Fischer-Tropsch Iron Catalyst Development

by

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UOP
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Abstract

The main objective of this contract is the development of the means of preparing 100 lb/day batches of a precipitated iron-based Fischer-Tropsch catalyst for slurry processing. The actual catalyst results from reduction of an iron oxide-based precursor in the slurry reactor. The final catalyst should be high in activity yet product less than 5 mol-% of methane and ethane.

An important part of the preparation of precipitated iron-based Fischer-Tropsch catalysts is the addition of potassium. Potassium is usually the metal of choice to enhance catalyst activity and control product selectivity. For the catalyst production method being developed for the present contract, potassium is added by a separate impregnation-calcination step using potassium carbonate prior to catalyst activation. This step is a separate one that if eliminated, would reduce the cost of preparing the catalyst.

A new method of adding potassium to slurry catalyst is reviewed. This method employs an oil-soluble salt of potassium, for instance, potassium laurate. Two variations of this method are discussed. In one case, the potassium laurate is added to a potassium-free catalyst precursor and the slurry oil at the beginning of the run. Following this addition, the catalyst is reduced in the usual fashion. In the other case, the potassium laurate is added in a suitable solvent during a run. So far three variations of this latter experiment have been performed, each with a different catalyst precursor: one with no potassium and two with potassium but at different levels. The addition of a solution of potassium laurate during a run works best if the catalyst precursor has a small amount of potassium present at the start. In such a case, lower methane and ethane selectivities were noted than with any of the catalysts that had the full amount of potassium present at the outset, either from potassium carbonate impregnation or potassium laurate addition.

Thus, the use of potassium laurate allows the elimination of one step in a traditional preparation method for a Fischer-Tropsch catalyst precursor based on iron oxide. In addition, it allows the preparation of catalysts exhibiting the targeted low methane and ethane selectivity. Finally, because a method to intermittently add it to the slurry reactor during the run is available, the catalyst performance can be modified *during a run*, for instance, if some potassium is present at the outset but more is found to be required during the run to meet the performance target.

Fischer-Tropsh Iron Catalyst Development

UOP 2145-1

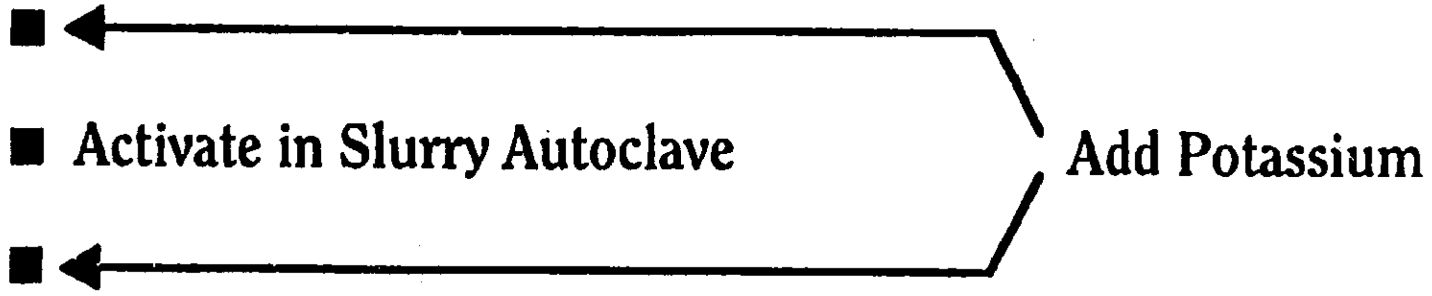
Contract Objective

- Develop Iron-Based F-T Catalyst for Slurry Bubble Reactor

UOP 2145-2

Approach

- Fe/Cu/(Si) Oxide Precursor via Precipitation



- Activate in Slurry Autoclave

Add Potassium

- Maximize Conversion and Minimize $C_1 + C_2$ Selectivity via:
  - Potassium Level & Method of Adding
  - Activation Procedure

UOP 2145-3

Catalyst Performance Targets

- Performance Conditions
  - 20 wt-% Catalyst in Slurry
  - Coal-Derived Syngas Feed at 2.4 NL/hr • g Fe
  - 265°C Slurry Temperature

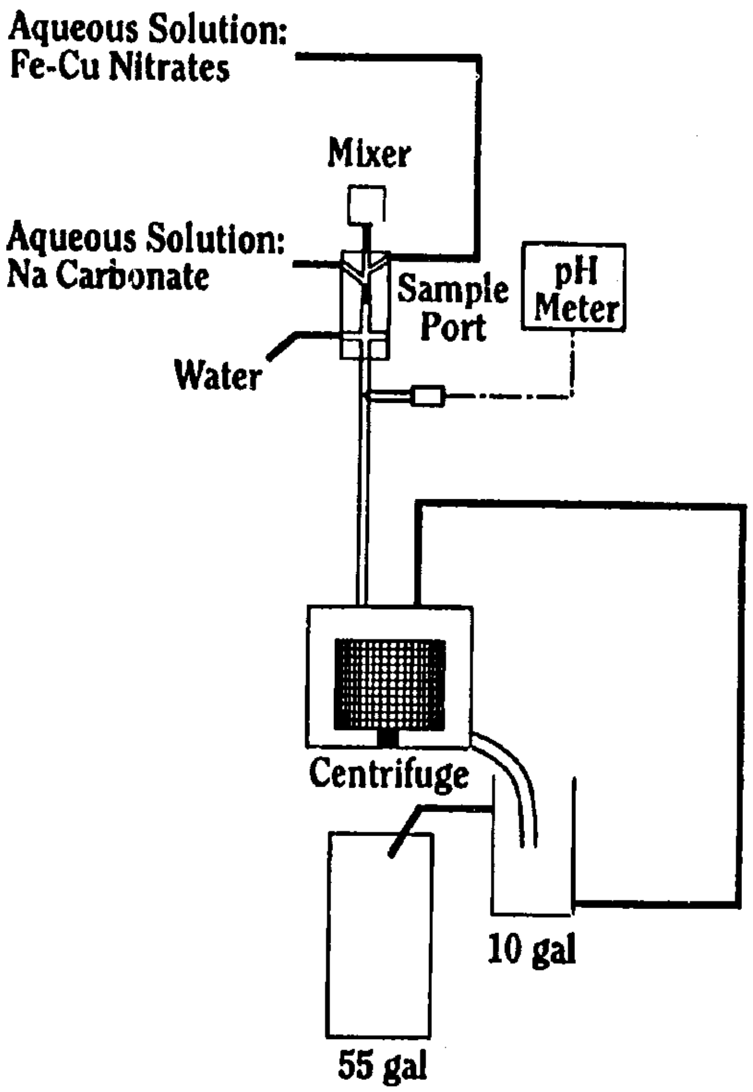
UOP 2145-4A

Catalyst Performance Targets

- Performance Conditions
  - 20 wt-% Catalyst in Slurry
  - Coal-Derived Syngas Feed at 2.4 NL/hr • g Fe
  - 265°C Slurry Temperature

