



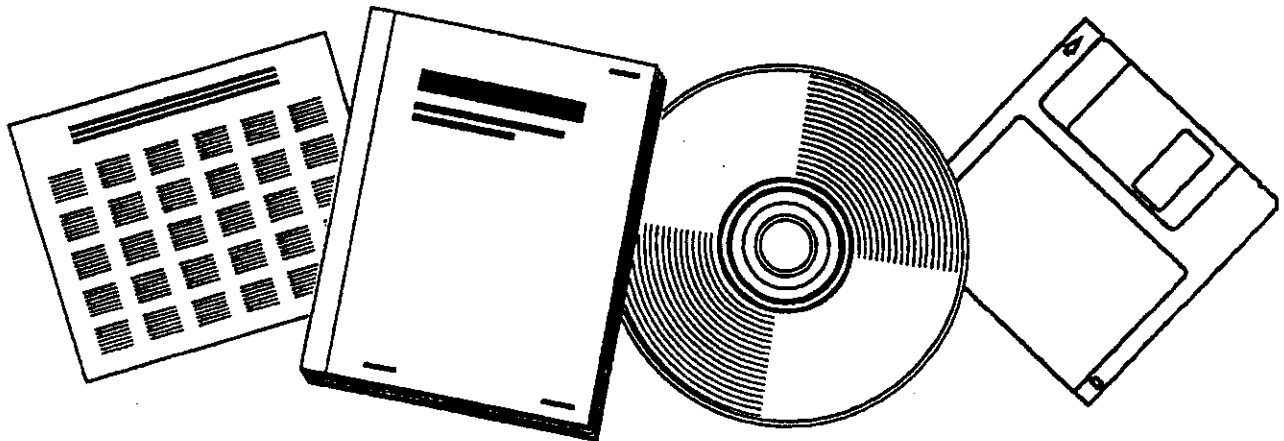
DE89009568

NTIS
Information is our business.

**IMPROVED FISCHER-TROPSCH SYNTHESIS
CATALYSTS FOR INDIRECT COAL LIQUEFACTION:
QUARTERLY TECHNICAL PROGRESS REPORT NO. 9,
1 OCTOBER-23 DECEMBER 1987**

SRI INTERNATIONAL
MENLO PARK, CA

1987



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

SRI International



Received 4-03

DOE/PC/80016--T7

DE89 009568

APR 03 1989

Quarterly Technical Progress Report No. 9
for the Period 1 October to 23 December 1987

IMPROVED FISCHER-TROPSCH SYNTHESIS CATALYSTS
FOR INDIRECT COAL LIQUEFACTION

By: G. T. Tong and J. G. McCarty

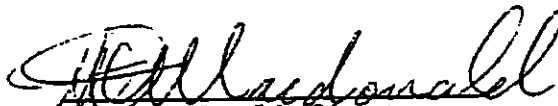
Prepared for:

UNITED STATES DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, Pennsylvania 15236-0940

Attention: Edgar B. Klunder, Project Manager

Contract No. DE-AC22-85PC80016
SRI Project No. 1245

Approved:


D. D. Macdonald, Director
Materials Research Laboratory

MASTER

333 Ravenswood Ave. • Menlo Park, CA 94025
415: 326-6200 • TWX: 910-373-2046 • Telex: 334-486
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *de*

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

SUMMARY

The medium-level sulfur-treated (50% monolayer sulfur coverage) iron and cobalt catalysts were tested for FTS activity, with the clean fused iron catalyst tested as a comparative standard for the fixed-bed reactor operated at high pressure (2 MPa). Of the four improved catalysts chosen for evaluation at high pressure FTS synthesis, the medium-level sulfur-treated fused iron catalyst seems most promising, with a 50% reduction in methane yield, a narrower product distribution, and a threefold increase in olefin selectivity. The sulfur-treated catalyst exhibited behavior at 2 MPa similar to the 0.1 MPa synthesis run; however, the olefin selectivity decreased with increasing temperature or pressure.

A 2 wt% ruthenium on alumina is being prepared and sulfur-treated for completion of the sulfur treatment task. The clean and sulfur-treated ruthenium catalyst will then be tested for FTS activity under high pressure to complete the project.

EXPERIMENTAL RESULTS

During this reporting period, we made progress on Tasks 2 and 4, as described below. Tasks 1 and 3 have been completed.

