MODELING OF FISCHER-TROPSCH SYNTHESIS IN A TUBULAR REACTOR

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***Abstract*— Fischer-Tropsch synthesis is an important chemical process for the production of liquid fuels and olefins. In recent years, the abundant availability of natural gas and the increasing demand of olefins and liquid fuels have led to a high interest to further develop this process. A mathematical model of a tubular reactor used for syngas polymerization was developed and the carbon monoxide polymerization was studied from a modeling point of view. Simulation results show that different parameters affect syngas conversion and carbon product distribution, such as operating pressure, gas velocity and syngas composition. Optimization of several hydrocarbon products were done in order to search for the best operating conditions for their production.**

***Keywords*— Multitubular Reactor, Fischer-Tropsch Synthesis, Liquid Fuels, Olefins**

I. INTRODUCTION

In recent years, the Fischer-Tropsch Synthesis (FTS) became a subject of renewed interest particularly in the context of the conversion of remote natural gas into liquid transportation fuels and due to an escalation in the price of oil. Natural gas, biomass and coal can be converted to carbon monoxide and hydrogen (synthesis gas) via the existing processes, such as steam reforming, carbon dioxide reforming, partial oxidation and catalytic partial oxidation. The syngas can be converted into hydrocarbons (paraffins and olefins) by the FT synthesis reaction:

$$CO + (1 + m/2n)H_2 \longrightarrow \frac{1}{n} C_n H_m + H_2O \cdot \qquad (1)$$

The FT synthesis can be carried out in iron, cobalt and ruthenium based catalysts. Fe-based catalysts are much less expensive than the Co-based catalysts, which can be an important economical factor for the process specially because the catalyst has to be replaced due to deactivation. When iron catalysts are used, the carbon monoxide polymerization occurs in combination with the water gas shift reaction (WGS):

$$CO + H_2O \longleftrightarrow CO_2 + H_2 . \qquad (2)$$

Many researchers have been working on catalyst development (Raje and Davis, 1997; van Steen and Schulz, 1999) and reactor design (Maretto and Krishna, 1999; Krishna and Sie, 2000; Krishna *et al.*, 2001; Wang *et al.*, 2003), but few investigations have been done in order to optimize the production of specific products.

The Fischer-Tropsch reaction yields predominately straight chain hydrocarbons (α-olefins and alkanes) where the main reaction products are α-olefins. There is general agreement that the reaction may be viewed as a methylene polymerization reaction where the monomer unit (=CH_2), is not initially present. The products are formed by hydrogenation of CO to generate the methylene monomer, *in situ*. Polymerization occurs through initiation of chains, competing chain propagation and chain termination steps. Theories on the CO polymerization mechanism are based in the superposition of two ASF (Anderson-Schulz-Flory) distributions and rely in the dual site theory (Madon and Taylor, 1981), secondary chain growth of readsorbed alkenes theory (Schulz and Claeys, 1990; Iglesia *et al.*, 1991), or the dual mechanism of chain growth theory (Patzlaff *et al.*, 1999, 2002). Iron catalysts are more likely to obey a dual mechanism of chain growth theory.

In this work a mathematical model of a tubular reactor used for CO polymerization was developed and the carbon monoxide polymerization was studied from a modeling point of view based on the kinetics of an iron catalyst obeying a dual mechanism theory.

II. TUBULAR REACTOR

The tubular reactor for Fischer-Tropsch synthesis consists of a multitube reactor where the synthesis gas is fed at the top of the reactor and passes through the bed of catalyst inside the tubes. The synthesis gas passes through the reactor in plug-flow regime. Water passes through the shell side of the multitube reactor to remove the heat released by the FTS reaction and to control the reactor temperature, ensuring an isothermal condition inside the reactor, in spite of the high heat of reaction (ΔH = - 170 kJ/mol CO).

III. MATHEMATICAL MODEL

A. Tubular Reactor Model

The basic assumptions made for the reactor were: steady-state operation, isothermal conditions, gas passing through the reactor in plug-flow regime due to its velocity, hydrocarbon products in the gas and in the liquid phases are assumed to be in equilibrium at the