LIQUID HYDROCARBON FUELS FROM SYNGAS

This contract calls for the direct catalytic conversion of syngas to liquid motor fuels including gasoline, turbine and diesel oil, with product selectivities and quality superior to those provided by the Fischer-Tropsch process. The catalyst consists of a Fischer-Tropsch metal component (MC) and a shape selective molecular sieve component (SSC) to control hydrocarbon boiling range and quality. Task 1 is aimed at the screening of molecular sieves as SSC candidates using small olefins as feed while in Task 2 the syngas is directly converted to liquid fuels using a combined MC + SSC catalyst system. At present, the Task 1 work has been successfully completed and several excellent SSC candidates are available for the formulation of Task 2 catalysts. The work is now concentrated on the optimization of several MC-SSC catalyst systems.

Catalysts comprised of promoted iron (MC) and either of Union Carbide's Molecular Sieves 101 or 104 (SSC) produce primarily gasoline range hydrocarbons from syngas. Cobalt containing catalysts, while producing more methane, have produced at least as much gasoline and more diesel oil than comparable iron containing catalysts. On a methane-free basis, promoted cobalt (MC) and either of Union Carbide's Molecular Sieves 101 or 108 (SSC) produce more total motor fuels than is possible from an exact Schulz-Flory distribution.

A catalyst consisting of Union Carbide's Molecular Sieve 103 and a promoted metal component is extremely durable. The catalyst remained on stream for three months partially under very severe reaction conditions and showed no significant deactivation.

LIQUID HYDROCARBON FUELS FROM SYNGAS
DE-AC22-81PC40077

Tarrytown Laboratory
Molecular Sieve Department
Engineering Products Division
Union Carbide Corporation

ORGANIZATION

TASK 1: Evaluate shape-selective catalyst (SSC) candidates for converting low molecular weight liquids and small olefins to LHF.

TASK 2: Evaluate combinations of transition metal component (MC) and SSC for converting syngas ($CO + H_2$) to LHF.

TASK 3: Study surface effects and reaction intermediates in the hydrogenation of carbon monoxide.

TASK 1

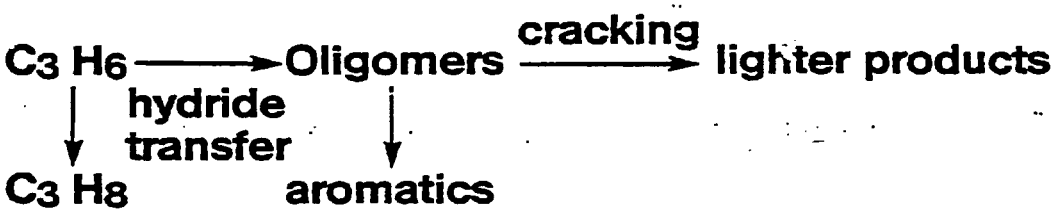
Evaluation of the molecular sieve, shape selective component, using propylene feed

