimethyl ether, which has the merit that H2/CO may be equal to 1 to reduce CO synthesis gas conversion load to achieve further energy-saving, which is more meaningful to coal gasification syngas synthesis dimethyl ether for IGCC power generation joint production, the following as one-step layered synthesis examples.

In the dimethyl ether synthesis system from syngas, methanol synthesis reactor uses the horizontal water-cooled reactor whose diameter is 4.0 meters, contains copper-based catalyst for methanol $160M^3$; methanol dehydration reactor uses gas-cooling reactor whose diameter is 3.2 meters, contains γ-alumina methanol dehydration Catalyst $75M^3$. The synthesis gas is compressed to 8.5MPa with cycle gas, heated to 230 ℃ into the methanol synthesis reactor, reacted on the methanol catalyst layer under 250 ℃. Reaction heat is taken away by water in the horizontal tubes to joint produce steam, the methanol content is 37% at the horizontal reactor outlet, the methanol dehydration reaction goes on in the next reactor at about 300 ℃. Under the volume of raw materials $583596Nm^3$/ h, dimethyl ether synthesis yield can be 167 tons / h, with an annual output 1,350,000 tons dimethyl ether, the data in Table 6.

Table 6 Data Sheet

Name		Fresh Gas	Cycle Gas	Methanol Reactor Outlet	DME Reactor Outlet
Total Flowrate Nm^3/h		583596	244485	473606	473606
	H_2	65.84	63.95	39.22	39.22
	CO	32.15	22.15	13.71	13.71
	CO_2	1.14	3.71	3.25	3.25
Components	N_2	0.25	3.12	1.92	1.92
%	CH_4	0.62	6.52	4.13	4.13
	H_2O	0	0.097	0.13	17.33
	CH_3OH	0	0.45	37.65	3.25
	$(CH_3)_2O$	0	0	0	17.20

4.3 syngas F-T reaction or layered one-step To Gasoline process

The ways of syngas to hydrocarbon from Natural gas or coal, such as Sasol company in South Africa can use F-T reaction to produce, which usually gets diesel with complex components, generates a lot of methane, also generally needs to be further refined and modified, so it has to need the large investment; and the other way is through the synthesis methanol from synthesis gas, and then dehydrating methanol to dimethyl ether, hydrocarbon generates from dimethyl ether at last, such as the Exxon Mobil's MTG technology, the main product of MTG is gasoline, good quality and generating less methane. The existing methanol synthesis technology, due to the strong reaction heat, and the copper-based catalyst can't expose to high temperature, it is necessary to remove heat in the reaction at the same time, such as tube-shell reactor removes heat by water absorbing heat to produce steam, but its limitation of heat transfer capacity, to be used the cycle of synthesis gas as much as 5 to 10 times than feedstock gas for the removal of reaction heat, then the methanol content of syngas at the reactor outlet is only 3~6%, it would be inappropriate to dehydrate to hydrocarbon directly, so MTG method uses synthesis gas to synthesize methanol, and then which cools by syngas, condensates and separates methanol from synthesis gas, makes liquid methanol vaporize for dehydration at last, as a result of the strong reaction heat of methanol dehydration, the Mobil's MTG method uses a high cycle ratio which is more than 9, leads to high power consumption.

By adopting the aforementioned Linda horizontal water-cooled reactor in methanol synthesis part, the cycle ratio can be reduced to <1 from the existing 5 to 10, the methanol content of methanol syngas at the reactor outlet from the existing 3 to 6% increases to 50%, So as to methanol at a high content of syngas methanol synthesis can be directly dehydrated to hydrocarbons without the separation and condensation, the same as the methanol dehydration is a strong exothermic reaction, the same can use horizontal water-cooled reactor, such as the ZSM-5 molecular sieve catalyst, reaction temperature is 280~380 ℃, and the use of water boiling heat transfer, the steam pressure can be 10Mpa high-pressure, the following as a case.

The layered one-step synthesizing gasoline from synthetic gas, methanol synthesis reactor uses Linda horizontal water-cooled reactor, 3.5 meters in diameter, which contains copper-based catalyst for methanol $110M^3$, methanol dehydration reactor uses horizontal water-cooled reactor tower, 3.3 meters in diameter which contains ZSM-5 molecular sieve catalyst $90M^3$. The syngas is compressed to 5.5MPa and heated to 220 ℃ into the methanol synthesis reactor, about 250 ℃ in temperature, reacts on methanol catalyst layer. Reaction heat is taken away by water in the horizontal tubes to joint produce steam, the methanol content is 46% at the horizontal reactor outlet, the methanol dehydration reaction goes on in the next reactor at about 300 ℃. In this case the cycle ratio is 0, purge gas flowrate is 2772 kmol / h all to IGCC power generation, the raw gas 10000kmol/h produces hydrocarbons 798.4 tons/day, with an annual output 265,000 tons of hydrocarbon, $1000Nm^3$ syngas to hydrocarbon 149kg, see data Table 7.