- Targets
  - CO + H_2 Conversion = 88% (≈93% CO Conversion)
  - Methane + Ethane Selectivity ≤ 5 mole-%

Iron & Copper Oxide Precipitation Plant



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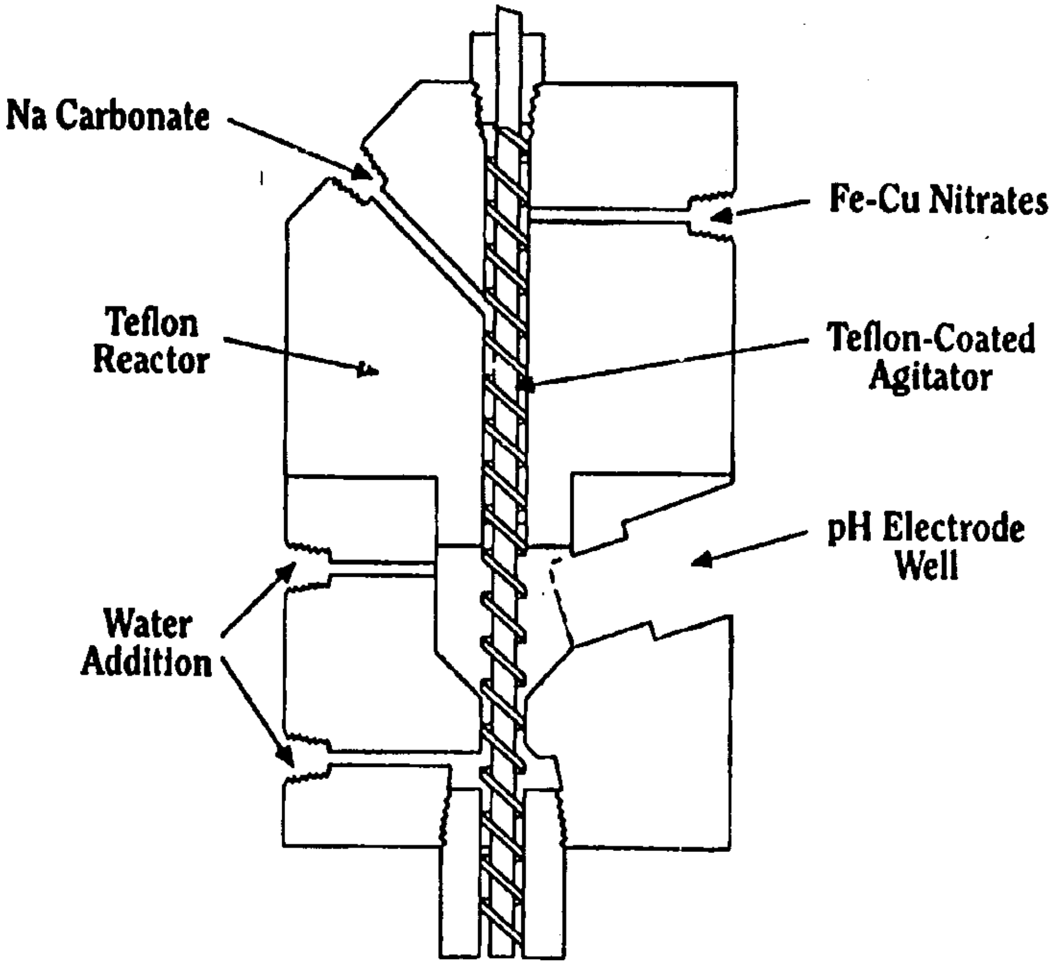
Precipitation Reactor



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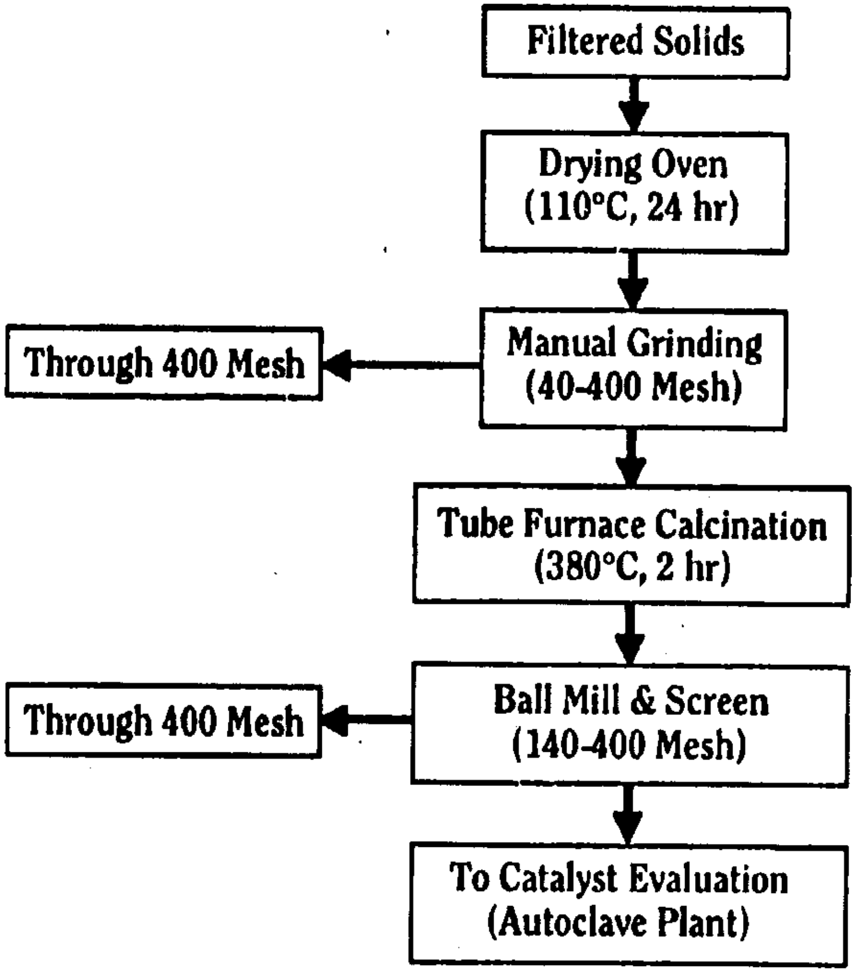
Workup of Water-Washed Precipitate



