4.5
5.0
5.6
6.3
7.1
8.0
9.0
10
11.2
12.5
14
16
18
20
22.4
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63
71
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180
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320
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400
450
500
560
630
710
800
900
1000

1 of 1

DOE/PC/90055-T11

TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSTS

CONTRACT DE-AC22-90PC90055

**Technical Progress Report No. 10
12/26/92-3/26/93**

prepared for

**Pittsburgh Energy Technology Center
Department of Energy
Pittsburgh, Pennsylvania**

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TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSTS

Contract No. DE-AC22-90PC90055

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Technical Progress Report No. 10
(12/26/92-3/26/93)

Contract Objective

The objectives of this contract are to develop a technology for the production of active and stable iron (Fe) Fischer-Tropsch catalysts for use in slurry-phase synthesis reactors and to develop a scaleup procedure for large-scale synthesis of such catalysts for process development and long-term testing in slurry bubble-column reactors. With a feed containing hydrogen (H_2) and carbon monoxide (CO) in the molar ratio of 0.5 to 1.0 to the slurry bubble-column reactor, the catalyst performance target is 88% CO+ H_2 conversion at a minimum space velocity of 2.4 NL/hr/gFe. The desired sum of methane and ethane selectivities is no more than 4%, and the conversion loss per week is not to exceed 1%.

Contract Tasks

Task 1.0: Catalyst development

- 1.1: Technology assessment
- 1.2: Precipitated catalyst preparation method development
- 1.3: Novel catalyst preparation methods investigation
- 1.4: Catalyst pretreatment
- 1.5: Catalyst characterization

Task 2.0: Catalyst testing

Task 3.0: Catalyst aging studies

Task 4.0: Preliminary design and cost estimate of a catalyst synthesis facility

Experimental

A slurry autoclave pilot plant is used for catalyst evaluations, the autoclave of which is contained in a 130°C hot box. The liquid and gaseous products are separately withdrawn but taken to the same traps. There are three traps in series, the first is in the hot box, the second and third are outside of the hot box and maintained at ice and dry ice/acetone temperatures respectively. A small slip stream of the product before the ice trap is taken to a GC (GC-1) for an on-line boiling point type of analysis. A second slip stream (after the ice trap) is taken to a second GC

(GC-2) for an analysis for gases (C_1 - C_4).

Scope of the Work during the Reporting Period

Task 1.2

Several preparation methods are being investigated as routes to iron oxide catalysts for use in Fischer-Tropsch processing of coal-based syn fuel. During this contract experimental catalysts have been evaluated in a slurry autoclave test that requires 73 g of catalyst per test. The amount of catalyst is governed both by the size of the autoclave reactor and the contractual target of a high (20%) loading of catalyst in the slurry. A screening test requiring less catalyst was needed because evaluating smaller quantities of catalyst would reduce the preparation time for experimental catalysts.

Task 2.0

Run 56

This was primarily a reference run in which a potassium-containing iron-copper oxide (25 g) was added to the slurry autoclave reactor along with 290 g of a C_{30} oil. Properties of the oxide are summarized in Table 1. The oxide was prepared via precipitation followed by calcination and sizing. The catalyst preparation method and properties correspond well with catalysts previously shown to exhibit good performance in the slurry autoclave test. Catalyst activation was by treatment with the feed (0.7 molar ratio of H_2 : CO) at the rate of 5.8 NL/hr · g Fe at 153 psig and 280°C for 24 hours. Following activation, the conditions were: feed, 7.0 NL/hr · g Fe, 290 psig and 265°C. Plots of conversions and selectivities as a function of hours-on-stream are in Appendix 1 as Figures A-1 to A- 6. The initial CO conversion was 55% after a brief line-out period. Following this there was some loss of conversion, for instance, the carbon monoxide conversion dropped to 50% at 160 hours-on-stream.

