

KINETICS OF SLURRY PHASE FISCHER-TROPSCH SYNTHESIS

First Annual Technical Progress Report

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## **Abstract**

This report covers the first year of this three-year research grant under the University Coal Research program. The overall objective of this project is to develop a comprehensive kinetic model for slurry phase Fischer-Tropsch synthesis on iron catalysts. This model will be validated with experimental data obtained in a stirred tank slurry reactor (STSR) over a wide range of process conditions. The model will be able to predict concentrations of all reactants and major product species ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , linear 1- and 2-olefins, and linear paraffins) as a function of reaction conditions in the STSR.

During the reporting period we have completed one STSR test with precipitated iron catalyst obtained from Ruhrchemie AG (Oberhausen-Holtien, Germany). This catalyst was initially in commercial fixed bed reactors at Sasol in South Africa. The catalyst was tested at 13 different sets of process conditions, and had experienced a moderate deactivation during the first 500 h of testing (decrease in conversion from 56% to 50% at baseline process conditions). The second STSR test has been initiated and after 270 h on stream, the catalyst was tested at 6 different sets of process conditions.

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## **Introduction**

The overall objective of this project is to develop a comprehensive kinetic model for slurry phase Fischer-Tropsch synthesis on iron catalysts. This model will be validated with experimental data obtained in a stirred tank slurry reactor (STSR) over a wide range of process conditions. This model will be able to predict concentrations of all reactants and major product species ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , linear 1- and 2-olefins, and linear paraffins) as a function of reaction conditions in the STSR. Kinetic model will be useful for preliminary reactor design and process economics study.

The overall program is divided into several tasks, and their timetable and brief descriptions are:

### Task 1. Development of Kinetic Models (November 1, 2002 - March 31, 2005)

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. These models will be continually updated on the basis of experimental data obtained in Task 3, and subsequent data analysis in Task 4.

### Task 2. Catalyst Synthesis (August 1, 2003 - October 30, 2003)

A precipitated iron catalyst with nominal composition 100 Fe/3 Cu/4 K/16  $\text{SiO}_2$  (in parts per weight) will be synthesized utilizing equipment and procedures developed in our laboratory at Texas A&M University (TAMU). As an alternative we may utilize a robust commercially available catalyst with similar performance characteristics to TAMU's catalyst.

### Task 3. Experiments in a Stirred Tank Slurry Reactor (January 15, 2003 - March 31, 2005)

Experiments will be conducted in a 1 dm<sup>3</sup> stirred tank slurry reactor (STSR) over a wide range of process conditions of industrial significance. Synthesis gas feed H<sub>2</sub>/CO molar ratio will vary from 0.67 (coal derived syngas) to 2 (natural gas derived syngas). Baseline conditions will be repeated periodically to assess the extent of catalyst deactivation.

### Task 4. Model Discrimination and Parameter Estimation (March 1, 2004 – August 31, 2005)

Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach and the concept of rate limiting step result in a large number of competing kinetic models. 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.

## **Current Status**

### Task 1. Development of Kinetic Models

Professors Bukur (PI) and Froment (Co-PI) have monitored current literature on F-T kinetics and/or mechanisms, and have had numerous discussions concerning kinetic model development. Junior researchers on the project have not participated in this task yet, since the main emphasis was on experimental work (Task 3) as described below. We expect to focus on this task during the next year.

### Task 2. Catalyst Synthesis

Instead of synthesizing a new batch of TAMU's precipitated catalyst 100 Fe/3 Cu/4 K/16 SiO<sub>2</sub> (in parts by weight) we have decided to use a precipitated iron catalyst prepared by Ruhrchemie AG (Oberhausen-Holtent, Germany). This catalyst (LP 33/81) has a nominal composition 100 Fe/4.3 Cu/4.1 K/25 SiO<sub>2</sub> (in parts by weight) and it was used initially in fixed bed reactors at Sasol in South Africa. It has been tested extensively at TAMU [1-4], and was used in previous

study of kinetics of Fischer-Tropsch (F-T) synthesis by Lox and Froment [5,6]. It is a robust catalyst and its selectivity is similar to that of TAMU's catalyst.