CONCLUSIONS

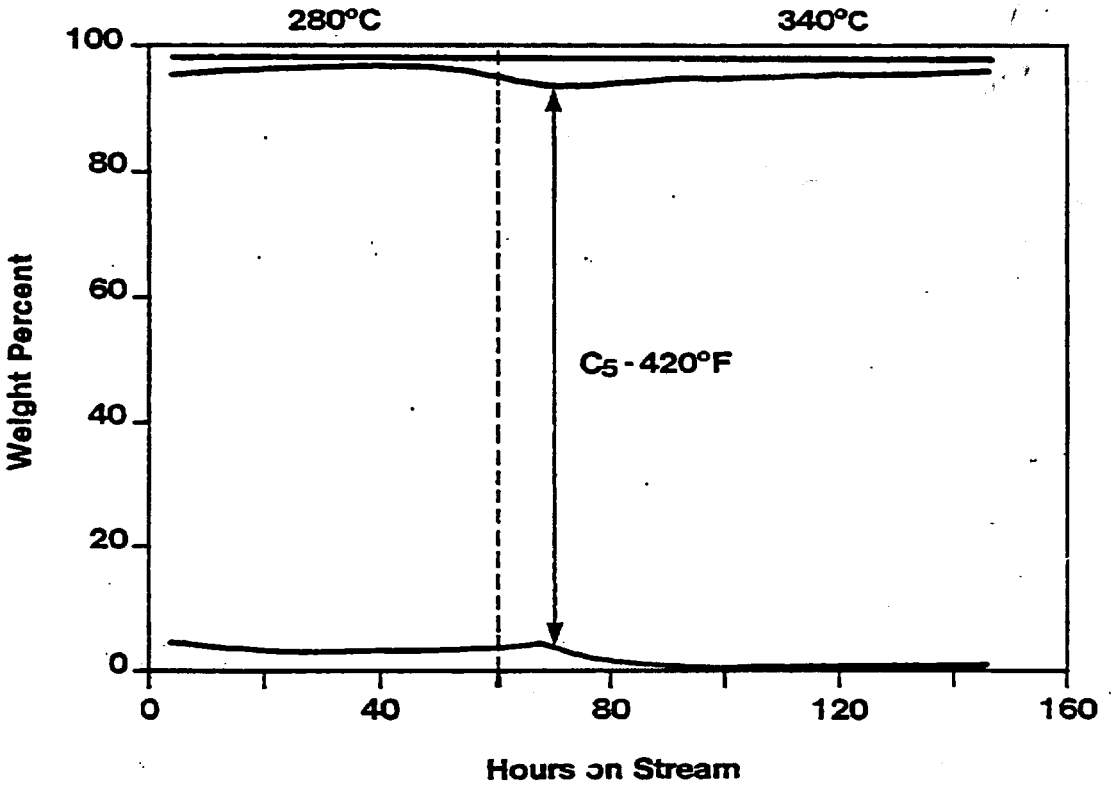
1. The molecular sieves UCC-104 and UCC-108 have outstanding selectivity ($\geq$ 95%) for the conversion of propylene to C_5^+ hydrocarbons boiling in the gasoline range. The selectivity of these catalysts to gasoline is substantially superior to ZSM-5.

