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Technology of Producing Dme

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Abstract: The use of natural gas as a feedstock for the production of dimethyl ether makes the project economically viable. One of the most promising methods of producing "synthesis gas" from natural gas is trireforming. "Synthesis gas" is a raw material for production. The selection of an efficient method for the production of dimethyl ether increases production productivity.

Keywords: dimethyl ether, DME, methanol dehydration, direct synthesis, indirect synthesis.

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Direct and indirect synthesis methods

The process of obtaining dimethyl ether from synthesis gas consists of three main stages: the reaction of the conversion of water gas, the reaction of methanol synthesis and the dehydration of methanol.

Indirect synthesis method

Traditionally, dimethyl ether is produced from synthesis gas in a two-step process in which methanol is obtained from synthesis gas, purified and then converted to dimethyl ether in another reactor. A diagram of this process is shown in Fig. 2-3. The commercial reaction of the process for the production of dimethyl ether from methanol dehydration is shown in the formula. (1):

$$2CO + 4H_2 \leftrightarrow 2CH_3OH \qquad \Delta H_{298} = -43{,}4\ kcal/mole \qquad (1)$$

$$CO_2 + 3H_2 \leftrightarrow 2CH_3OH + H_2O \qquad \Delta H_{298} = -11{,}9\ kcal/mole \qquad (2)$$

Then DME is obtained by dehydration of methanol in the following reaction:

$$2CH_3OH \leftrightarrow CH_3OH + H_2O \qquad \Delta H_{298} = -5{,}6\ kcal/mole \qquad (3)$$

Numerous studies of the kinetics of dimethyl ether synthesis by methanol dehydration on solid acid catalysts have been published. Most of the authors agree that the mechanism follows either the Langmuir-Hinshelwood [2] or the Eli-Rideal kinetic model [3], with water and dimethyl ether acting as reaction

inhibitors [4].

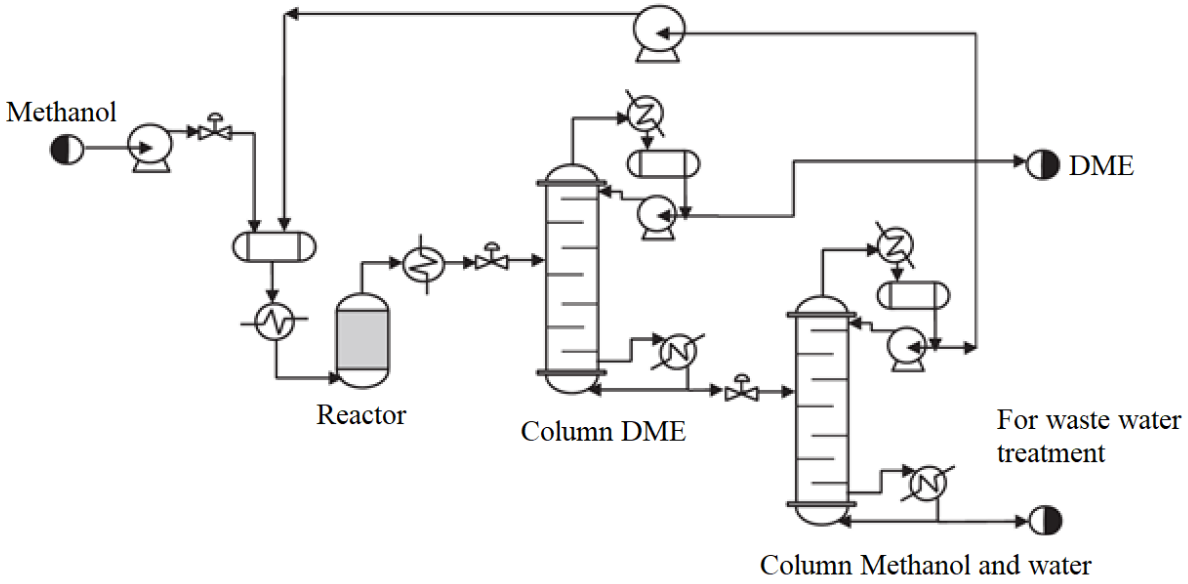

Fig. 3 – Scheme of indirect synthesis

Synthesis gas can be obtained by steam reforming. Currently, Haldor Topsoe, Lurgi, Mitsubishi Gas Chemical Company, Southwest Research Institute of the Chemical Industry of China, Toyo Engineering Corporation and China Energy (Jiutai Group) are the main companies in possession of the necessary technology for the production of DME using indirect synthesis.

Methanol production worldwide is mainly controlled by two companies: Johnson Matthey (ICI process) and Lurgi. This takes place in the presence of a Cu/Al/ZnO heterogeneous catalyst. The final stage, obtaining dimethyl ether, is carried out in the presence of solid acids. Zeolites, γ-alumina and silica-alumina catalysts are the most commonly used.