Filtered Solids

Drying Oven
(110°C, 24 hr)

Manual Grinding
(40-400 Mesh)

Through 400 Mesh

Tube Furnace Calcination
(380°C, 2 hr)

Ball Mill & Screen
(140-400 Mesh)

Through 400 Mesh

To Catalyst Evaluation
(Autoclave Plant)

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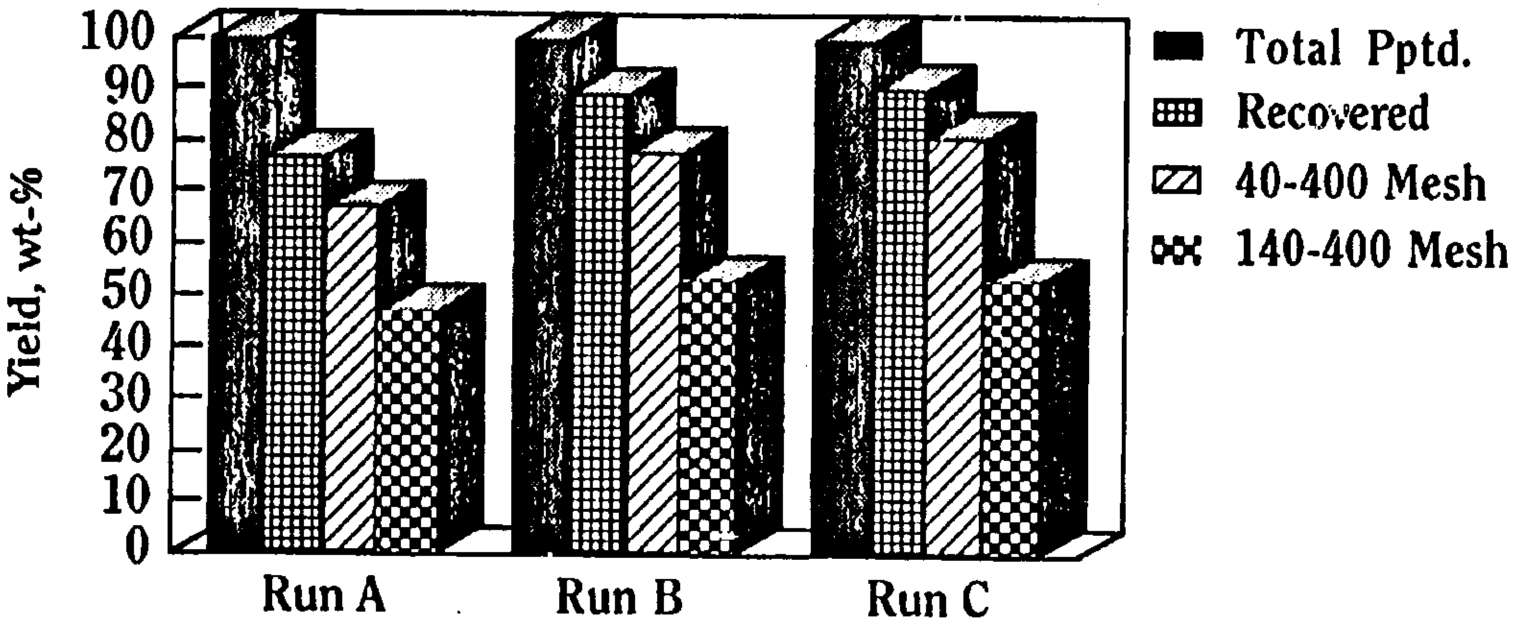
F-T Fe Catalyst Yield



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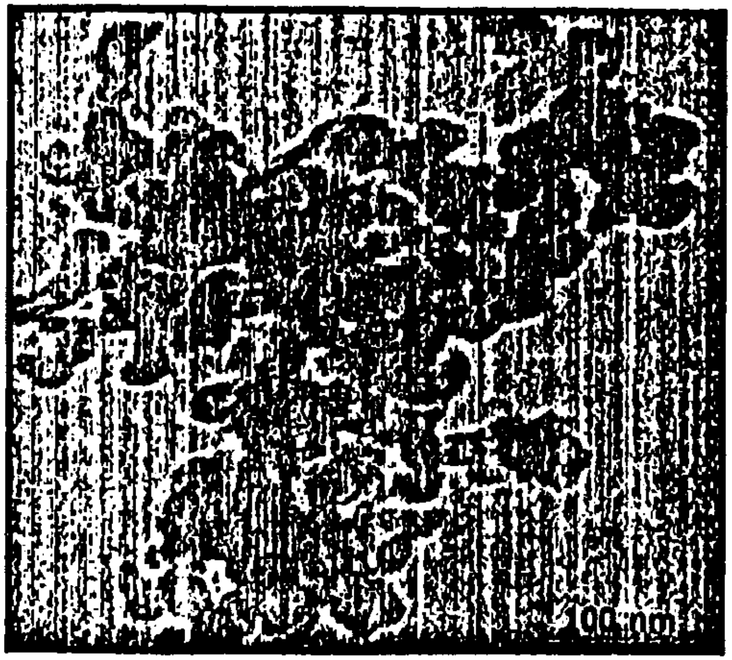
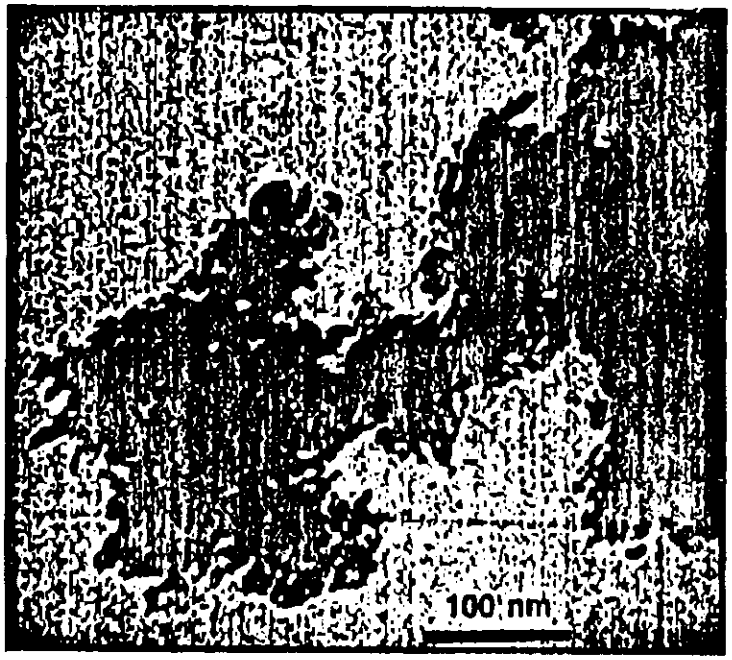
Catalyst Physical Properties