At 160 hours-on-stream a second feed was introduced, namely pure hydrogen at the rate of 1.08 NL/hr/gFe. The purpose of this addition was twofold. First, the recently installed second feed system needed to be certified for a gas feed. Second, catalyst performance data at a variety of H_2 :CO ratios was desired. Introduction of the hydrogen feed resulted in an instantaneous increase in the carbon monoxide conversion from 50 to 62%. However, from 195 to 240 hours-on-stream the carbon monoxide conversion declined to 48%, thereafter it appeared to be stable.

Conversion calculations were based on feed and product carbon monoxide, hydrogen and argon concentrations. When the second, pure hydrogen, feed was started a new feed concentration was calculated based on the compositions and rates of the two feeds. The conversions and selectivities reported after 160 hours-on-stream were based on this new feed composition.

The reason for the peculiar performance after introduction of the separate hydrogen feed is unknown. The initial increase in carbon monoxide conversion was instantaneous and occurred in spite of the fact that the added hydrogen feed reduced the carbon monoxide residence time in the reactor. Since the nature of the catalyst probably could not have changed over such a short period of time the most likely explanation is that the added hydrogen facilitated some step in the carbon monoxide conversion process, perhaps the hydrogenation of surface-bound carbon monoxide. The subsequent loss in carbon monoxide conversion occurred over a longer period of time and could have been due to a gradual change in the nature of the catalyst itself. The working catalyst is a mixture of iron oxides and carbides, the composition of which might be expected to be a function of the hydrogen to carbon monoxide ratio, however, subsequent experiments below show that significant conversion losses can occur during a run at these conditions even without a feed change.

Introduction of the separate hydrogen feed resulted in increased selectivity to methane, ethane and propane. These increases occurred immediately upon addition of the hydrogen. In the case of methane the selectivity decreased during the catalyst deactivation period which occurred after the initial increase in activity, although prior to this it had increased somewhat with the initial increase in conversion. The ethane selectivity behaved in a similar fashion. Although the propane and butane selectivities also increased when the hydrogen feed was started, the loss in selectivity during the time the catalyst lost activity was minimal. The olefin selectivities also changed somewhat after the hydrogen feed was started. The propylene and butylene selectivities were most severely affected and both decreased substantially during the time the catalyst was losing activity.

Just past 320 hours-on-stream there was an unscheduled feed shutdown which lasted for several hours, during this time the stirrer was shut off. The conversions did not recoup to their former levels after restart.

Run 57

The catalyst used in this run was experimental, resulting from precipitation and further treatments of metal oxalates. The preparation conditions for this material will be separately reported, although some of its properties are outlined in Table 1. As prepared this catalyst had no potassium; potassium was added to the autoclave as potassium laurate at the same time as the iron/copper oxide and C₃₀ oil. This mode of potassium addition was described in Quarterly Report No. 9 of this contract. When evaluated under the same conditions as the reference catalyst of Run 56 good initial activity was observed, but rapid catalyst deactivation ensued. Plots of conversions and selectivities vs hours-on-stream are in Figures A-7 to A-12 in Appendix 1. The reason for the deactivation could be related to the small amount of catalyst and the high feed rate (see Conclusion section). During the time the catalyst operated at high conversion (55% CO + H₂ conversion at 40 hours-on-stream compared to 50% CO + H₂ conversion at 80 hours-on-stream in Run 56) the methane selectivity was very low (2 mol % vs 4.5 mol %, in other words at the time of each catalyst's optimum performance the conversions were similar, but there was a large difference in the methane selectivities). The ethane selectivity was also

very low (0.23 mol % vs 1.5 mol % in Run 56).

This catalyst exhibited promise. It was evaluated a second time in Run 60 (below) after two additional runs with oxides prepared similarly to that used in Run 56.

