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Prospective Ways Of Methanol Application

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Abstract – The article presents the search for promising ways of using and processing methanol, the technology creation and development for new environmentally friendly, highly effective octane-increasing additives production. It was presented a technological scheme for the methyl tertiary butyl ether production.

Keywords – Methanol, Octane-Enhancing Additives, Gasoline, Methyl Tertiary Butyl Ether, Technological Scheme, Ether, Catalysis.

Methanol is one of the most important products of the chemical industry, in production volumes, the leading places are occupied by Saudi Arabia, China, Trinidad and Tobago, Russia and the United States. Mainly methanol is used as raw material for many of organic synthesis products production, mostly formaldehyde (up to 50%), which serves as one of the components for the plastics and resins production [1]. About 65% in the methanol consumption structure in the world falls on the chemical industry - production of formalin, acetic acid, methyl methacrylate, methyl mercaptan, DL- methionine and etc. In the petrochemical industry, the main consumers are the isoprene and methyl tertiary butyl ether production (MTBE) [2]. Also methanol is actively used in the gas industry as a reagent in the fight against hydrate formation and a reagent for drying natural gas. In addition, the use of methanol in the olefins production on MTO and MTP technologies is being discussed today (ethylene and propylene) [3-5].

The most important problem at the present time is the search for alternative energy sources. This is due not only to the upcoming oil raw materials shortage, but also to environmental problems. Transport consumes about 40% of the oil produced in the world [6]. Use of hydrocarbon fuels in internal combustion engines accompanied by emissions into the atmosphere of a huge amount of harmful substances: nitrogen oxides, carbon monoxide, etc. The possibility of using alcohols as motor fuel seems to be very attractive. At the same time, harmful emissions are significantly reduced. The very problem of using alcohols as a fuel is not new, and in some European countries in the 1920s and 1930s, laws were passed that prescribe the alcohol addition to gasoline [7–8].

At the beginning of its development, the valuable hydrocarbons obtaining technology from synthesis gas was considered as a productive method for producing high-octane gasoline from coal. In fact, with this technology from coal or natural gas almost all hydrocarbons can be obtained, which could be obtained from petroleum raw materials. Methanol is dehydrated, forming an equilibrium mixture of methanol, DME and water, which, depending on the reaction conditions and catalyst can be directed or to obtain lower olefins (MTO process), or for the liquid hydrocarbons production (MTG process).

Although methanol itself is a potential motor fuel or can be used as an additive to gasoline, however, high financial costs are required to solve technical problems, associated with the use of methanol as a vehicle fuel.

1973 year was the year of the energy crisis, at the same time, interest in new synthetic fuels increased, and continued research on converting methanol to hydrocarbons was approved.

In the same year, MTG and MTO processes are carried out on an industrial scale, because for this there are technological and economic prerequisites. “Mobil” MOGD firm process (methanol-olefins-gasoline-distillate process) (Fig. 1) [9] was originally developed as a refinery process, which can be well combined with the MTO process. In the MOGD process on a ZSM catalyst the lower olefins oligomerization occurs, which enter the reactor from refinery streams, or converting olefins from the MTO process to high molecular weight olefins. The later fall within the boiling range of gasoline and distillate.

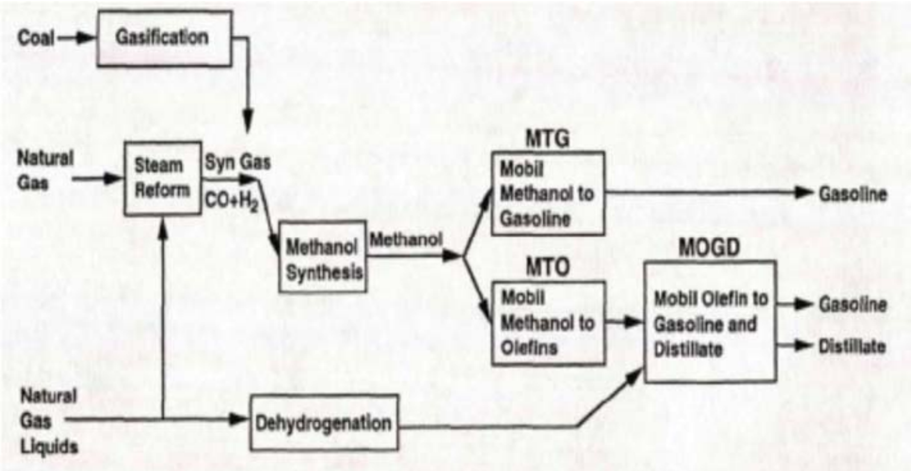

Fig. 1. Getting gasoline and distillate from methanol by technology of «Mobil» firm [10]

Synthesis gas is obtained from natural gas by steam reforming, which converts to methanol. The methanol is then sent to the MTG and/or MTO processes. The formed olefins are oligomerized with the natural gas dehydrogenation products by the MOGD process into gasoline and distillate.