Components of physical properties

The following table summarizes the physical properties of all pure components from the Aspen Plus database:

Table 1 - Physical properties [5]

Component name	Physical properties						
	Formula	Molecular mass(kg/ kmol)	Normal boiling point (K)	Critical pressure (bar)	Critical temperature(K)	Melting point (K)	Density of liquid at 25ºC (Kmole / m^3)
Methanol	CH_3OH	32.04	337.67	80.32	512.68	175.53	20.98
Oxygen	O_2	31.998	90.19	50.43	154.65	54.36	-
DME	C_2H_6O	46.07	248.36	53.1	400.05	131.62	-
Methane	CH_4	16.043	111.65	46.00	190.56	90.69	-
Hydrogen	H_2	2.02	20.397	12.93	33.18	13.96	-
Carbon dioxide	CO_2	44.01	185.35	73.81	304.15	216.59	21.15
Carbon oxide	CO	28.01	81.62	37.04	134.18	68.05	-
Water	H_2O	18.02	373.15	220.77	647.11	273.16	46.53

Stoichiometry and kinetics reaction

The first stage of the reaction is synthesis gas production. Produced by steam reforming of methane. Equations and kinetics of reaction are shown below.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{4}$$

$$r = 1.527exp\left(\frac{-14.820}{RT}\right) P_{CH4}^{1.014}\ P_{H2O}^{-0.9577} \tag{5}$$

Taking the order 1.014 as 1 and the order -0.9577 as -1, the velocity equations become:

$$r = 1.527exp\left(\frac{-14.820}{RT}\right) P_{CH4}\, P_{H2O} \tag{6}$$

Where

$E_a = 14,82$ *kcal/g mole*

$K = 1,527$ *g mole/gkat*h* [3]

Although steam reforming is carried out at high temperatures, a catalyst (Ni / α-alumina) is still needed to accelerate the reaction due to the very high stability of methane [5].

After carbon monoxide is obtained from methane, it is partially converted to carbon dioxide by the water-gas shift reaction [1].

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{7}$$

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$$r = k\frac{P_{H2O}}{1 + K_{eq}P_{H2O}/P_{H2O}}$$

Where; $K_{eq} = exp\left(\frac{4577{,}8}{T - 4{,}33}\right)$ (8)

The synthesis gas then undergoes two reactions in which methanol is formed.

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad (9)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad (10)$$

The initial catalyst for methanol synthesis was $ZnO\text{-}Cr_2O_3$, which is active only at high temperatures. New catalysts based on copper oxides mixed with alumina have been developed. They are more active at lower temperatures and pressures and resist sintering. This process uses a Cu/Al/ZnO heterogeneous catalyst. ZnO promotes the activity of Cu in these systems. Only copper based catalysts are not active for the production of methanol. Although methanol synthesis is a very old process, there is still no consensus about the nature of active sites and the behavior of ZnO. The typical atomic composition for these catalysts is 6/3/1. Aluminum is responsible for increasing the dispersion of copper and prevents it from sintering. The reaction mechanism is also unclear, and controversial theses have been presented by various authors in the literature. The bifunctional mechanism is generally accepted and there are several models depending on the composition of the synthesis gas.

The kinetics of the reaction is shown below [8]:

$$r = \frac{kP_{CO}^{1.9}P_{H2}^{0.9}}{(1 + P_{CO2}^{1.7}K_{CO2} + P_{CO}^{1.5}K_{CO}} \qquad (11)$$

Where; $k = 2{,}034 * 108exp\left(-\frac{14061}{RT}\right)$ (12)

$$K_{CO} = 66.63\exp\left(\frac{1588.2}{RT}\right) \qquad (13)$$

$$K_{CO2} = 139507\exp\left(\frac{-17551}{RT}\right) \qquad (14)$$

Finally, the synthesis of dimethyl ether takes place in the presence of an α-alumina catalyst according to the following reaction.

$$2CH_3OH = CH_3OCH_3 + H_2O \qquad (15)$$

For catalysts with Lewis acidity, such as $\gamma\text{-}Al_2O_3$, the dehydration mechanism proposed by Jain et al. Is the most common. Oxygen anions with an excess of electrons exhibit basic behavior, while aluminum has no electrons (acid behavior). Methanol molecules are adsorbed on basic and acidic neighboring centers. Both adsorbed substances immediately react via the Langmuir-Hinshelwood mechanism, forming a DME molecule in the main center. One proton reacts with adsorbed OH^- at the acid site to form an H_2O molecule. The following figure illustrates this mechanism:

The mechanism of methanol dehydration according to DME [9]

$$R = k_0 \exp(\frac{-E_a}{RT}) P_{Метанол}$$

The kinetic equations are expressed below [10].