Task 2: Preparation of Ru/Al₂O₃ Catalyst

An unpromoted ruthenium catalyst was prepared from an aqueous solution of ruthenium chloride (RuCl₃) by the method of incipient wetness on Harshaw AL-0104 alumina crushed and screened to 0.3-0.5 mm. The catalyst was then dried in air at 400 K for 24 hours. The final weight ratio was Ru:Al₂O₃ = 2:100.

Task 4: Evaluation of Improved FTS Catalysts

The FTS performance of the medium-level sulfur-treated fused iron catalyst, medium-level sulfur-treated alumina-supported cobalt, and fused iron standard catalyst was examined in a fixed-bed reactor at 2 MPa and 525-575 K (Table 1 and Figures 1 and 2). Typically, the CO conversion was about 20%. After 24 h at 575 K, the methane yield of the sulfur-treated fused iron catalyst was less than 15 wt% at low conversion (Figure 3) while the clean fused iron catalyst showed nearly 28 wt% CH₄ under the same reaction conditions. Also, the sulfur treated catalysts showed high selectivity for olefins (Figure 4). However, the FTS CO conversion rate declined from 1200 to 400 nmol/g/s because of the sulfur treatment, and the chain growth parameter (for C₃-C₉), α , decreased from 0.65 to 0.52 (Figure 5).

The sulfur-treated catalyst shows nearly the same level of improvements in methane selectivity (decreased by a factor of about 2) at 2 MPa as previously found at 100 kPa, with roughly a factor of two decline in overall rate at 575 K. After 24 h, the total hydrocarbon rate for the medium-level sulfur-treated catalyst was about 49.6% of the rate

Table 1

FIXED-BED FTS PERFORMANCE OF CLEAN AND SULFUR-TREATED
FUSED IRON AND SULFUR-TREATED ALUMINA-SUPPORTED
COBALT CATALYSTS AT 20-ATM

Catalyst	Clean Fused Fe		Medium-Level Sulfur-Treated Fused Iron		Medium Level Sulfur-Treated Co/Al ₂ O ₃		
	573	548	573	548	573	548	523
Temperature (K)	573	548	573	548	573	548	523
H ₂ /CO Ratio	1	1	1	1	2	2	1
Run Duration (h)	24	24	24	24	24	24	24
Product Rate ^a (mmol/g/s)							
C ₁	332.36	90.41	53.86	7.75	32.55	11.58	124.05
C ₂	42.44	25.43	43.07	8.27	22.82	9.75	7.95
C ₃	79.45	27.21	34.70	6.24	16.58	7.04	15.63
C ₄	47.77	17.72	17.30	3.57	7.81	3.59	13.14
C ₅	24.56	10.87	6.81	1.27	2.89	1.32	10.19
C ₆	16.91	7.49	3.80	0.78	1.53	0.75	8.75
C ₇	10.98	5.36	1.86	0.42	0.77	0.38	7.71
C ₈	7.28	3.77	1.04	0.24	0.42	0.23	7.06
C ₉	5.37	2.98	0.65	0.14	0.24	0.13	7.08
C ₁₀	4.71	3.12	0.37	0.09	0.11	0.09	-
TOTAL	1201.43	518.08	401.16	75.34	194.85	84.21	517.02 ^e
Chain Growth Factor ^b	0.65	0.72	0.52	0.54	0.50	0.53	0.85
Olefin to n-Paraffin Ratio ^c	1.67	1.58	3.67	5.23	3.34	4.69	0.93
Methane Selectivity ^d	28	19	15	11.6	18.6	15.4	26 ^e