2. The molecular sieve UCC-101 converts propylene to both gasoline and diesel oil.

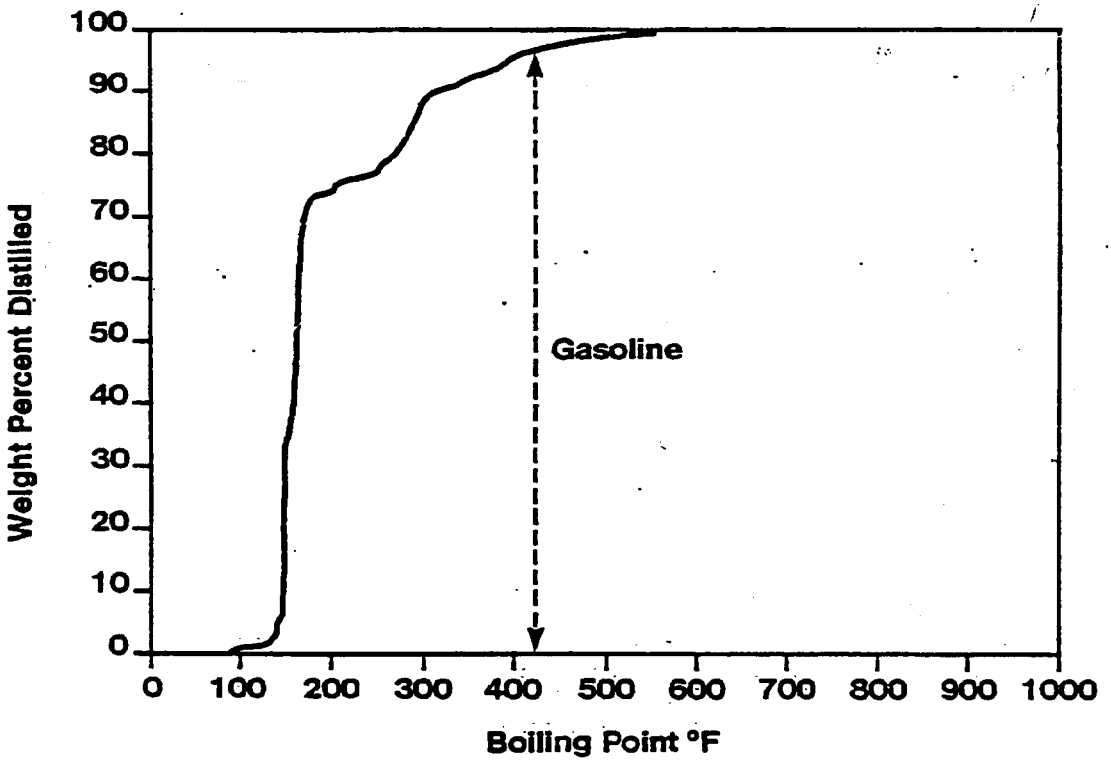
PROPYLENE OLIGOMERIZATION



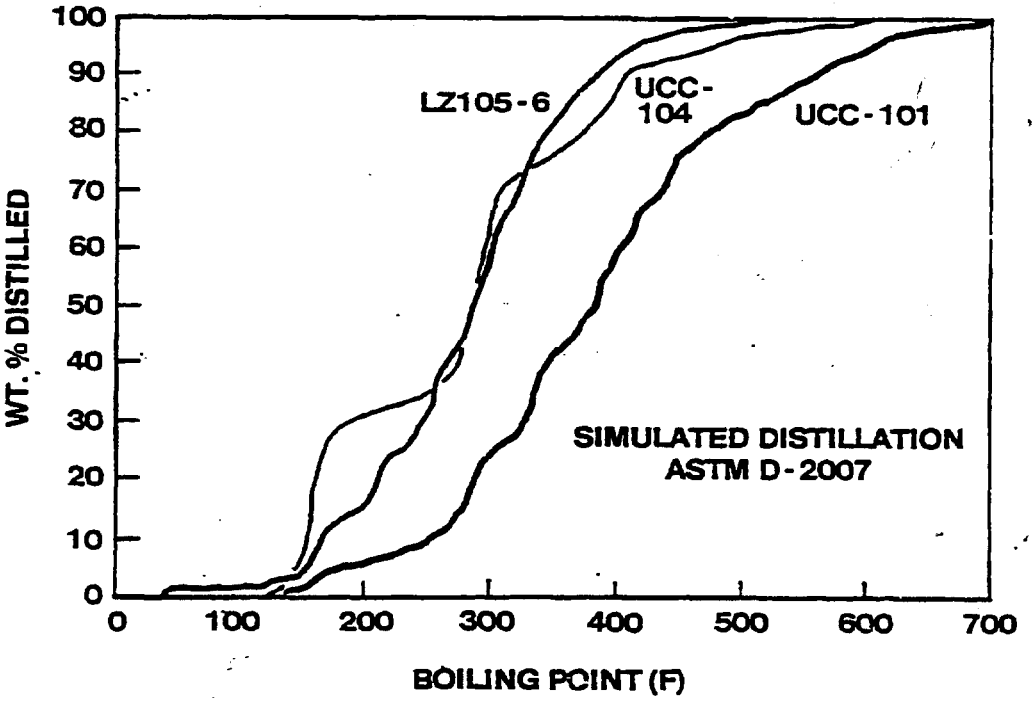
SELECTIVITY OF UCC-108 IN PROPYLENE OLIGOMERIZATION AT REACTION TEMPERATURES OF 280°C AND 340°C.



SIMULATED DISTILLATION OF THE C_5^+ PRODUCT FROM PROPYLENE OLIGOMERIZATION WITH UCC-108 CATALYST



BOILING POINT DISTRIBUTION OF THE LIQUID PRODUCT OF PROPYLENE OLIGOMERIZATION USING LZ105-6, UCC 101,AND UCC 104 AS CATALYSTS.



CATALYST	GASOLINE (100-420°F)	DIESEL (420-700°F)
LZ105	96	4
UCC-101	68	32
UCC-104	90	8

PROPYLENE OLIGOMERIZATION

CATALYST	HOS	CONVERSION	SELECTIVITY TO C_5^+
		AT 280°C	
UCC-104	24	41.2	90.5
UCC-108	21	72.2	96.9
ZSM-5	27	65.7	86.3
		AT 340°C	
UCC-104	78	63.1	95.6
UCC-108	68	74.6	94.2
ZSM-5	72	84.5	79.7

TASK 2

Evaluation of the molecular sieve component in combination with the metal component.