	Metals, wt-%			BET	
Fe/Cu Oxides	Fe	Cu	Na, ppm	SA, m^2/g	PV, cc/g
Run A, on Filter	65.5	2.1	47	97	0.47
Run A, Overflow	66.0	2.3	<100	108	0.44
Run B, on Filter	64.5	2.2	19	133	0.30
Run B, Overflow	64.3	2.3	<100	157	0.36

Stem Analysis for Run A



Run A, on Filter



Run A, Overflow

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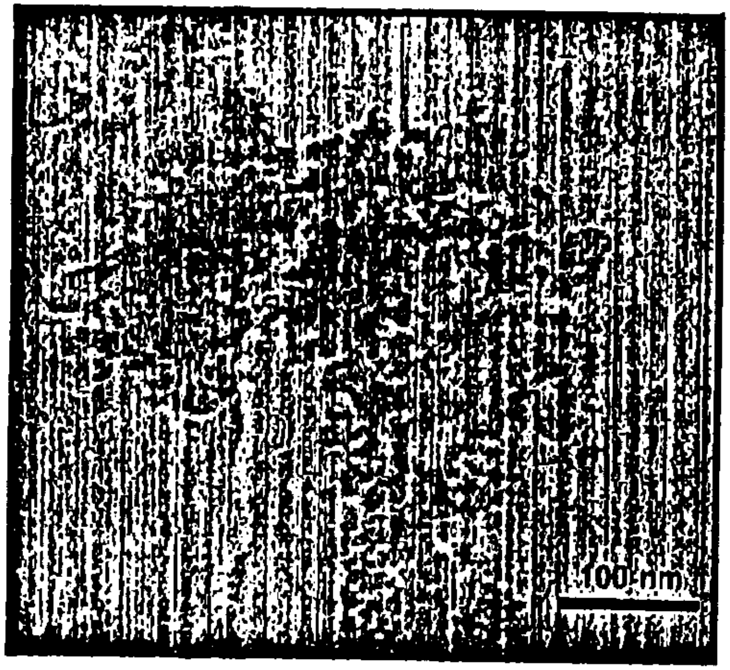
Stem Analysis for Run B



Run B, on Filter

Run B, Overflow

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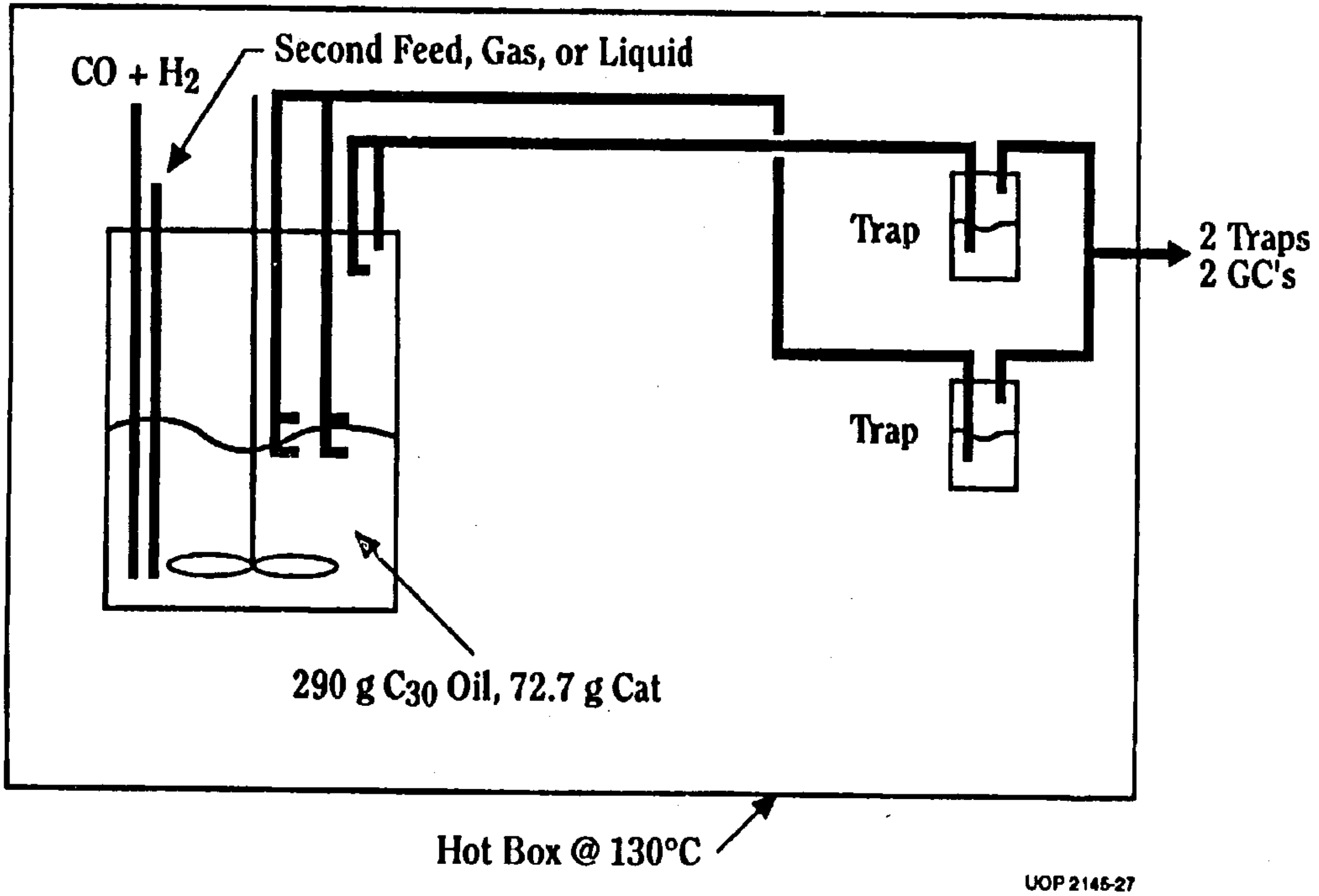
Schematic of Slurry Autoclave Plant