### Task 3. Experiments in a Stirred Tank Slurry Reactor

The work on this task was initiated in January 2003. Mr. Jian Wang (a Ph. D. graduate student who joined TAMU in September 2002) was recruited for this project, and was trained in operation of the STSR and gas chromatographs for product analysis by Dr. Wen-Ping Ma. Dr. Ma has been in our laboratory since August 2001, working on development of attrition resistant catalysts for F-T synthesis. Mr. Wang was expected to complete the current project as a part of his Ph. D. thesis research. Unfortunately, Mr. Wang decided to do research in the field of biotechnology, and he resigned from the project in June 2003. At this time Dr. Ma's appointment also had expired, but we were fortunate to have Dr. Lech Nowicki (University of Lodz, Poland) for a four-month period July – October 2003. Dr. Nowicki has collaborated with Professor Bukur on F-T synthesis since 1992, and he was familiar with the equipment, instruments and software for data analysis at TAMU.

During July – September 2003 period we finished one run (696 h on stream, 15 mass balances), and completed 275 hours on stream in the second test (6 mass balances). Details of these experiments are presented in other sections of this report (Experimental and Results and Discussion).

### Task 4. Model Discrimination and Parameter Estimation

The work on this task has not been scheduled to begin during the reporting period.

## **Experimental**

Two tests (runs SB-21903 and SB-26203) were conducted in a 1 dm<sup>3</sup> stirred tank slurry reactor (Autoclave Engineers). The feed gas flow rate was adjusted with a mass flow controller and passed through a series of oxygen removal, alumina and activated charcoal traps to remove trace

impurities. After leaving the reactor, the exit gas passed through a series of high and low (ambient) pressure traps to condense liquid products. High molecular weight hydrocarbons (wax), withdrawn from a slurry reactor through a porous cylindrical sintered metal filter, and liquid products, collected in the high and low pressure traps, were analyzed by capillary gas chromatography. The reactants and noncondensable products leaving the ice traps were analyzed on an on-line GC (Carle AGC 400) with multiple columns using both flame ionization and thermal conductivity detectors. Further details on the experimental set up, operating procedures and product quantification can be found elsewhere [1,2,5,8].

Ruhrchemie catalyst (15 g in run SB-21903 and 11.2 g in run SB-26203) 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,  $\sim C_{30}$  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 ( $\sim 60$  h on stream) the catalyst was tested at different process conditions. A minimum length of time between changes in process conditions was 20 h.

## Results and Discussion

List of process conditions and conversions achieved in these two tests is given in Tables 1 and 2. Conversions at baseline conditions (260°C, 1.5 MPa, 4 NL/g-Fe/h,  $H_2/CO = 2/3$ ) are shown in Figures 1 and 2.

Run SB-21903 lasted 696 h, and during this time period 15 mass balances were performed, and the catalyst was tested at 13 different sets of process conditions (Table 1). Baseline conditions were repeated after 245 h and 480 h on stream. Conversions at baseline conditions are shown in Figure 1. After the pretreatment the syngas conversion increased with time and then stabilized at about 56% after 50 h on stream. When the baseline conditions were repeated between 245 and 270 h on stream the syngas conversion was about 50%. Thus, the catalyst had experienced



moderate deactivation between 80 and 245 h on stream, during testing under different process conditions (see Table 1). After 270 h the catalyst was tested under different process conditions (Table 1) and another check for deactivation was made during 480 and 505 h on stream. During this period, the syngas conversion at the baseline process conditions, was about 50%. Thus, the catalyst did not experience any further deactivation between 270 and 480 h on stream. The baseline conditions were repeated again after 676 h on stream, and the syngas conversion was about 46% (Figure 1).

Several experimental problems were encountered during this run. There was a leak in the reactor head at about 400 h on stream, and the run was temporarily suspended by introducing N<sub>2</sub> and stopping syngas flow. After cooling the reactor temperature to 100°C, the leak was fixed and the run resumed. Between 513 and 579 h a fume hood did was out of order (mechanical/electrical failure) and the run was temporarily suspended by introducing flowing N<sub>2</sub> and stopping the syngas flow.

The second test (run SB-26203) was conducted with a new catalyst, using the same activation procedure as in run SB-21903. As can be seen in Figure 2, the catalyst activity was quite reproducible, and after 57 h on stream the syngas conversion was about 57%. At the end of the reporting period six mass balances were completed (Table 2).