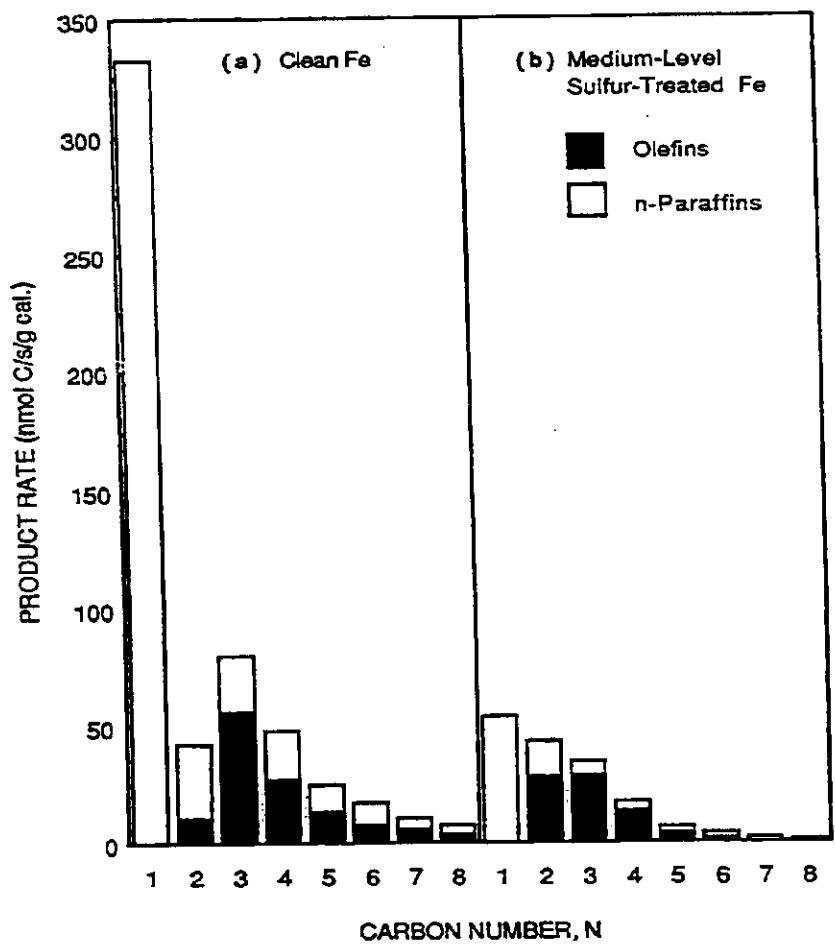
^aGHSV = 600 h⁻¹ and P = 20 MPa; Product rate for each carbon number includes n-paraffins and α - and β -olefins; total product rate is on a carbon-atom basis.

^bAverage chain growth parameter (α) for C₃₊ hydrocarbons.

^cAverage olefin to paraffin ratio for C₂ to C₆ hydrocarbons.

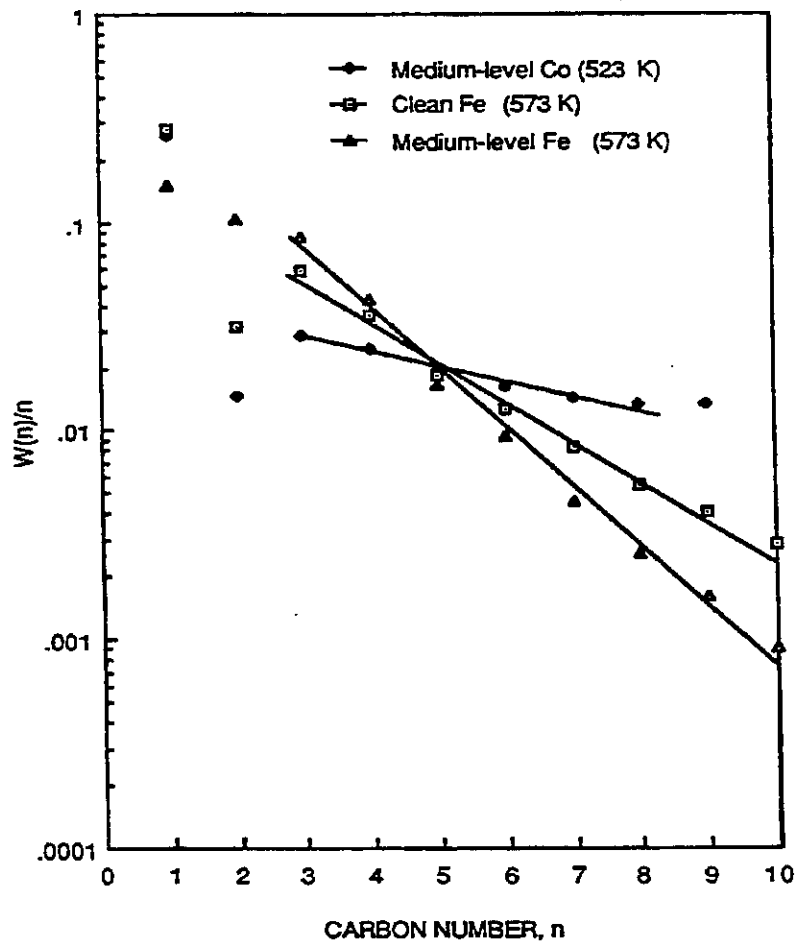
^dC₁ rate/(total rate) x 100%.