Runs 58 and 59

A major objective of the current contract is development of the means to continuously prepare iron/copper oxide catalyst precursors at the rate of 100 lbs/week. Earlier work during this contract showed it was possible to prepare iron/copper oxides via precipitation from an iron/copper nitrate solution followed by calcination and sizing. In this earlier work means were found to operate the precipitation plant so that very high yields of oxide were formed---catalysts such as the one used in Run 56 resulted. Runs 58 and 59 were done with iron copper oxide from a more recent precipitation plant run designed to be the first of several to illustrate that the plant can be run several days in a row under identical operating conditions and producing each time a high yield of precipitate.

Although Runs 58 and 59 were performed with samples of iron/copper oxide from the same precipitation plant run the catalyst particle size range was different in the two runs. Run 58 used through 140 mesh/on 400 mesh material and Run 59 used through 400 mesh material. The former mesh range is that desired for a commercial catalyst for slurry autoclave processing (fluidized catalyst)---the target of this contract. This size is roughly the same as the nominal 70 micron diameter catalyst currently used for cracking which is also done in a fluidized bed reactor, albeit gas rather than liquid phase. The through 400 mesh material is that normally rejected during processing of the iron/copper oxide precipitate, however, it is a fine powder, similar in size to the experimental catalyst evaluated in Run 57.

Potassium was added as potassium laurate in Runs 58 and 59. The conditions for these two runs were the same as the conditions during Runs 56 and 57. The hydrogen to carbon monoxide usage ratio and conversions during these two runs are compared in Figure A-13. These plots illustrate that the two catalysts behaved similarly early in the runs. However, from about 50 hours-on-stream the finer mesh material was more active and exhibited a lower hydrogen/carbon monoxide usage ratio. This is indirect evidence that the two catalysts were not attrited to the same mesh range during the run, otherwise similar, end-of-run performance would have been expected.

The conversions at the end of Run 59 were not much different than the conversions at the end of Run 57---the run which used the fine mesh experimental catalyst. On the other hand, there was a difference in performance between the Run 56 and Run 58 catalysts which could have been due to the different oxide lots used in their preparation or to the use of potassium carbonate in Run 56 vs. potassium laurate in Run 58. The Run 56 catalyst appeared to run for a longer period of time at a stable conversion before losing activity.

Conclusions

The runs described in this report used approximately one third the amount of iron/copper oxide catalyst precursor as previous ones. This allowed testing of a novel experimental catalyst which was available only in small quantity. The experimental oxide resulted from decomposition and further processing of an iron/copper oxalate mixture. Two runs were performed with this catalyst, of which the second produced the best results. In addition, several catalysts resulting from oxides prepared by precipitation from iron/copper nitrate solutions were evaluated. Such catalysts are the standard type of catalyst prepared under this contract.

The iron/copper nitrate-derived catalysts were of two types differing in the mode of potassium addition. The first type was a reference catalyst which contained potassium from potassium carbonate impregnation/calcination, the second type were catalysts resulting from addition of potassium as solid potassium laurate at the beginning of the run. There were two catalysts of this latter type, both resulting from the same iron/copper oxide preparation but differing in particle size (through 140/over 400 mesh vs. through 400 mesh). The latter, fine mesh, catalyst was similar in size to the above experimental catalyst from metal oxalate decomposition.

The experimental and through 400 mesh catalysts were operated with potassium resulting from solid potassium laurate. The two catalysts were of similar activity, but the experimental catalyst exhibited lower selectivities to the measured light products (C_1 to C_4). Finally, the potassium carbonate impregnated catalyst appeared to maintain activity better than the potassium laurate-containing catalysts, although all catalysts eventually suffered deactivation. The conversion process is first order and at low catalyst loading/high feed rate a small change in activity is witnessed by a large change in conversion--in other words one is on the steep part of the conversion/contact time plot and small changes in activity at a given contact time produce large changes in conversion.

Plans for the Next Quarter

Evaluate additional catalyst precursors prepared in the iron/copper oxide precipitation plant. Evaluate other potassium-containing organic molecules to better understand the results in this report and Report No. 9 which covered the early work with potassium laurate.