Reactor Loading

Catalyst, g	25
Fe:K, wt	100:1.8
C_{30} Oil, g	290

Performance Evaluation Conditions

	Activation (20 hr)	Rest of Run
Feed, H_2 : CO, Molar	0.7	0.7
Feed Rate, NL/hr•g Fe	5.8	7.0
Temperature,°C	280	265
Pressure, psig	153	290

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Performance Overview at Lineout

Fe/Cu Oxides	CO Conv., %	Selectivities, mol-%		
		C_1	C_2	$C_2^=$
Run A, on Filter	20	1.8	0.1	0.8
Run A, Overflow	28	2.9	0.5	3.0
Run B, on Filter	40	3.6	0.7	3.6
Run B, Overflow	46	3.5	0.8	4.5

Reasons for Potassium

- Activate Catalyst
- Lower Light Ends

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How Added in Current Work

- K_2CO_3 Impregnation & Calcine

or

- Potassium Laurate
  - As Solid at Start-Up
  - As Solution during Run

or

- Combinations of Above

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Potassium Laurate

$CH_3(CH_2)_{10}CO_2^- K^+$

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Reactor Loading for Potassium Study

Catalyst, g	73
Fe:K, wt	Varies
C_{30} Oil, g	290

Performance Evaluation Conditions for Potassium Study

	Activation (20 hr)	Rest of Run
Feed, H_2 : CO, molar	0.7	0.7
Feed Rate, NL/hr•g Fe	2.0	2.4
Temperature,°C	280	265
Pressure, psig	153	290

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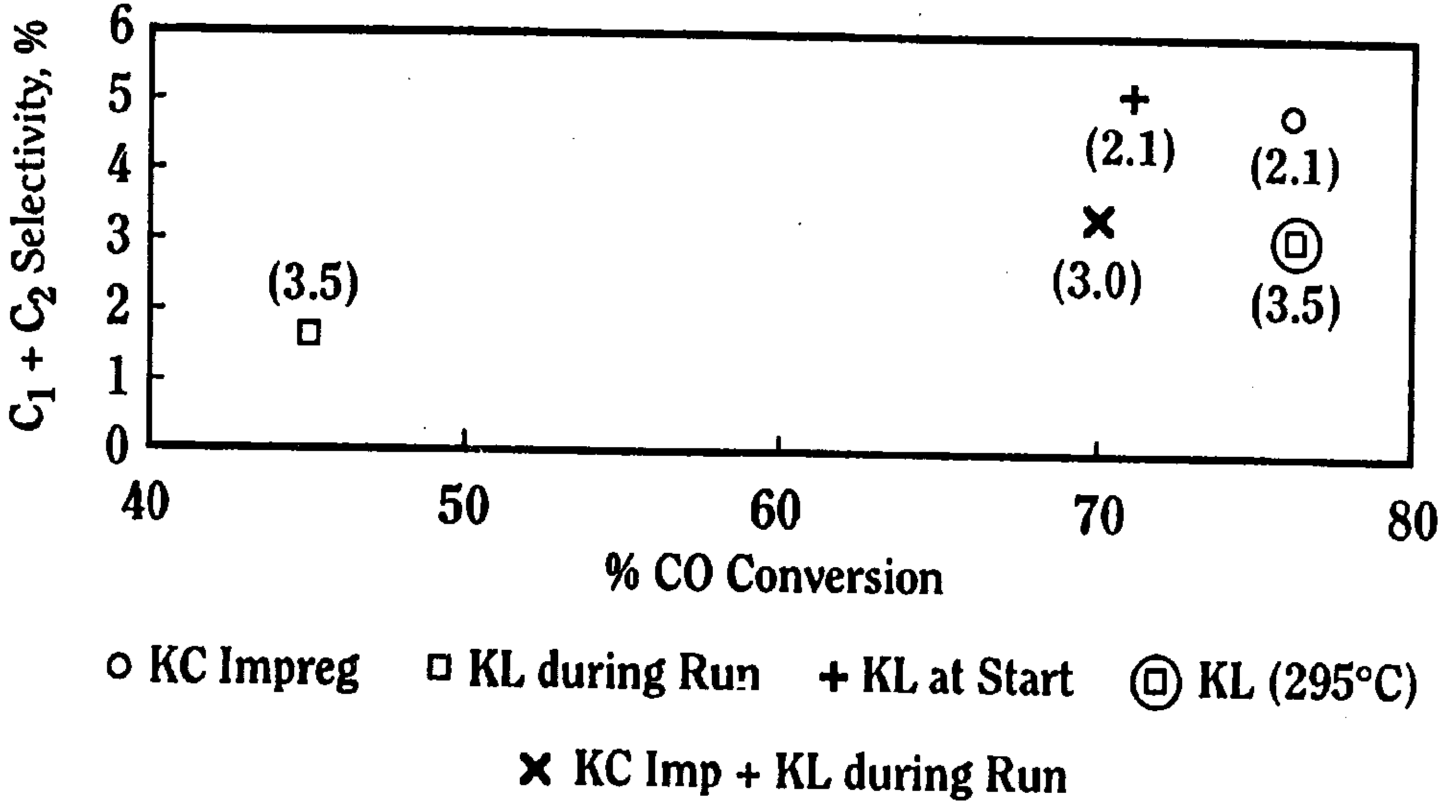
Best Performance with Various Potassium Sources