^eThrough Co only.



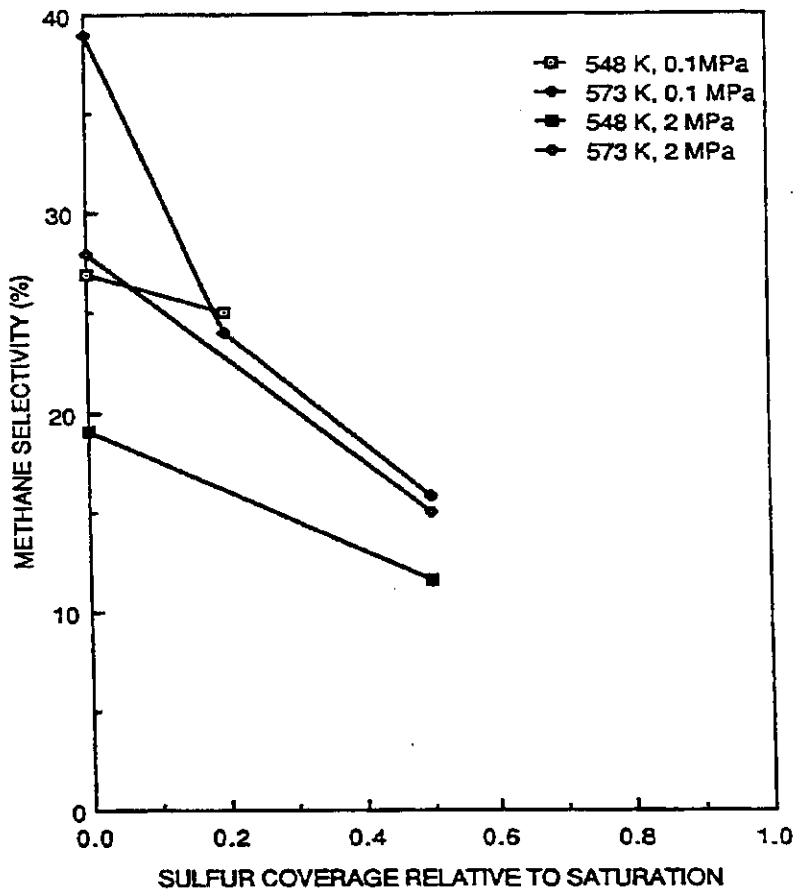
RA-M-1245-20

Figure 1. Fischer-Tropsch synthesis at 2 MPa, 573 K, and H_2/CO ratio = 1.0 on clean and medium-level sulfur-treated fused iron catalysts.



