WATER-GAS SHIFT REACTION AT MEDIUM TEMPERATURE: A NEW APPROACH IN THE INDUSTRIAL H2 PRODUCTION

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In recent years, fuel market and environmental policies have reinforced the key role of hydrogen, increasing dramatically the demand and the research on its application in fuel-cell systems. Hydrogen is not an energy source, but an energy carrier, therefore, it must be produced: currently, the Steam Reforming (SR) of hydrocarbons is the largest and most economical way to produce H2 [1]. Fundamental in the steam reforming plant, is the Water-Gas Shift (WGS) reaction, a catalytic step to convert CO and obtain additional H2 by reaction with steam, which is moderately exothermic and favoured at low temperature [2]. Currently, the WGS reaction is performed using two units [2]: a) a 1st unit using Fe2O3/Cr2O3, known as High Temperature Shift (HTS) catalyst, that operates at high inlet temperature (370-400 °C); b) a 2nd unit operating at the lowest possible inlet temperature (200 °C), by using a CuO/ZnO/Al2O3 catalyst, Low Temperature Shift (LTS) catalyst. In this way, it is possible to achieve exit CO concentrations as low as 0.1-0.3 %. For the shift catalyst, the criticality comes on lower temperature activity and thermal stability [3]. Thus, it may be advantageous to combine these two steps in only one unit, operating at Medium Temperature (MTS), with an exit temperature of about 320 °C. The shift from HTS to MTS processes offers further advantages, low steam to carbon ratios can be achieved, without sintering and Fisher-Tropsch side reactions.

In this preliminary study, some Cu-based commercial catalysts has been studied as a function of different parameters (pressure, temperature, steam to dry gas ratio (S/DG) and contact time (τ), not only to check the catalytic activity at middle temperature, but also to define best operating conditions for a good CO conversion, operating at low S/DG ratio and contact time values, thus ensuring a lower overhead of the plant.

A critical point in the WGS unit is the catalyst deactivation, caused by a sintering accelerated by poisoning, because in the presence of sulphur and chlorine, low-melting-point compounds are formed on the catalyst surface. Thus, in a second step a deactivation study has been performed to predict the volume required to operate for a desired time. The temperature profile along the reactor gave precious information on the catalyst activity: the top of the catalytic bed is quickly deactivated, acting as a guard layer, in which poisons are preferentially adsorbed.

A design tool has been programmed with Visual Basic for Applications (VBA) to simulate the WGS reactor. The fitting of temperature profiles regarding the origin load in a MTS plant was very good in all the ranges of time-on-stream below 3 years of aging. Using the simulation tool with the deactivation law determined from the plant data, it was possible to link the volume of active catalyst (excluding the catalytic guard, assumed to be fully deactivated) to the approach to equilibrium. The catalyst volume was calculated to achieve 90 % of maximum conversion after 3 years of time-on-stream; however, these calculated values should be considered with care, because the results depend on deactivation laws based on the profiles measured along the MTS reactor. Moreover, this tool cannot be extrapolated to cases with different specification.

References