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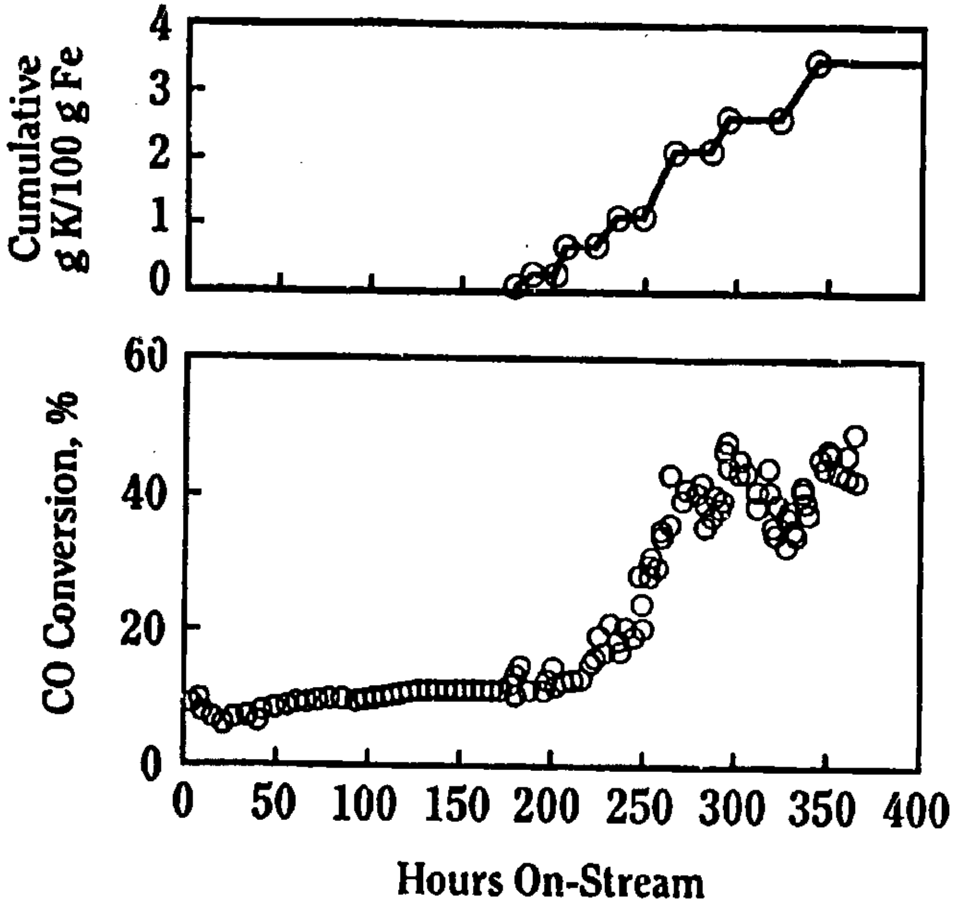
Effect of Potassium Laurate Addition on CO Conversion



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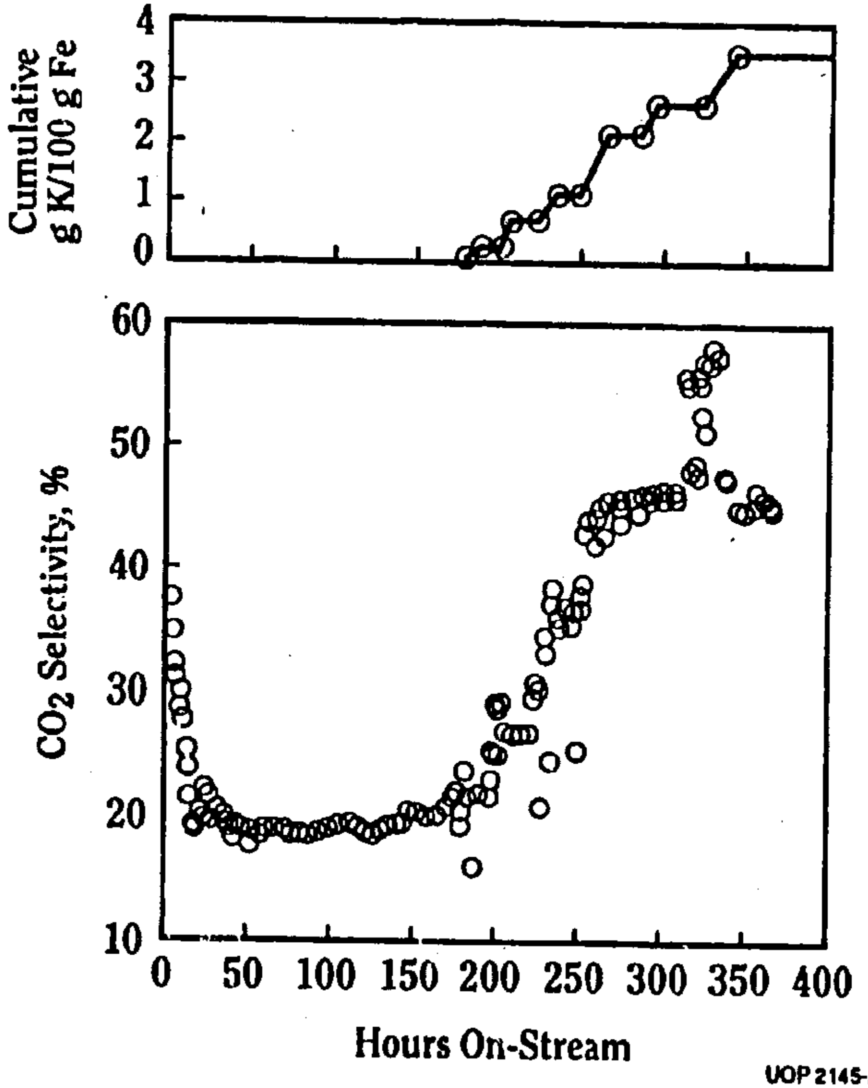
Effect of Potassium Laurate Addition on CO_2 Selectivity