## **Conclusions**

During the first year of the project we have completed one STSR test (13 sets of conditions), and initiated the second STSR test (6 sets of process conditions completed). This is a significant progress in terms of our goal of having about 24 different sets of process conditions for estimation of kinetic parameters. At this point we have not conducted any extensive evaluation of experimental data, to assess their quality. This will be done during the next period.

## Future Work

Our plan for the next period (second year of the project) is to complete planned experiments, and initiate data analysis (preliminary estimation of kinetic parameters). Also, we'll continue to review the current literature and update our kinetic models.

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Table 1. Process conditions during STSR run SB-21903

MB#	TOS	T	P	H <sub>2</sub> /CO	SV	Syngas	CO
	(h)	(°C)	(bar)	(-)	(NL/g-Fe/h)	conversion	conversion
1	79	260	15	0.67	4	56.9	54.1
2	103	260	15	0.67	1.7	82.1	83.5
3	127	260	15	0.67	9.2	31.4	26.7
4	169	240	15	0.67	2	44.6	38.9
5	215	240	15	0.67	1	58.9	56.2
6	241	240	15	0.67	5.5	18.4	14
7	272	260	15	0.67	4	50	46
8	312	240	15	2	4.2	40	50
9	343	240	15	2	2.1	64	80
10	369	240	15	2	10.8	20.6	24.4
11	408	260	15	2	3.5	63	82.5
12	433	260	15	2	8	47	58.8
13	489	260	15	0.67	4	50	46.5
14	601	260	22	0.67	6.1	42.4	36.1
15	647	260	22	0.67	1.4	82.6	83.7

Table 2. Process conditions during STSR run SB-26203

MB#	TOS	T	P	H <sub>2</sub> /CO	SV	Syngas	CO
	(h)	(°C)	(bar)	(-)	(NL/g-Fe/h)	conversion	conversion
0	55	260	15	0.67	4	56.8	53.5
1	86	260	15	2	1.7	51.4	76.1
2	118	260	15	2	9.2	46.3	66.5
3	142	260	15	2	2	31.5	41.2
4	175	240	15	2	1	42.1	55.2
5	224	260	25	2	5.5	50	43.6
6	264	260	25	2	4	28.3	19.8

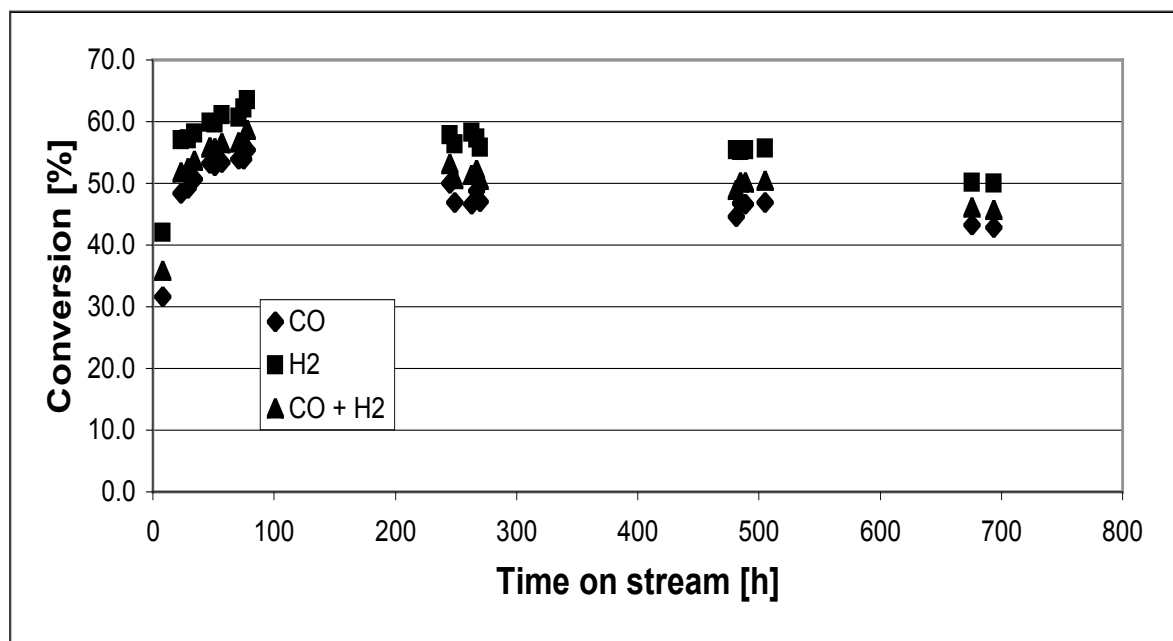


Figure 1. Syngas, hydrogen and CO conversions at baseline process conditions (SB-21903).