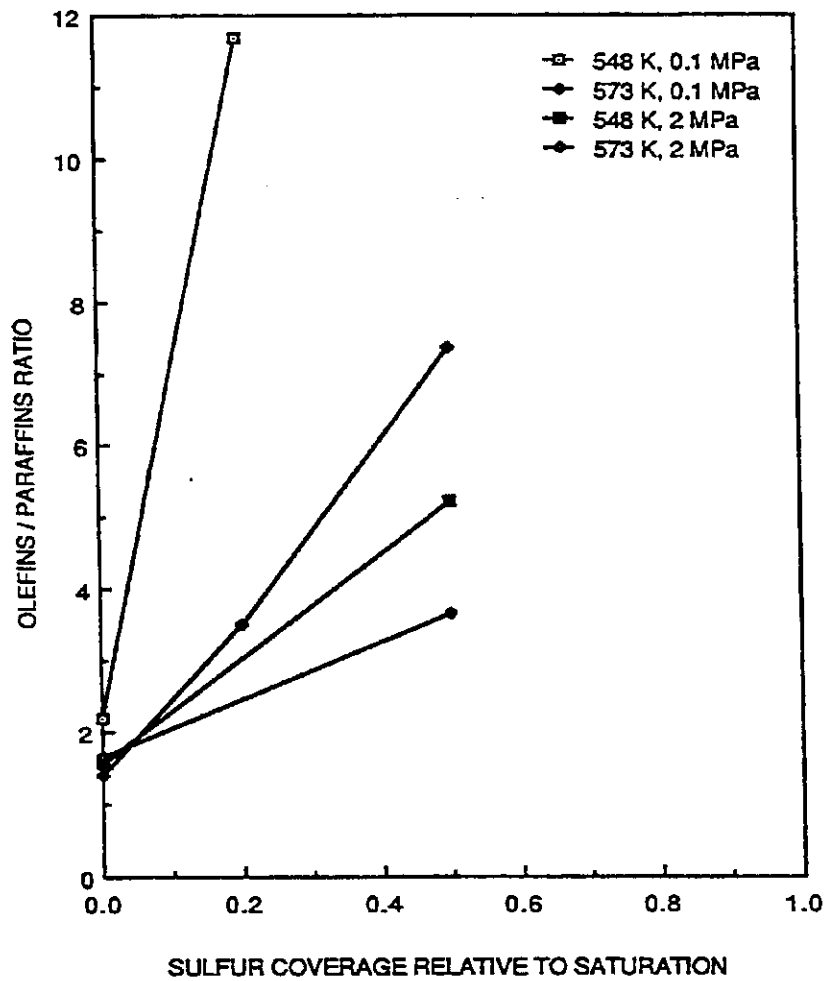
RA-M-1245-21

Figure 2. Schutz-Flory-Anderson plot of the hydrocarbon product distribution for fused clean iron, medium-level sulfur-treated iron, and medium-level sulfur-treated cobalt catalysts at 2 MPa, $H_2/CO = 1$, and 573 K and 523 K, respectively.



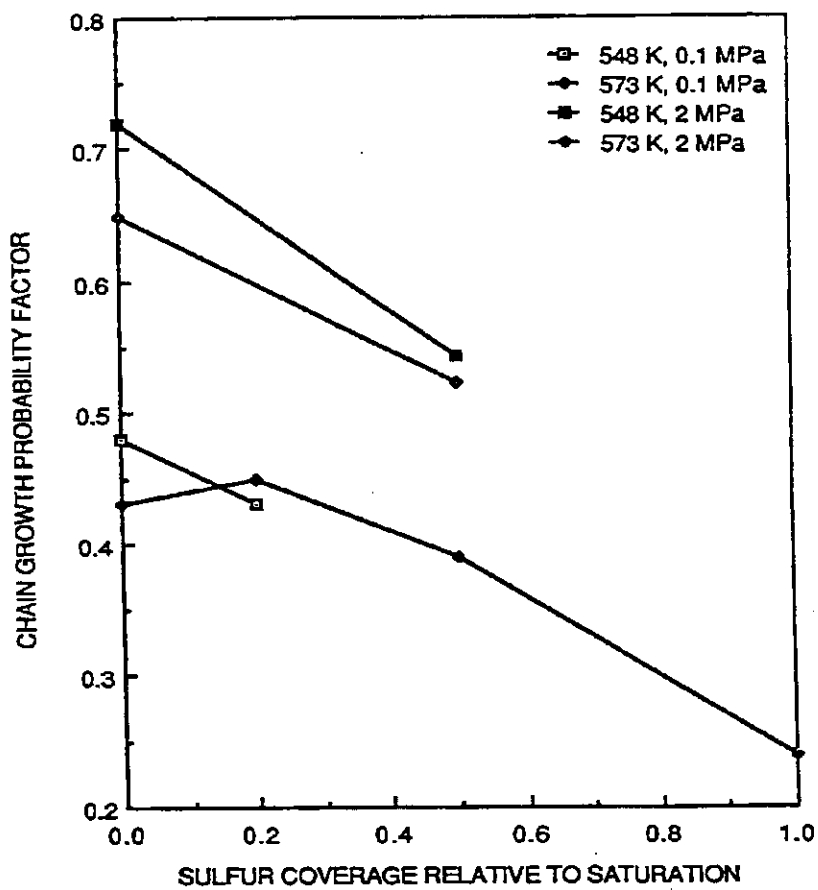
RA-M-1244-23

Figure 3. Methane selectivity for fixed-bed FTS by clean and sulfur-treated fused iron catalysts with H_2/CO ratio = 1.0.



RA-M-1245-24

Figure 4. Light olefin selectivity for fixed-bed FTS by clean and sulfur-treated fused iron catalysts with H_2/CO ratio = 1.0.



RA-M-1245-22

Figure 5. Chain growth probability factor for clean and sulfur-treated fused iron catalysts with H_2/CO ratio = 1.0.

of the untreated catalyst. If only C₂ through C₁₀ total hydrocarbon rates were considered, the activity of the medium level sulfur-treated catalyst was 66.8% of the clean catalyst.