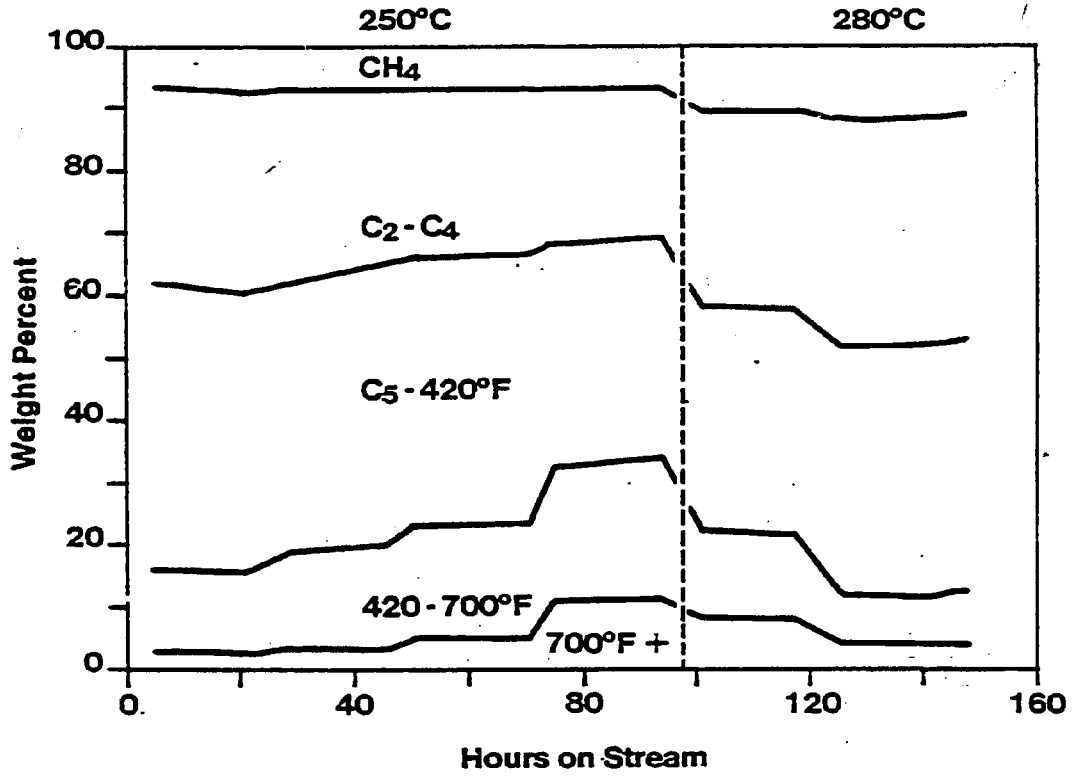
HIGHLIGHTS

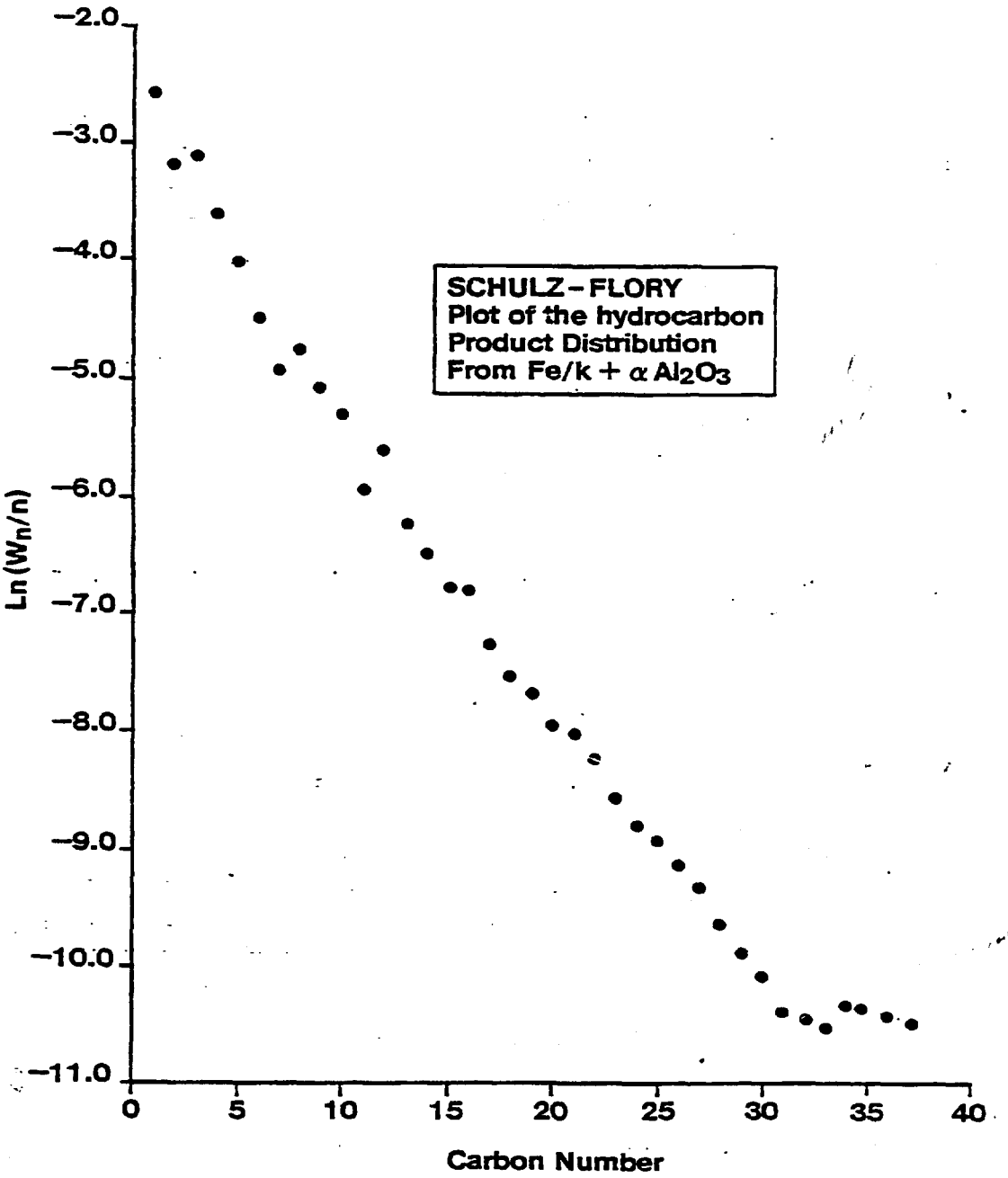
Promoted Cobalt and UCC-101 or UCC-108 have excellent selectivity to motor fuels producing a wax-free liquid hydrocarbon product.