Table 7 Data Sheet

Name		Methanol Reactor Inlet	Hydrocarbylation Reactor Inlet	Hydrocarbylation Reactor Outlet	Purge
Flowrate kmol/h	Total	10000	5208.8	5208.8	2772.3
	H_2	6524.8	1731.7	1731.7	1718.4
	N_2	21.7	21.7	21.7	21.4
	CH_4	43.4	43.4	73.4	73.4
	CO	3290	896.3	896.3	882.0
	CO_2	120	118.1	118.1	85.2
	H_2O	0	1.9	2378.2	4.1
	CH_3OH	0	2395.5	19.2	19.2
	Hydrocarbon	0	0	33268kg	

4.4 Methanol, DME and gasoline-IGCC combined production without circulation.

The technology of chemicals-power combined production is generally acknowledged with high efficiency and energy saving. The focus is researching on combined production of methanol-IGCC, DME-IGCC and gasoline-IGCC. The energy saving is very high when methanol to DME reacted with low cycle ratio or no circulation. It goes with the problem that the increased vent gas would result to increasing the waste gas that affects on economic benefit. So using the vent gas to make power –IGCC will bring much more benefit then producing chemicals and power respectively. Fig 4 explains this technology.

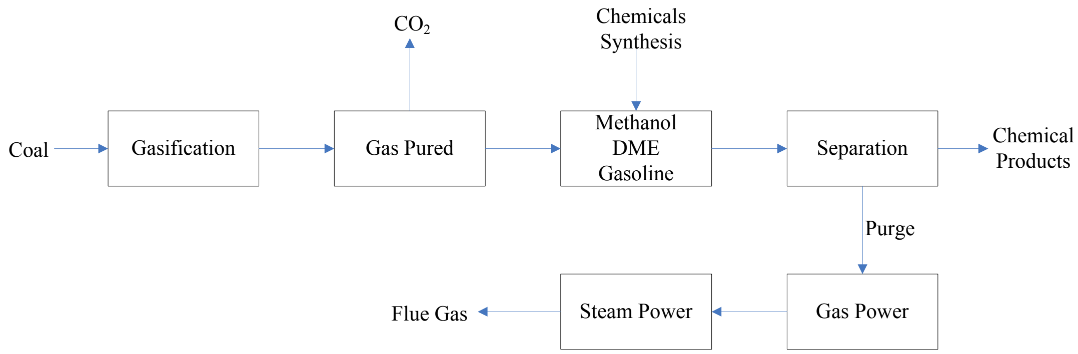


Fig 4 Chemicals-power Combined Production

Note：1. Chemicals synthesis contains methanol, DME and gasoline synthesis. The chemicals can be achieved with one step or two steps methods.

2. The by-product of steam could be generated power produced in gasification, purification and synthesis process.

The followed example explains how to make use of the horizontal water cooling reactor to produce methanol, DME and gasoline-IGCC combined production without circulation.

Example1: Material coal consumes 31.6kg/s and the total exergy is 883.3MW with the condition of coal gasification-power combined production. The flowrate of pured syngas is 2.778kmol/s. Table 1 lists the gas components and flowrate. The syngas passes the methanol synthesis device for one time. The gas is heated to 220℃ in heat exchanger at 5Mpa and then fed into the reactor with the catalyst of $100M^3$. The gas reacts at 220~270℃. We can control water boiloff temperature in reactor to keep the uniform temperature and small temperature difference in catalyst beds. The gas from the reactor is cooed to 35℃ in heat exchanger and condenser with the methanol concentration of 25.1%. Liquid methanol and purge can be gained after separating in gas-liquid separator. The yield of methanol is 14.66kg/s and the purge is burned to generate the power of 188MW. See example 1 in table 9.

