TITLE: KINETICS OF SLURRY PHASE FISCHER-TROPSCH SYNTHESIS

AUTHORS: Dragomir B. Bukur (PI), Gilbert F. Froment (Co-PI) and Lech Nowicki

STUDENT: Madhav Nyapathi

INSTITUTION: Texas A&M University
Department of Chemical Engineering
College Station, TX 77843-3122

PHONE NO.: (979) 845-3401

FAX NO: (979) 845-6446

E-MAIL: d-bukur@tamu.edu

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1. ABSTRACT

Program Introduction: Rationale and Objectives

The overall objective of this project is to develop a comprehensive kinetic model for slurry phase Fischer-Tropsch synthesis on iron catalysts. After a thorough review of literature kinetic models will be formulated utilizing the current state-of-the-art understanding of reaction mechanisms for formation of reaction intermediates and hydrocarbon products. Models will be based on adsorption/desorption phenomena for reactants and product species. Discrimination between the rival models will be based upon the goodness of fit, supplemented with statistical tests on parameter values and the physicochemical meaningfulness of the estimated parameter values. Kinetic models will be validated with experimental data obtained in a stirred tank slurry reactor (STSR) over a wide range of process conditions. These models will be able to predict concentrations of all reactants and major product species (H_2O, CO_2, linear 1- and 2-olefins, and linear paraffins) as a function of reaction conditions in the STSR.

Accomplishments Achieved During the Current Period of Performance

During the reporting period (October 2002 – March 2004) we have completed three STSR tests with a precipitated iron catalyst obtained from Ruhrchemie AG (Oberhausen-Holten, Germany). This catalyst was initially in commercial fixed bed reactors at Sasol in South Africa. Ruhrchemie

catalyst (11-25 g) was calcined in air at 300°C and a fraction between 140-325 mesh was loaded into the reactor filled with 300-320 g of Durasyn 164 oil (a hydrogenated 1-decene homopolymer, ~ C_{30} obtained from Albemarle Co.). The catalyst was pretreated in CO at 280°C, 0.8 MPa (100 psig), 3 Nl/g-cat/h for 12 hours. After the pretreatment the catalyst was tested initially at 260°C, 1.5 MPa (200 psig), 4 NL/g-Fe/h (where, NL/h, denotes volumetric gas flow rate at 0°C and 1 bar) using CO rich synthesis gas (H_2/CO molar feed ratio of 0.67). After reaching a stable steady state value (~60 h on stream) the catalyst was tested at different process conditions. A minimum length of time between changes in process conditions was 20 h. Experiments were conducted in a 1 dm^3 STSR (Autoclave Engineers) at: P = 8, 15 and 25 bar, T = 220, 240 and 260 °C, H_2/CO = 2/3 and 2/1 at different gas space velocities to obtain conversions of a limiting reactant ranging from 9% to 84%. Data were obtained at 26 sets of process conditions. Test duration was from 337 to 696 h. Reproducibility of catalyst performance (activity and selectivity) in three tests was excellent, and the catalyst deactivation was moderate. We are currently analyzing experimental data to determine the effects of process conditions on hydrocarbon product distribution (lumped hydrocarbon distribution, 1-olefin and 2-olefin selectivity). These results will be discussed at the Contractors Review Conference. Also we are continuing to review the current literature on kinetic modeling of Fischer-Tropsch synthesis.

Plans for the Remaining Period of Performance

- The work planned for the remainder of this grant will focus on development of kinetic models and estimation of kinetic parameters from experimental data in STSR tests. Discrimination between the rival models will be based upon the goodness of fit, supplemented with statistical tests on parameter values and the physicochemical meaningfulness of the estimated parameter values.

2. LIST OF PUBLISHED JOURNAL ARTICLES, COMPLETED PRESENTATIONS AND STUDENTS SUPPORTED FROM THE GRANT

Conference Presentations

- Kinetic models for hydrocarbon selectivity on iron Fischer-Tropsch catalysts in a stirred tank slurry reactor, D. B. Bukur and L. Nowicki, paper to be presented at the Annual AIChE Meeting, November 2004, Austin, Texas.

Students Supported Under this Grant

- Madhav Nyapathi, graduate student in the Department of Chemical Engineering, Texas A&M University.

- Lech Nowicki, post-doctoral fellow.