TABLE 1
CATALYST PRECURSOR PROPERTIES

PLT/RUN NO.	701/56	701/57	701/58	701/59	701/60
K ADD. METHOD	K ₂ CO ₃ IMPREG.	SOLID K LAURATE TO RX AT STARTUP			
<u>CATALYST PRECUR.</u>					
<u>OXIDE PART¹</u>					
ELEMENTAL ANAL.					
Fe, WT %	57.0	62.7	65.5	65.9	62.7
Cu, WT %	1.27	2.77	2.14	2.14	2.77
K, WT %	1.18	0.12	—	—	0.12
Fe:K, WT	100 : 2.1	100 : 0.19	—	—	100 : 0.19
NITROGEN POROS.					
SA, m ² /g	196	206	97	94	206
PV, cc/g	0.24	0.10	0.47	0.41	0.10
MESH RANGE	THRU 140 ON 400	FINE POWDER	THRU 140 ON 400	THRU 400	FINE POWDER
<u>K LAURATE PART², g</u>	0.0	1.9	2.1	2.1	1.9
Fe:K, WT (TOTAL)	2.1	2.2	2.1	2.1	2.2

1. ALL RUNS USED 25 g OF PRECURSOR.
2. K LAURATE = 16.6 wt% K.

FIGURE A-1

UOP REF.CAT: LOWER % SOLIDS

PLT 700B R-56 25.0g 6616-160 in 290g C₃₀ oil

H₂:CO in feed = 0.7, stirrer rpm = 1100

REACTOR TEMP, °C

REACTOR PRESSURE, psig

H₂ FEED, NL/Hr g Fe

CO FEED, NL/Hr g Fe

STIRRER rpm

CO + H₂
CONVERSION

FIGURE A-2

UOP REF.CAT: LOWER % SOLIDS

PLT 700B R-56 25.0g 6616-160 in 290g C₃₀ oil

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE A-3

UOP REF.CAT: LOWER % SOLIDS

PLT 700B R-56 25.0g 6616-160 in 290g C₃₀ oil

H₂:CO in feed = 0.7, stirrer rpm = 1100

TARGET TEMP, °C
PRESSURE, psig
H₂, NL/Hr g Fe
EED, NL/Hr g Fe
STIRRER rpm

FIGURE A-4

UOP REF.CAT: LOWER % SOLIDS
 PLT 700B R-56 25.0g 6616-160 in 290g C₃₀ oil
 H₂:CO in feed = 0.7, stirrer rpm = 1100

REACTOR TEMP, °C
 PRESSURE, psig
 H₂, NL/Hr g Fe
 CO, NL/Hr g Fe
 STIRRER rpm

FIGURE A-5

UOP REF.CAT: LOWER % SOLIDS
 PLT 700B R-56 25.0g 6616-160 in 290g C₃₀ oil

H₂:CO in feed = 0.7, stirrer rpm = 1100

TARGET TEMP, °C
 PRESSURE, psig
 H₂, NL/Hr g Fe
 CO, NL/Hr g Fe
 STIRRER rpm

CO
 CONVERSION

H₂/CO
 OUTLET

GC2 C3
 SELECTIVITY

GC2 C3
 PAR SELECTIVITY

HOURS ON STREAM

FIGURE A-6

UOP REF.CAT: LOWER % SOLIDS
 PLT 700B R-56 25.0g 6616-160 in 290g C₃₀ oil
 H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE A-7

PLANT 700B RUN 57 EVALUATION OF NOVEL CATALYST

25g 6827-69 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm

TARGET TEMP, °C	← 280 →	← 265 →
PRESSURE, psig	← 153 →	← 200 →
FEED, NL/Hr g Fe	← 5.82 →	← 6.97 →