The «Mobil Research», «Development Corporation», «Union Rheinische Braunkohlen KraftstoffAG» and "Ubde GmbH" firms jointly created in Wesseling (Germany) a demonstration unit for the MTG process with a fluidized bed of catalyst [11], which from December 1982 to the end of 1985 worked with a liquid fuel 15.9 m^3/day capacities (Fig. 2). This project is described in detail in [12] and [13]. This project was partially funded by the American and German governments.

A simplified diagram of the installation with a fluidized catalyst bed is shown in Fig. 2 shows that methanol is converted to steam and fed to the reactor. To improve the economy process, methanol is dehydrated. The reaction temperature can be used to produce high pressure steam; The MTG process is carried out on a ZSM-5 catalyst at about 400 °C temperature, partial pressure of methanol is 0.4-1 MPa.

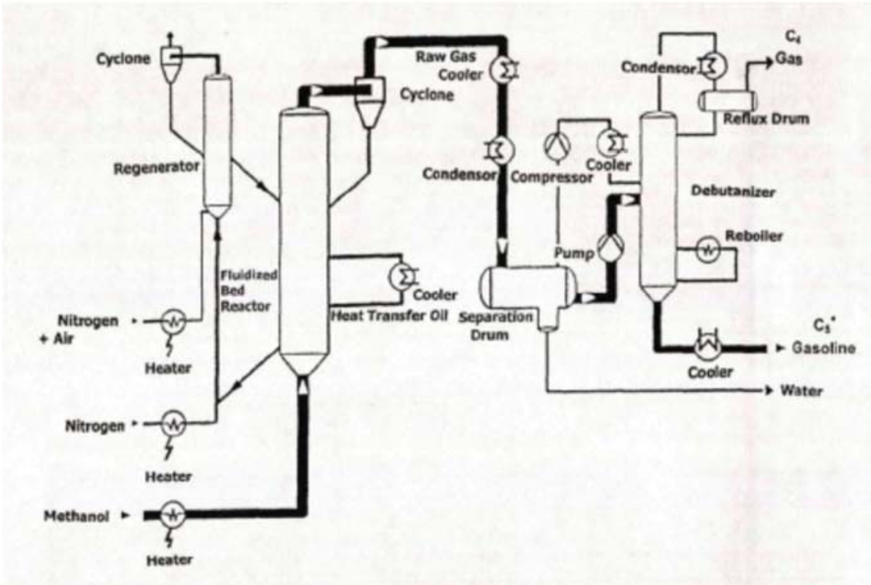

Fig. 2. Demonstration installation of MTG (Mobil)

For some physical and chemical properties (heat of combustion, octane number, etc.) methanol is approaching, and in such an important characteristic as the heat of vaporization, it even surpasses the best hydrocarbon fuels. However, the high methanol, toxicity, aggressiveness hydrophilicity towards some metals, low heat capacity inhibits its use for internal combustion engines. In addition, the use of methanol as a clean fuel requires significant engine re-equipment. The more economical way seems, therefore, the methanol processing into gasoline. The gasoline formation process from methanol on the ZSM-5 catalyst proceeds through the methanol dehydration stage into dimethyl ether, which is further converted into a mixture of hydrocarbons (gasoline), consisting of more than 50% of valuable highly branched paraffins: $2CH_3OH$ и CH_3OCH_3. Currently, the problem of using methanol as an additive to fuel for power plants is being seriously considered. In addition to the use of methanol as a fuel, we note its use as a raw material for obtaining high-octane additives to gasoline, primarily methyl tert-butyl ether (MTBE), which replaced the toxic tetraethyl lead in this capacity. The addition of small amounts of this antiknock agent allows the use of gasolines without adding such a toxic substance as tetraethyl lead. MTBE, the industrial production of which is rapidly growing in the world, is obtained by the interaction of methanol with isobutylene in the presence of acid catalysts [10, 14, 15].

It is known that the bulk of the oil produced in Uzbekistan is characterized by a high content of asphaltenes and resinous compounds and a low content of aromatic hydrocarbons and hydrocarbons of the iso-construction industry. Gasoline obtained by direct distillation of a mixture of oil and gas condensate has an octane number of about 50 RON (motor octane number).

