ABSTRACT

Many reports in the open literature have focused on Fischer-Tropsch (FT) kinetics, yet none of them appear to be able to explain FTS completely. Few of the FT models consider the production of olefins and paraffins separately. To study whether the selectivity to olefins and paraffins follows similar trends and if kinetics alone suffices to explain FT phenomena, a series of FT experiments were conducted in a fixed bed reactor loaded with 10% Co/TiO_2. FT feeds were periodically switched from syngas to syngas + N_2 by adjusting the total reactor pressure so that the reactant partial pressures (P_{CO} and P_{H2}) remained constant.

During the initial deactivation (the first 1200 hours), it was found that the formation rates of olefins remained fairly constant (in some cases they increased) while those of paraffins decreased. This indicates the deactivation is mainly caused by the decrease in the paraffin formation rate. Currently, none of the published kinetic models can explain the phenomenon that the decay of the reaction rates of olefins and paraffins were not the same during the deactivation. At steady state (1055 to 2700 hours, overall reaction rate fairly constant), adding extra N_2 decreased the selectivity to the light hydrocarbons. These results suggest that by feeding the extra N_2 there could be an increase in selectivity and formation rates to long chain hydrocarbons (C_{5+}).

Plotting molar ratios of paraffin to olefin (P/O) with carbon number n+1 versus the ratio with carbon number n revealed linear relationships which are independent of feed gases, catalyst activity and reaction temperature. These results imply that product distributions might be determined by some sort of equilibrium. Another plot of normalised mole fractions of C_nH_{2n}, $C_{n+1}H_{2n+2}$, and C_nH_{2n+2} in ternary diagrams showed that after disturbances these product distributions tended to stable points. It is suggested that this could be due to slow changes in the liquid composition after the disturbances.

Although not all the results are explained, the researcher emphasises that normal kinetics alone cannot explain these results completely. There might be factors, including vapour-liquid equilibrium or reactive distillation, which are worthy of consideration to explain FTS.