Table8 The Feedin Gas Component

component	H_2	CO	N_2	CH_4	CO_2	H_2O	CH_3OH	total
mol %	40.04	57.21	2.1	0.06	0.59	0	0	100
Kmol/s	1.122	1.589	0.058	0.002	0.016	0	0	2.778

Building the gas of same flowrate listed in example 1 without producing power, we make the ratio of hydrogen to carbon to be 2 after transform and decarbonization. Methanol synthesis can take the Lurgi reactor. The ratio of cycle gas to flesh gasis 5. The fuel exergy is 665.2MW when make the same yield of methanol (14.66kg/s) and the energy consumption is 45.3GJ/T while the combined production is 30.77GJ/T. The energy conversion is 48%. The fuel is 432.2MW when producing power of 188 MW by IGCC. The total fuel is 665.2＋432.2＝1097.4MW when produce power and methanol respectively. It means the energy efficiency is 46.2% while combined production is 57.4%. Relative energy saving ratio is 1－883.3/1097.4＝0.195. See example 1 in table 9.

Example2: DME-power combined production use bifunctional catalyst of 150M3 consisting of copper-based methanol catalyst and γ-alumina or molecular sieve dehydration catalyst. We can get the DME of 10.43kg/s and power of 157MW at 6 Mpa and 280 ℃. It consumes energy of 46.21GJ/T per ton DME and the efficiency of total exergy is 53.59%. If produce the products respectively, the energy consumption is 63.2GJ/T for the same yield of DME and the fuel exergy is 402.3MW for the same yield of power. Combined production saves energy about 16.76% more than Producing respectively. See table 9 eg2.

Example3: Gasoline-power combined production use F-T catalyst of 120M^3 on the condition of the same gas flowrate and component listed in table 1. We can get the gasoline of 6.1kg/s and power of 172MW at 4 Mpa and 250 ℃. Combined production saves energy about 15.8% more than Producing respectively. See table 9.：

Table9 the capability of chemical-power combined production

	Example1			Example 2			Example 3		
	Methanol-power combined production	Produce respectively		DME-power combined production	Produce respectively		Gasoline-power combined production	Produce respectively	
		IGCC	Methanol		IGCC	DME		IGCC	gasoline
Fuel energy MW	883.3	1097.4		883.3	1061.3		883.3	1049.3	
		432.2	665.2		402.3	659		395.4	653.9
yield kg/s	14.66		14.66	10.43		10.43	6.1		6.1
power MW	188	188		175	175		172	172	
Energy consumption GJ/T	30.77		45.38	46.21		63.2	79.98		107.2
Efficiency of total energy %	57.4	46.23		53.59	44.6		52.04	44.66	
Relative energy saving rate %	19.5	0		16.76			15.8		

4.5 The technology of H2S to sulfur and producing nature gas with high pressure steam as by-product

The synthesis nature gas can be gained by methanation reaction. The material gas is get from coal gasification. Methanation reaction can use the sulfur-tolerant molybdenum sulfide catalyst or nickel catalyst with alumina as charge. The strong reaction heat will be the main problem.

$$CO + 3H_2 = CH_4 + H_2O \qquad +206KJ/mol \qquad (1)$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \qquad +165KJ/mol \qquad (2)$$

The (1) and (2) are strong exothermic reactions and the adiabatic temperature rise of reaction (1) is 72 ℃. As the heat of reaction of synthetic nature gas is tens times as much as the heat of methanation in ammonia synthesis. Preventing the catalysts from overheating by controlling the temperature of methanation reactor turns into a technical problem. At present, controlling the temperature needs a number of complex devices containing heat exchangers and gas cycle machines. The patents of US4016189,US4205961 and US4298694 is about methanation reaction with a number of adiabatic reactors and heat transfer reactors in series. We should increase the number of devices because of strong reaction heat. Decreasing the CO content of feeding gas by gas cycling to control temperature will increase the consumption of power.

example1：The methanation reactor is horizontal water cooling reactor. The diameter is 4.2m and the volume of catalysts (Ni 60%) is 250M^3 with alumina as charge. The pressure of purged gas from Lurgi coal gasification is 5 Mpa. The gas heated to 290℃ come into the reactor and then react in 320℃ in the catalysts bed. The high pressure steam is build by heating the boiler water form heat of reaction. The CH4 content of gas from methanation reactor is 94.2% after cooling and dehydrating. The volume of material gas is 282584Nm^3/h, from which we can get the reacted gas of 100000Nm^3/h while get the steam of 350t/h as by-product, i.e.5 tons high pressure steam per ton material gas. The data is listed in table 10.