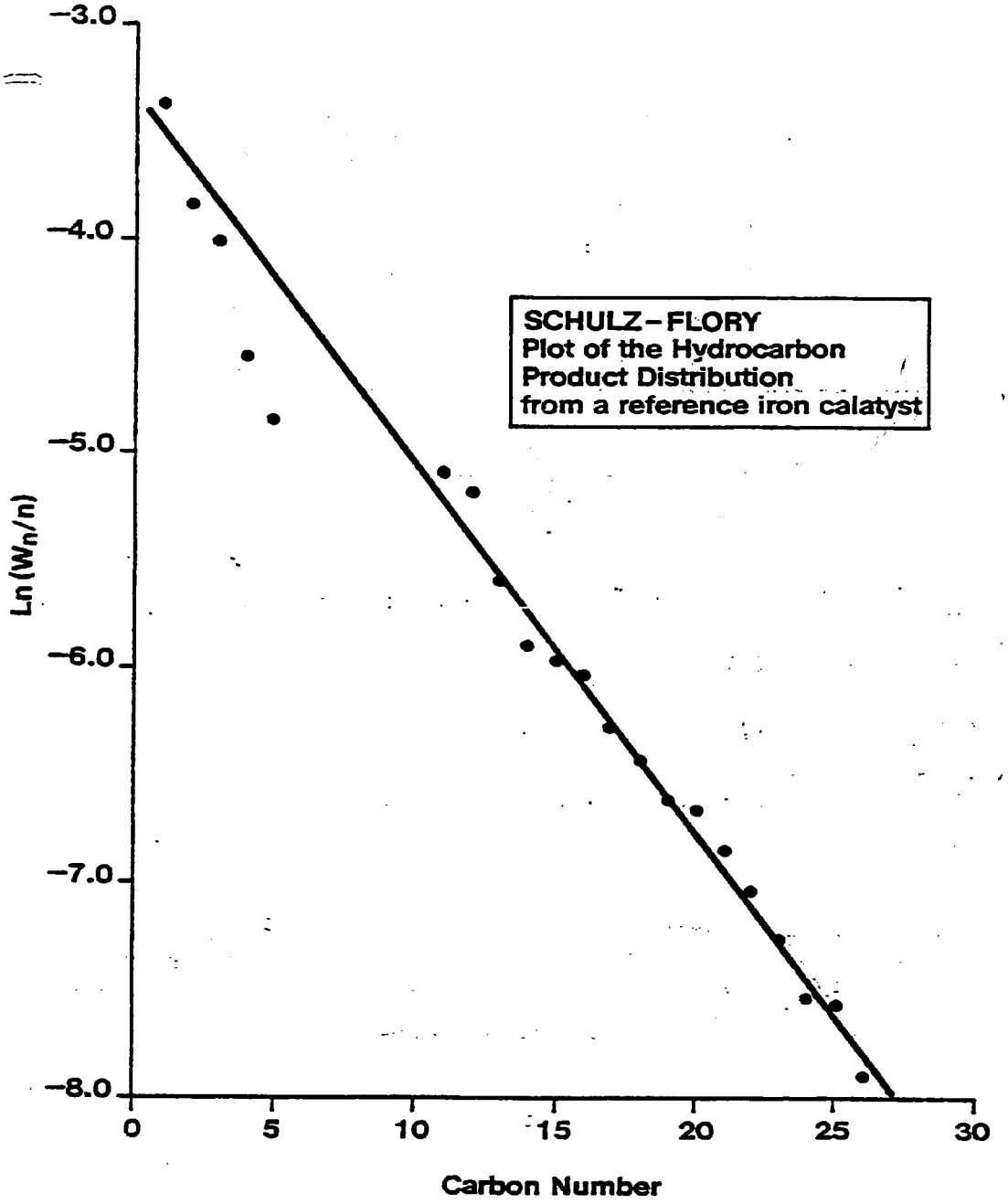
Promoted iron and UCC-101 produces both gasoline and diesel oil while promoted iron and UCC-104 produces a isomerized gasoline product.