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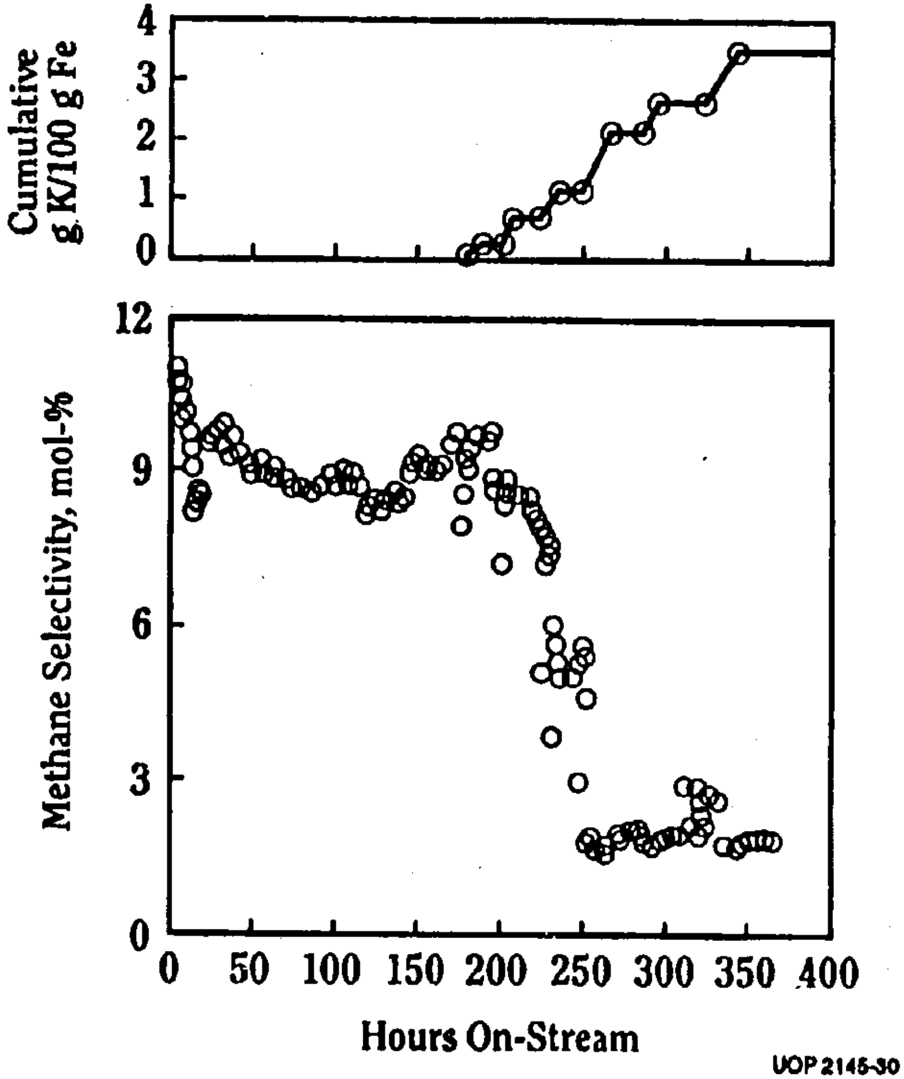
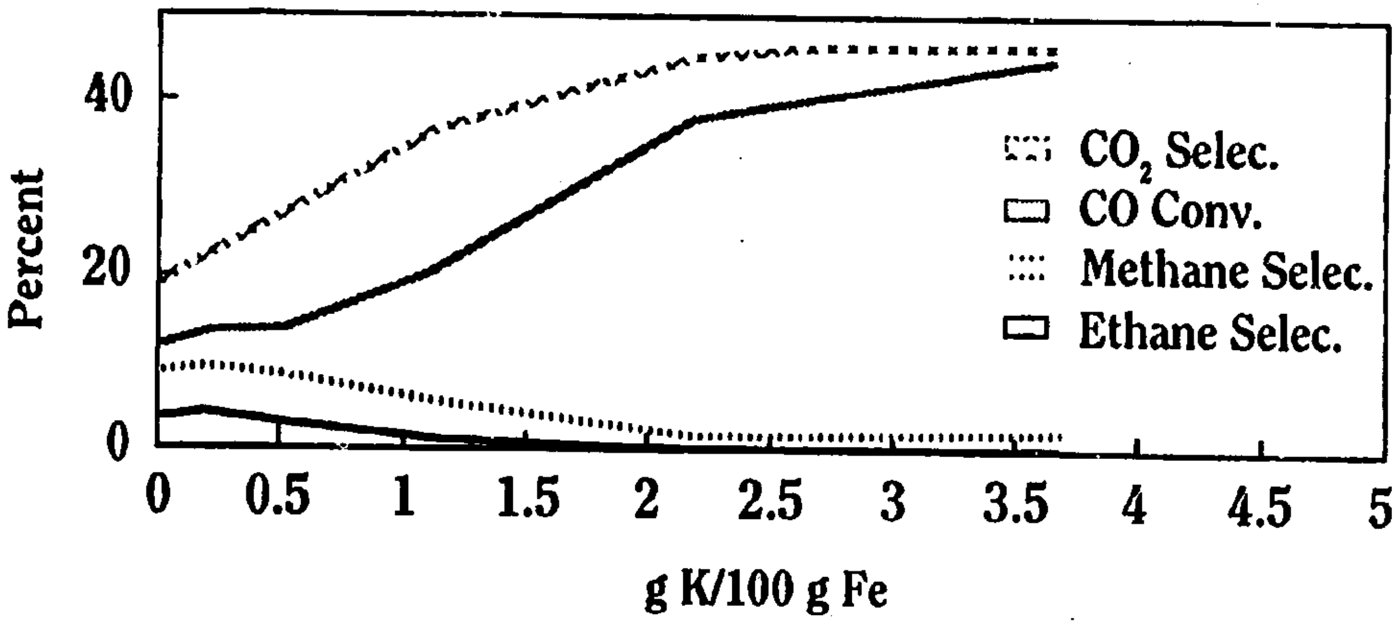
Effect of Potassium Laurate Addition on Methane Selectivity