Table10 Data Sheet

Name		Inlet	Outlet	Methanation
Gas vol Nm^3/h		282584	162022	100000
Component%	H_2	65.10	0.85	1.38
	CO	20.90	0.32	0.52
	CO_2	1.00	0.67	1.08
	CH_4	12.00	58.14	94.20
	N_2	1.00	1.74	2.82
	H_2O	0	38.28	49838kg/h（L）

In the process of syngas purification from coal gasification, we need oxidate the H_2S to sulfur for recovery. This is a strong exothermic reaction with adiabatic temperature rise of 70 ℃ for 1%H_2S. Some plants employ the Linde spiral water cooling reactor and the content of H_2S in syngas should be hold a low concentration. Using the Linda horizontal reactor with TiO selective oxidation catalyst, we can achieve the uniform temperature reaction with high concentration of H_2S at 230 ~ 280 ℃ while get the by-product of medium-pressure steam.

5 The engineering performance of Linda large-scale methanol synthesis, DME synthesis, methanation in ammonia plant

Linda uniform temperature methanol synthesis technology, ammonia synthesis and methanol methanation technology in ammonia plant, widely is used for many years and promoted. There are a large number of projects or applications in the combined methanol in ammonia plant, ammonia synthesis and methanol methanation. Linda low pressure methanol synthesis technology is also used for more than 20 applications (see Table 11). Linda not only signed a technology and equipment contract which is 600kt/a large-scale water-cooled horizontal methanol synthesis project with Ningxia Pagoda Petrochemical Group, and in addition to the first horizontal methanol water tower put into operation successfully, there had been Longchang φ1600 reactor in Sichuan, Sulige φ2800 reactor in Inner Mongolia which are two vertical water cooled reactors put into operation successfully and achieved good results. At the same time, Tow sets of 100kt/a dimethyl ether plant has successfully put into operation and got good results in Henan Asia New Energy Company, which used Linda dimethyl ether synthesis technology. These series of projects brought the experience to Linda engineering for future large-scale methanol, dimethyl ether, synthesis oil and other new technologies.

Table 11-1: A list of Linda low pressure methanol reactors which have been put into operation

No.	Clients	Diameter	Productivity	Delivery and running starting time
1	Harbin Gasification Plant	2000	60	2000
2	Harbin Gasification Plant	2000	80	2001
3	Henan Zhongyuan Gasification Plant	2000	70	2003
4	Shandong Kenli Fertilizer Plant	1600	30	2003
5	Jiangsu Wujin Chemical Plant	1400	20	2004
6	Hebei Handan Xinyangguang	1400	20	2004
7	Yunnan Qujing Jiaohua	2000	80	2004
8	Inner Mongolia Tianye Group	3000	200	2005
9	Shanxi Weihua Group	3000	200	2006
10	Henan Junma Group	2000	80	2006
11	Liaoning Benxi Group	1900	30	2006
12	Fujian Zhangzhou Changtai	1600	30	2007
13	Shanxi Yulin Group	2100	100	2007
14	Yunnan Yunwei Group	3200	200	2007
15	Shanxi Tianhao Group	2100	100	2007
16	Shanxi Lanhua Group	3000	200	2007
17	Hulunbeier Dongneng	3000	200	2008

18	Shandong Kenli	1800	60	2008
19	Sulige Natural Gas Chemical Plant in Inner Mongolia	2800	150	2008
20	Shanxi Jintong	2100	100	2008
21	Sulige Natural Gas Chemical Plant in Inner Mongolia	3400	180	2008
22	Sichuan Longchang	1400	20	2008
23	Yunnan Dawei	3200	200	2007

Table 11-2 The list of Linda low-pressure methanol reactor being manufacturing

No.	Clients	Productivity	Project progress	Date of signing
10	Hebei Tangshan Guyu	100 kt/a	Φ2200 vertical water-cooled reactor，designing	2008
9	Sichuan Panzhihua Coal	100 kt/a	Φ2100，designing	2008
8	Shandong Rongxin	250 kt/a	Φ3400，designing	2008
7	Ningxia Pagoda	600kt/a	Φ3800，Ministry of Science and Technology Support Program	2008
6	Qingdao Hengyuan	60kt/a	Φ1800，Equipment manufacturers	2007
5	Wulanchabu Xinao group	20kt/a	Φ1400, Design	2007
4	Inner Mongolia Zekai	1000kt/a	Experts have successfully passed the examination and signing	2007
3	Liaoning Dandong Wantong	60kt/a	Φ1800, signed a contract	2007
2	Sichuan Shehong	40 kt/a	Φ1600，Design	2007
1	Dalian Dahua	300 kt/a	Φ3200，completed the installation	2004