In order to bring it to the SS requirement, there are two ways: chemical processing - reforming, platforming, destructive hydrogenation, etc., which requires huge capital costs. The second method is the use of octane-enhancing additives and additives. The FORP reformers capacities do not allow the gasoline production with an AI-80 octane rating and higher. Therefore, at present, the Fergana oil refinery plant uses imported reagents imported from foreign countries for foreign currency in the amount of about 70 million US dollars to increase the octane number of low-octane gasolines.

Currently in developed countries to increase the octane number of gasoline used aliphatic alcohols - methanol, ethanol, isopropanol; simple ethers - methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), amyl tert-butyl ether (ATBE), diisopropyl ether (DIPE); aromatic amines - monomethylaniline (MMA), ashless highly effective additive - AEA (70% MMA + 30% methanol), metallocenes - ferrocene, manganese, organic compounds (Hitech-3OOO), ADA, Ferrada and etc.

In JSC "Navoiazot" there is a methanol production from synthesis gas with 35 thousand tons capacity per year, which has no proper application.

Many works have been devoted to the use of aliphatic alcohols, including methanol and ethers such as dimethyl, methyl tert-butyl, aromatic amines and metallocenes as octane-increasing additives.

However, the use of aliphatic polyamines, esters, 1,1,3-trimethoxy and 1,1,3-triethoxybutanes, acetone, acetonitrile and sodium, potassium, magnesium, manganese acetates; ammonium nitrate and others as octane-increasing additives have not been studied.

The purpose of the research is to find promising ways of using and processing methanol, creating and developing a technology for new environmentally friendly, highly effective octane-increasing additives production.

Technological process for the production of octane-increasing additives (OIA) based on methanol developed by Tashkent chemical-technological institute jointly with CLO “Navoiazot” JSC,TADI and FORP. To test the process at the TCTI and CLO of JSC "Navoiazot", pilot plants have been mounted.

The production consists of three technological lines:

1. MTBE production installation based on butane fraction.
2. 1,1,3 - triethoxybutane production setup.
3. Installation for the chromium-alumina catalyst production.

The anti-knock properties of the developed octane-increasing additives have been tested at the TADI, FORP and Kuchlyuk oil depot laboratories. The process is periodic.

The developed method for obtaining octane-increasing additives consists of obtaining MTBE, 1,1,3-triethoxybutane and mixing them with acetone, methanol, acetonitrile, urotropine and manganese acetate.

In the octane-increasing additives, gaseous, liquid and solid wastes obtaining process are not formed.

Esters have a number of advantages over alcohols. The ethanol use is not advisable, which creates difficulties in exceeding the saturated vapor pressure norms, especially in the summer. Although methanol is the most readily available and cheapest of the known alcohols, it is unacceptable due to environmental considerations and its high water solubility. The ethers advantage over alcohols is that the latter have sufficiently high octane numbers and low saturated vapor pressure; they replace aromatics and butanes in gasoline. Methyl tert-butyl ether (MTBE) is the most widely used in practice. Its additive to gasoline reduces the carbon monoxide (to 27%) and hydrocarbons content in car exhaust gases. The tests carried out at Fergana ORP showed that the most economical MTBE additive is about 11%.

In the USA, it is allowed to use MTBE in compounded gasolines up to 15% by volume, which corresponds to 2.7% of the oxygen mass.

In some countries, due to groundwater contamination incidents with MTBE, due to the non-compliance of the tank farm for underground gasoline storage, a company was deployed to limit and even exclude this oxygenate use. The analytical company SRJJnHrnatinal connects the noted facts with the tank farm improving problem. Currently, MTBE is produced in Russia in the amount of 400 thousand tons per year.

Although MTBE is the most effective additive with good performance characteristics, its production is associated with nuances number. The demand of Fergana ORP for MTBE is about 100 thousand tons per year. The “Navoiazot” JSC operates a methanol production facility with 35 thousand tons capacity per year.

This amount can be used to obtain MTBE up to 80 thousand tons per year. SJSC "Uzkimyosanoat" is ready to increase the methanol capacity up to 100 thousand tons per year, if there is a consumer.

A technological scheme for the octane-increasing additives production by the n-butane and i-butane dehydrogenation is proposed followed by isobutylene esterification with methanol in the presence of a cation exchanger in H^+ is shown in the following sequence (Fig. 3).