FIGURE A-8

PLANT 700B RUN 57 EVALUATION OF NOVEL CATALYST

25g 6827-69 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm

TARGET TEMP, °C

PRESSURE, psig

FEED, NL/Hr g Fe

← 280 →

← 153 →

← 5.82 →

265

200

6.97

CO
CONVERSION

H₂
CONVERSION

CO + H₂
CONVERSION

H₂/CO
USAGE

HOURS ON STREAM

FIGURE A-9

PLANT 700B RUN 57 EVALUATION OF NOVEL CATALYST

25g 6827-69 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm

FIGURE A-10

PLANT 700B RUN 57 EVALUATION OF NOVEL CATALYST

25g 6827-69 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm

FIGURE A-11

PLANT 700B RUN 57 EVALUATION OF NOVEL CATALYST

25g 6827-69 in 290g C₃₀ oil
H₂:CO in feed=0.7, 1100 rpm

FIGURE A-12

PLANT 700B RUN 57 EVALUATION OF NOVEL CATALYST

25g 6827-69 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm

FIGURE A-13

PERFORMANCE COMPARISON

○ RUN 58, THROUGH 140 ON 400 MESH.

□ RUN 59, THROUGH 400 MESH

TARGET TEMP, °C

← 280 →

265

PRESSURE, psig

← 153 →

290

FEED, NL/Hr g Fe

← 5.82 →

6.97

H₂/CO
USAGE

CO

CONVERSION

H₂

CONVERSION

CO + H₂

CONVERSION

HOURS ON STREAM

FIGURE A-14
PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE

PLANT 701 R-58 25g 6827-93 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm

TARGET TEMP, °C	280	265
PRESSURE, psig	153	290
FEED, NL/Hr g Fe	5.82	6.97

FIGURE A-15

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE

PLANT 701 R-58 25g 6827-93 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm

TARGET TEMP, °C

≤ 280

265

PRESSURE, psig

≤ 153

290

FEED, NL/Hr g Fe

≤ 5.82

6.97

FIGURE A-16

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE

PLANT 701 R-58 25g 6827-93 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm

FIGURE A-17

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE

PLANT 701 R-58 25g 6827-93 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm

TARGET TEMP, °C	<280>	265
PRESSURE, psig	<153>	290
FEED, NL/Hr g Fe	<3.82>	6.97

FIGURE A-18

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE

PLANT 701 R-58 25g 6827-93 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm

TARGET TEMP, °C	<280>	265	→
PRESSURE, psig	<153>	290	→
FEED, NL/Hr g Fe	<3.82>	6.97	→

FIGURE A-19

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE

PLANT 701 R-58 25g 6827-93 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm

FIGURE A-20

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE

PLT 701 R-59 25.0g 6827-93-A in 290g C₃₀ oil

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE A-21

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE

PLT 701 R-59 25.0g 6827-93-A in 290g C₃₀ oil

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE A-22

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE

PLT 701 R-59 25.0g 6827-93-A in 290g C₃₀ oil

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE A-23

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE

PLT 701 R-59 25.0g 6827-93-A in 290g C₃₀ oil

H₂:CO In feed = 0.7, stirrer rpm = 1100

FIGURE A-24

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE

PLT 701 R-59 25.0g 6827-93-A in 290g C₃₀ oil

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE A-25

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE

PLT 701 R-59 25.0g 6827-93-A in 290g C₃₀ oil

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE A-26

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

$H_2:CO$ in feed = 0.7, stirrer rpm = 1100

FIGURE A-27

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE A-28

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

□ RUN 59

○ RUN 60

TARGET TEMP, °C

← 280 →

265

PRESSURE, psig

← 153 →

290

FEED, NL/Hr g Fe

← 5.82 →

6.97

FIGURE A-29

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE A-30

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

□ RUN 59

○ RUN 60

TARGET TEMP, °C

<280>

265

PRESSURE, psig

<153>

290

FEED, NL/Hr g Fe

<5.82>

6.97

FIGURE A-31

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

□ RUN 59

○ RUN 60

TARGET TEMP, °C

280

265

PRESSURE, psig

153

290

FEED, NL/Hr g Fe

5.82

6.97

FIGURE A-32

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE A-33

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

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