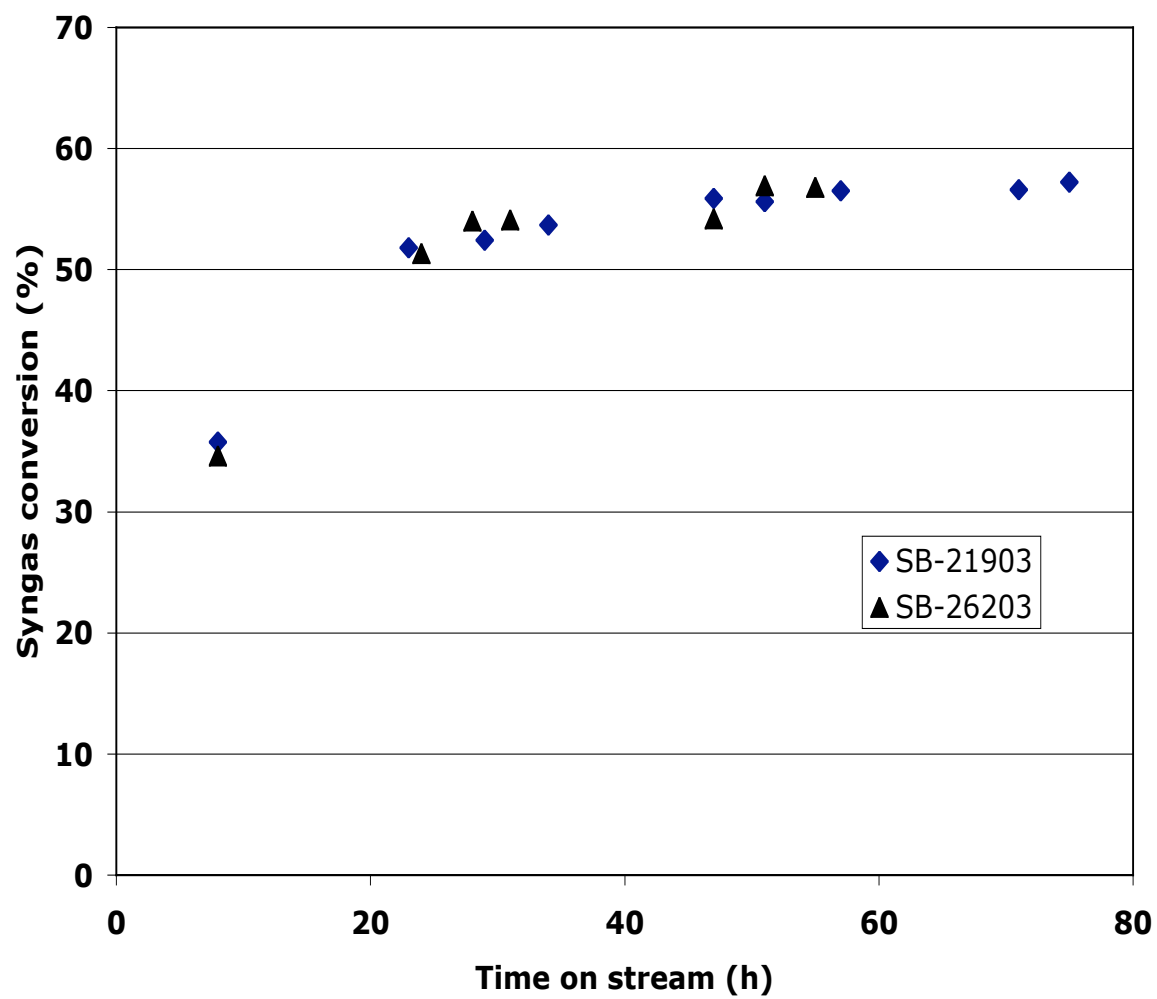


Figure 2. Comparison of conversions at baseline process conditions in tests SB-21903 and SB-26203.