Iron and UCC-103 is a very durable catalyst even under demanding reaction conditions.

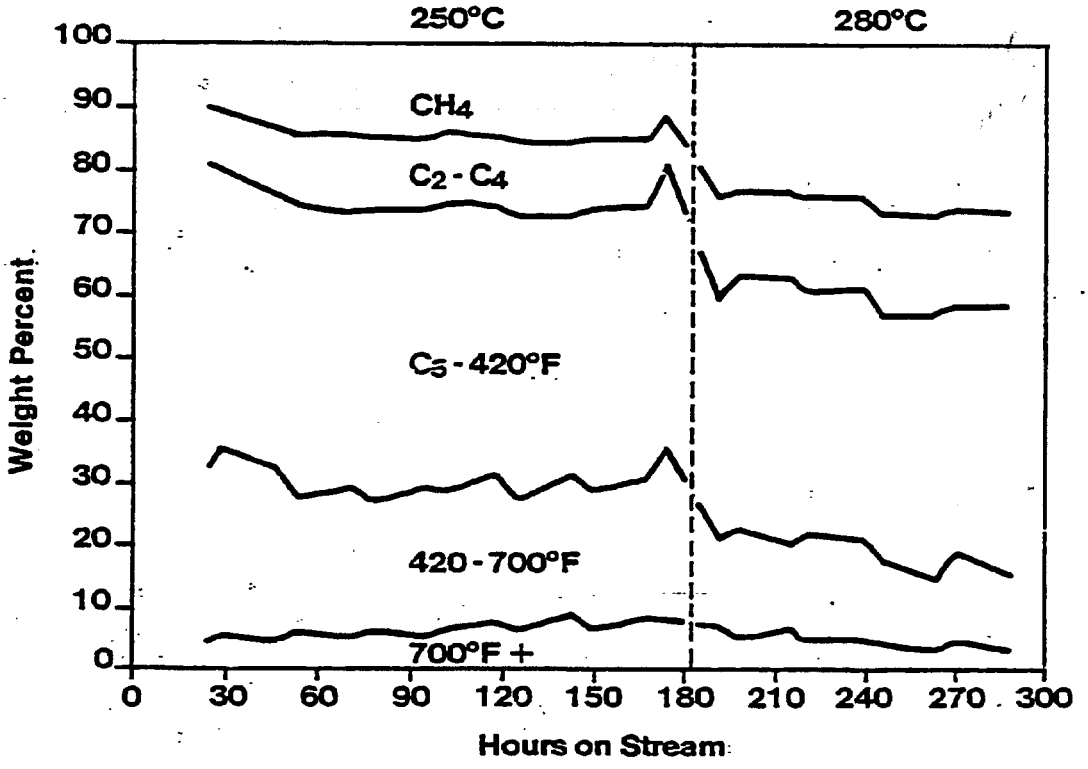
THE PRODUCT DISTRIBUTION FROM THE CONVERSION OF 1:1 H_2:CO SYNGAS TO HYDROCARBONS USING A PROMOTED IRON AND α Al_2O_3 AS THE CATALYST