Where; $E_a=80,48 kJ/mol$; $k=1,21*10^6$ $kmole/kat*h*kPa\ m^3$

Direct synthesis method

Direct synthesis, a relatively new synthesis route, takes place in only one step and uses one reactor. Within it, several reactions take place to convert the syngas into dimethyl ether. A diagram of this process is shown in Fig. 7. Several companies, including Haldor Topsoe, Japan JFE Holdings Company and Korea Gas Corporation, have developed technologies for the direct synthesis of DME [3]. The following reactions occur:

$$2CO + 4H_2 \rightarrow 2CH_3OH \qquad \Delta H_{298} = -43,4\ kcal/mole \qquad (16)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H_{298} = -5,6\ kcal/mole \qquad (17)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H_{298} = -9,8\ kcal/mole \qquad (18)$$

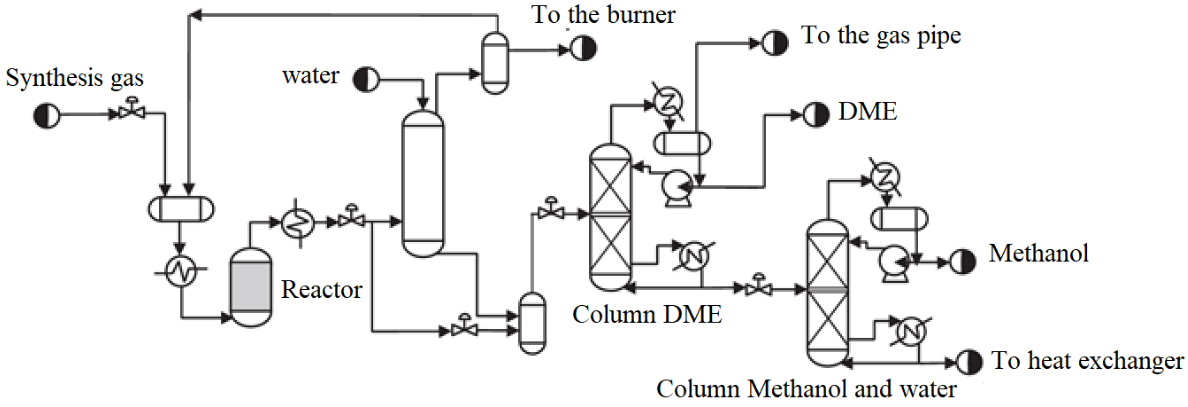

Fig 7 – Scheme of indirect synthesis

The methanol synthesis reaction, methanol dehydration and the water gas shift reaction (the last of the above) take place in the same reaction vessel after the synthesis gas has been produced earlier. The general equation can be expressed as:

$$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2 \qquad \Delta H_{298} = -58,8\ kcal/mole \qquad (19)$$

One of the most notable direct syntheses is the JFE process at the Ohno plant in Japan. The reactions take place in a slurry bed reactor. The synthesis catalyst developed by the JFE group is active and selective for three-stage reactions at 260 ° C and 5 MPa. As can be seen from equation (16), the molar ratio of CO and H_2 in this process is 1: 1.

The previous steam reforming reaction to produce synthesis gas is shown below. With conventional reforming or even autothermal reforming, higher H2 / CO levels are obtained. Therefore, the required molar ratio of 1 can be achieved by recycling the CO_2 by-product.

$$2CH_4 + O_2 + CO_2 \rightarrow 3CO + 3H_2 + H_2O \qquad (20)$$

Due to two catalytic steps, bifunctional catalysts are required for the direct synthesis of dimethyl ether. One function of Cu based methanol synthesis and acid solid based methanol dehydration function. Thus, methanol synthesis reactions and water gas shift reactions occur on a Cu based catalyst, while methanol dehydration to DME occurs on an acid catalyst. Recently, new materials have been investigated, such as catalysts based on heteropoly acids (HPA), which have excellent acidic properties, which is very important for the synthesis of dimethyl ether.

The complexity of this process can be viewed as a disadvantage. This requires more equipment and threads, which entails a higher process cost. However, the indirect method provides a great deal of flexibility in the process as it takes place in different stages and in reactors. Any anomaly in raw material flow or in higher processes can be easily compensated for.

In addition, catalysts can be different in both reactors, implying reasonable costs and not interfering with other reactions. If all reactions take place in the same vessel with a bifunctional catalyst, any problem or disturbance in activity can destroy the process. In addition, higher temperatures are required for direct synthesis efficiency and catalyst activity. This limits the reaction from a thermodynamic point of view, since the global reaction is highly exothermic. In addition, a significant reduction in volume results in high operating pressures, typically above 4 MPa. Therefore, it becomes difficult to control the reaction.

The indirect synthesis method is easier to control and manage. Moreover, since it is the most widely used at present, there is more information in the reference literature for realizing operating and process conditions. For all these reasons, indirect synthesis was chosen for this project.

In general, dimethyl ether will be obtained from natural gas as it is more beneficial from both environmental and economic points of view, and indirect synthesis is used. Steam reforming of crude methane is preferred for process simulations.

CONCLUSIONS

Thus, there are currently two main methods of producing environmentally friendly diesel fuel from natural gas - dimethyl ether. The production of synthetic fuels (two-stage synthesis of DME from syngas) is expected to be more competitive and economically competitive than conventional fuels.

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