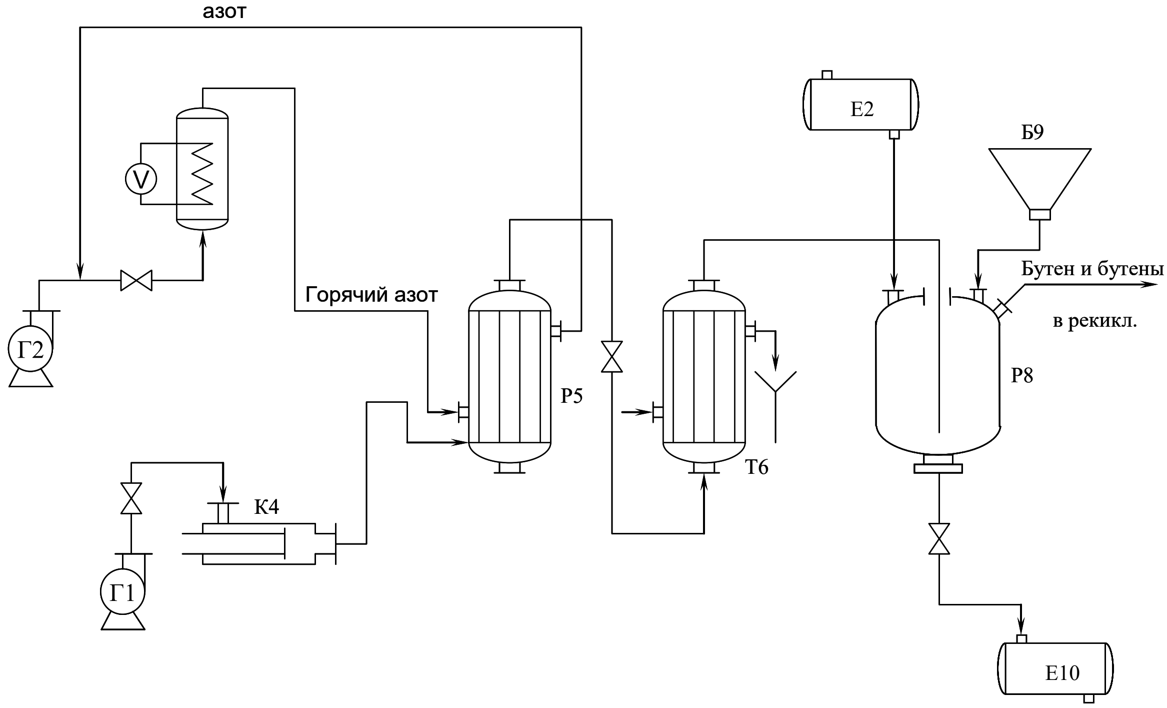

Fig.3. Basic technological scheme for the methyl tert-butyl ether (MTBE) production based on butanes: G1 and G2 - gas holders for butane and nitrogen; T3 - TEH (thermoelectric heater); K4 - compressor; P5 - dehydrogenation reactor; T6 - heat exchanger; E2 - container for methanol; P8 - ether reactor; B9 - catalyst hopper; E10 - container for the finished product.

A n-butane with isobutane mixture from the G1 gas tank is fed to the lower reactor part position P5, with the help of a compressor position K4. Hot nitrogen is supplied to the annular space from position T3. Reactor position P5 is a cylindrical tube-in-tube apparatus.Pipe diameter is 55 mm, length 5000 mm. The pipes number is 52 pieces. The butanes dehydrogenation reaction is carried out at 550 - 570 °C temperature, the volumetric velocity of a butanes mixture is 1000-1200 $ч^{-1}$. The resulting butenes and hydrogen mixture is fed to the heat exchanger position T6, where they are cooled to 90-100 ºC and then enter the lower the reactor - etherizer part, position P8.

When the MTBE content in the etherizer reaches 90% and above, the process is stopped, the catalysis is poured into the finished product container, position E10. At this point, the butenes mixture is sent to the reactor at position P11, operating in parallel with reactor P8. Every 2 months the process is stopped, the system is purged with nitrogen, and then the chromia-alumina catalyst is regenerated. Oxygen in the air at 600ºC as follows. After purging the system with nitrogen, nitrogen and air mixture is fed into the reactor at nitrogen: air ratio of 8: 2. Then the air content is gradually increased. Clean air falls into the system into the regeneration cone. The regeneration completeness is determined by the carbon dioxide in the exhaust gases and when its content is reduced to 0.4%, the regeneration process is terminated.

An analytical review of the methanol use has been carried out. The basic technological scheme for the methyl tert-butyl ether (MTBE) production based on butanes is presented.

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