Summary of Data



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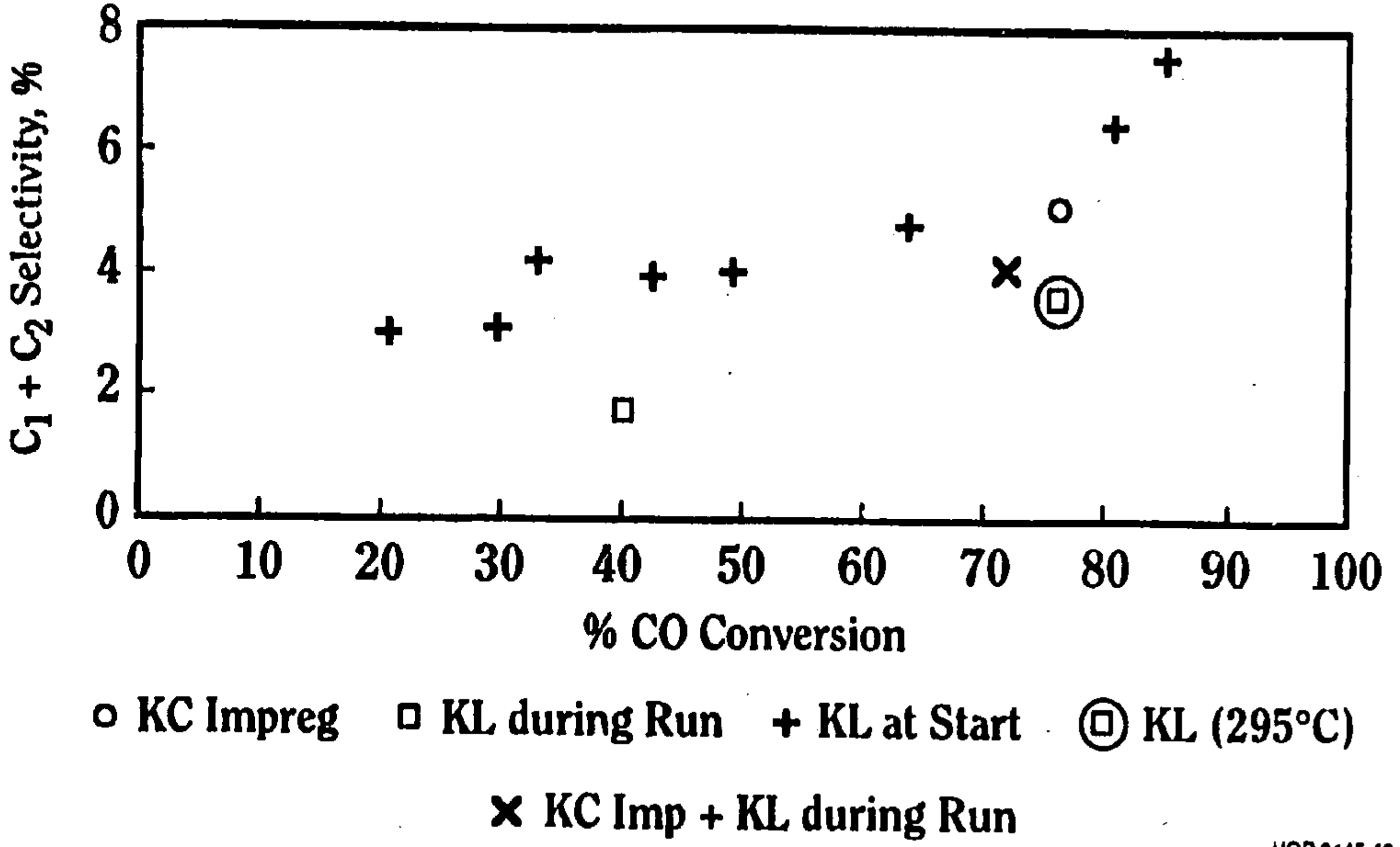
Activity Selectivity Relationship



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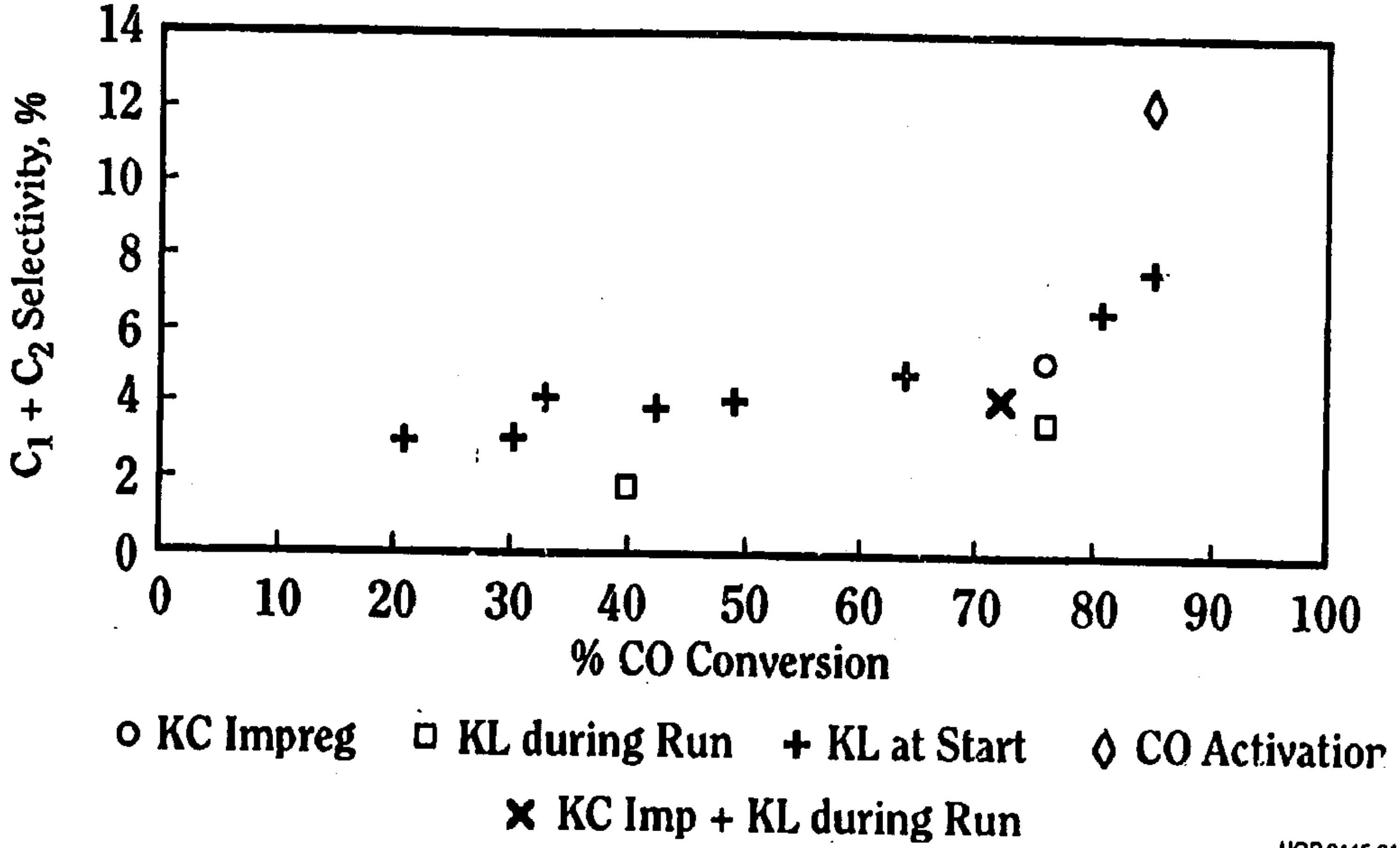
Reactor Loading for CO Activation

Catalyst, g	73
Fe:K, wt	No Potassium
C_{30} Oil, g	290

Performance Evaluation Conditions for CO Activation

	Activation (30 hr)	Rest of Run
Feed, H_2 : CO, molar	Only CO	0.7
Feed Rate, NL/hr • g Fe	2.0	2.4
Temperature,°C	265	265
Pressure, psig	200	200

Comparison of CO and Syngas Activation



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Conclusions

- Precipitation Method Proven for Fe Oxide-Based Precursor
- Catalyst Activity Increased Significantly over Previous Contract
- Potassium Addition Technique Developed to Control Selectivity