BIOETHANOL – GREEN FEEDSTOCK FOR PETROCHEMICAL INDUSTRY

Y.I. Makarfi[1], M.S. Yakimova[1], L.M. Koval[2], V.I. Erofeev[2], R.M. Talyshinsky[1], A.S. Lermontov[1], V.F. Tretyakov[1]

1 - A.V. Topchiev Institute of Petrochemical synthesis, RAS, Moscow

2 - Tomsk State University, Chemistry Department, Tomsk

tretjakov@ips.ac.ru

One of the most important problems of basic petrochemicals production besides the rise of oil prices is ecology non-friendliness of this process. From "green chemistry" viewpoint overall petroleum-based production is an infinite source of various pollutants. The major one is carbon dioxide which is a final point of any fuel or petrochemical life cycle. The only way to decrease the amount of CO_2 in petrochemicals production is the use of renewable biological substances which are produced from atmospheric carbon dioxide during the growth of green biomass.

Bio-ethanol is one of the most abundant substances which can be produced by fermentation of various types of biomass or food industry wastes with low production cost. There was a short period in the history before WWII when bio-ethanol was used as a raw material for synthetic rubber production via the Lebedev process. After finding rich crude oil deposits in the east of Russia, ethanol was forced out by cheap hydrocarbons from petroleum cracking and even bio-ethanol was substituted in industry by ethanol produced via catalytic hydration of ethylene. Currently, world market trends show that prices of bio-ethanol are lower than that of ethylene or any other petrochemicals with potential to organize the industrial technology of ethanol conversion. Despite economical and ecological advantages there is no industrial realization of bio-ethanol conversion to ordinary petrochemicals.

Olefins and aromatic hydrocarbons formation from bio-ethanol was studied over pure and industrial HZSM-5 zeolite catalysts in fixed-bed continuous flow reactor. It was shown that the pure HZSM-5 have reasonable catalytic activity in ethanol conversion to a range of olefins and aromatics. The conversion of ethanol was near 100% in all experiments but the composition of products depends on the catalyst and reaction conditions. The 30% yield of liquid hydrocarbon product contained more than 88% of methyl and ethyl-substituted benzenes, mainly xylenes and toluene, were

obtained at 380 ^{O}C, WHSV = 10 h^{-1}, and atmospheric pressure. The gaseous phase products are C_3-C_4 hydrocarbons. Ethanol conversion on HZSM-5 is pressure sensitive – the yield of liquid hydrocarbons can be increased to 40% at 3-5 bar, but further increase of pressure to 10 bar leads to fast zeolite deactivation due to pore blocking by heavy hydrocarbons and coke formation.

The conversion of ethanol over unmodified industrial zeolite catalysts which contain 60-70% of HZSM-5 pressed with low surface area alumina at the same conditions shows decrease of liquid hydrocarbons yield to 10-20% with high percentage of ethylene in the products. It was found that the modification of industrial catalyst with 4% of ZnO or Ga_2O_3 promotes liquid hydrocarbon formation with up to 50% yield. Moreover, it was found that these oxides have different influence on product composition. In the case of ZnO modified catalyst the content of aromatics in liquid product was near 60% giving preference to C_6-C_8 hydrocarbons. Ga_2O_3 promotion does not change products distribution significantly compared to unmodified zeolite giving 85-90% of aromatics in liquid product. Another possibility of changing catalyst selectivity is the use of water-ethanol mixtures instead of pure ethanol. We have shown that under the same reaction conditions (T = 350 ^{O}C, $WHSV_{eth}$ = 2 h^{-1}, P = 1 bar) on the same ZnO/HZSM-5/Al_2O_3 catalyst the yield of products is changed from pure ethylene (water ethanol ratio > 6:1), through 80% of C_3-C_4 at (W/E ~ 1:2) to liquid hydrocarbons in the case of pure ethanol.

Thus, bio-ethanol conversion on HZSM-5 based catalysts provides a great opportunity to aromatics and olefins production from renewable biomass sources preventing additional CO_2 formation in Earth atmosphere which is one of the key points of “green chemistry”-based technologies.