A hot-wax trap was installed at the exit of the FTS reactor. The trap was designed to collect C₁₂₊ hydrocarbons when operated at 393 K. The condensed wax was dissolved in toluene and analyzed by FIMS to determine the distribution and chain growth probability factor of higher hydrocarbons. Hydrocarbons wax contains both paraffins and olefins and exhibits chain growth probability of up to carbon number C₅₀. Samples from slurry reactor runs using cobalt and fused iron catalyst were kindly provided by Professor Satterfield of MIT and were used as the comparative standard and calibration for our FIMS data. In using the FIMS technique to analyze the MIT cobalt sample, which was composed almost entirely of normal paraffins, we obtained results (weight %) for C₃₀ through C₄₅ very similar to the data in the accompanying analysis.¹ Therefore, we were able to obtain the weight fractions of C₃₀ and C₄₀ in the sample from the hot wax trap for the fixed-bed synthesis run with clean fused iron at 573 K, 2 MPa, and H₂/CO ratio of 1 (Table 2).

Table 2
FIMS ANALYSIS OF FTS WAX

<u>Carbon Number</u>	<u>FIMS Result (weight %)</u>	<u>Predicted Value (weight %)</u>
30	3.07 x 10 ⁻⁴	1.32 x 10 ⁻³
40	4.34 x 10 ⁻⁵	2.36 x 10 ⁻⁵

We compared the FIMS results in Table 2 to the values predicted by extrapolating to the wax range using the calculated (for C₃ to C₉) chain

¹D. K. Matsumoto, MIT, private communication.

growth probability factor ($\alpha = 0.649$). FIMS results indicate a longer chain growth and therefore a higher probability factor ($\alpha = 0.8$) for the wax range than the light hydrocarbon range.

DISCUSSION

The results for the fixed-bed FTS performance of the medium-level sulfur-treated fused iron FTS catalyst are encouraging. The sulfur-treated catalyst shows nearly the same level of improvement in methane selectivity (decreased by a factor of about 2.5) at 2 MPa as previously found at 100 kPa, with a decline in overall rate of only a factor of 2 at 575 K.

Matsumoto and Satterfield reported a study similar to our fixed-bed FTS results with sulfur-treated fused iron catalyst;² they used dibenzothiophene as the poison in a slurry reactor operating at 536 K, 1.48 MPa, and H₂/CO ratio of 0.7 to 1.0. They observed that methane selectivity of the poisoned fused magnetite catalyst was significantly lower than that of the unpoisoned catalyst and that the olefin to paraffin ratio was higher on the poisoned catalyst than the clean catalyst. They also reported that methane selectivity increased and olefin to paraffin ratio decreased with increasing CO conversion and that both parameters were unaffected by temperature or pressure.

Our study also showed that methane selectivity decreased for the sulfur-treated fused iron catalysts, but in contrast to the results reported by Matsumoto and Satterfield, the methane selectivity decreased further with increasing temperature or pressure (see Figure 3). In addition, in our study the olefin to paraffin ratio increased for the sulfur-treated catalyst but decreased with increasing temperature or pressure (see Figure 4). Dictor and Bell³ also reported that olefin selectivity decreased with increasing temperature and decreasing H₂ partial pressure for a fixed-bed reactor. Perhaps their smaller pressure range (from 0.79 to 1.48 MPa, as compared to our 0.1 to 2 MPa) would

²D. K. Matsumoto and C. N. Satterfield, *Energy & Fuels* 1, 203-210 (1987).

³R. A. Dictor and A. T. Bell, *Applied Catalysis* 20, 145-162 (1986).

explain why Matsumoto and Satterfield observed no effect on methane selectivity or olefin to paraffin ratio. Moreover, the temperature range (505-536 K) at which their slurry reactor was operated showed a high methane yield (about 30 mol% for the clean catalyst and 15 mol% for the poisoned catalyst, both at about 20% CO conversion) compared to other studies that reported about 5% methane selectivity (Pennline et al.: 4.7 wt% CH₄ for fused iron catalyst in a slurry reactor at 523 K, 1.38 MPa and 21.8% conversion).⁴

Our study showed that the primary products were linear 1-olefins and paraffins, with the majority of the olefins being terminal (i.e., α - and β -olefins). We also observed that the β -olefin/ α -olefin ratio increases with increasing carbon number and that the olefin to paraffin ratio remains high (O/P ratio = 1) in the wax range. All these findings are in agreement with the results reported by Dictor and Bell.³

⁴H. W. Pennline, M. F. Zarochak, R. E. Tischer, and R. R. Schehl, Applied Catalysis 21, 313-318 (1986).