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Modeling and optimization study of Fischer-Tropsch synthesis for diesel production

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Biofuel is considered as a relevant technology for both developing and industrialized countries due to the sustainability and environmental issues, impacts on energy security and socio-economic concerns related to the rural sector. Diesel produced from biomass by Fischer-Tropsch (FT) synthesis shows a great potential for the production of environment friendly high-quality transportation fuels. Fischer-Tropsch synthesis products are excellent high-performance, clean diesel fuels due to the absence of sulphur, NO_x and their aromatic compounds. The Fischer-Tropsch synthesis consists of a three-phase phenomenon: Gaseous phase (syngas, water vapor, carbon dioxide and light hydrocarbons); Liquid phase (heavy hydrocarbons); Solid phase (catalyst). A two-phase heterogeneous gas-liquid flow model was developed to simulate a fixed bed Fischer-Tropsch reactor. In this study, the main objective was to optimize the process conditions to achieve the maximum yield of desired products (i.e., diesel fuels) and to reduce the rate of production of unwanted CO_2 and CH_4. A mathematical modeling and chemical kinetics study were carried out for both gaseous and liquid production using simulated N2-rich syngas (17% CO, 33% H_2 and 50% N_2). The experiments were conducted over an in-house 37% Co-based catalyst on a SiO_2 support over a wide range of operating conditions (i.e., temperature of 503-543 K, total pressure of 10-25 bar and WHSV of 1.8-3.6 NL g_{cat}^{-1} h^{-1}). The chemical reaction kinetics was developed for the total paraffins and olefins' production of each carbon number in both gaseous and liquid phase with a comprehensive product distribution scheme. The model was based on a carbon number dependent chain growth concept and stoichiometric relationship between the hydrocarbons produced and the syngas converted. The product distribution obtained from the model includes the light hydrocarbons CH_4, ethene (C_2H_4) and ethane (C_2H_6), LPG (C_3-C_4), gasoline (C_5-C_{12}), diesel fuel (C_{12}-C_{22}) and waxes (C_{23+}). The rate of syngas conversion (i.e., CO and H_2) was developed by using a Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate expression. The water gas shift reaction was also taken into account in order to simulate the rate of change of CO_2 species along the reactor bed length. The kinetic parameters and the physical properties were estimated by fitting the experimental data under a variety of operating conditions using advance Global Optimization technique. The accuracy of model relative to the experimental results was determined by the statistical analyses quantitatively (i.e., using a mean absolute relative residual (MARR) and F-test method) and qualitatively (i.e., using a party diagram). The simulated values of the reactants' conversion and products' selectivity were in good agreement with the experimental data. It was found that the temperature, gas flow rate (per unit mass of catalyst) and H_2/CO ratio are the significant operating conditions that affect the syngas conversion and the entire product distribution specially the liquid production rate.

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