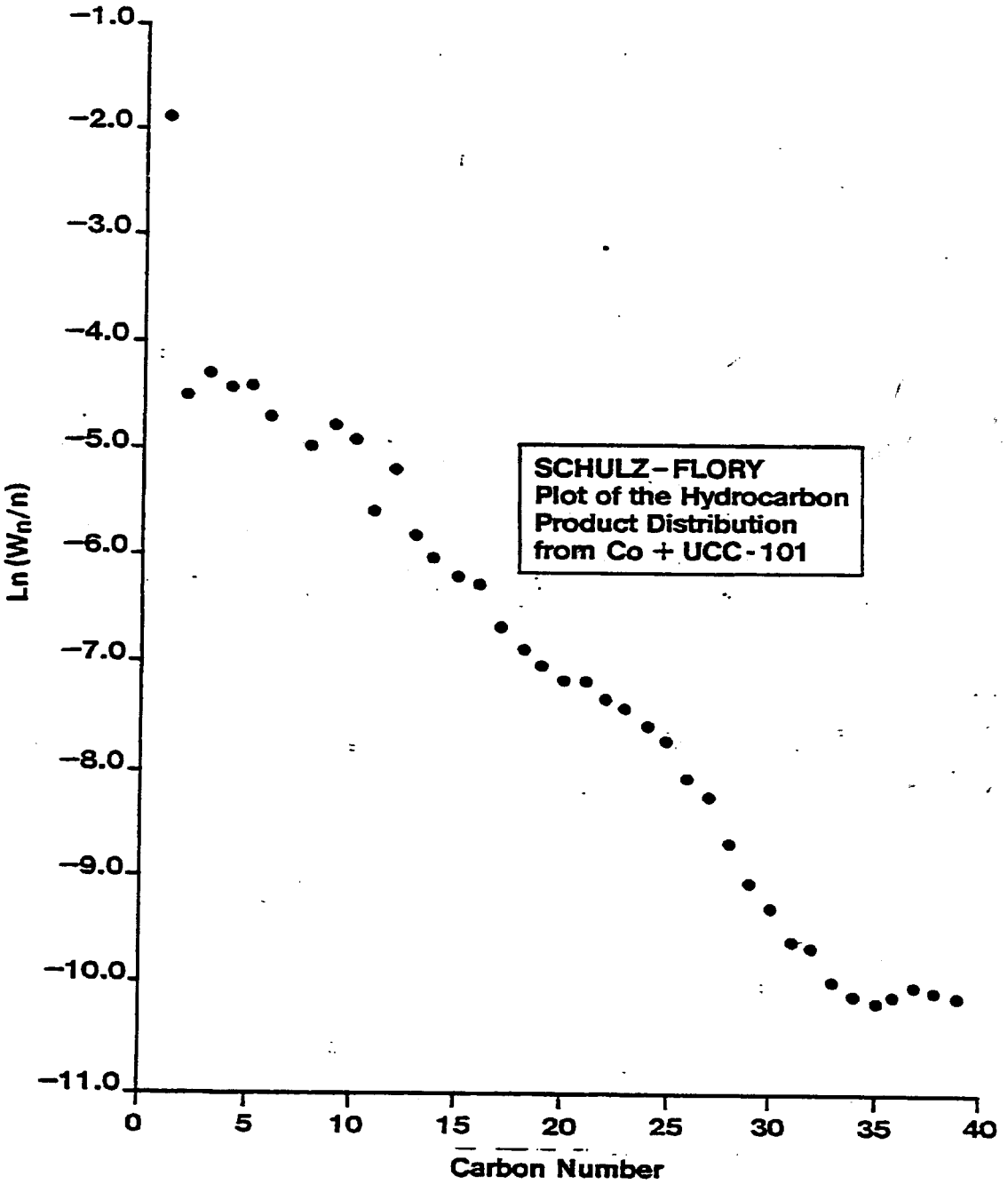



SCHULZ-FLORY
Plot of the hydrocarbon
Product Distribution
From Fe/k + α Al2O3
Ln (Wn/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number


SCHULZ-FLORY
Plot of the Hydrocarbon
Product Distribution
from a reference iron calatyst
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
Ln (Wn/n)
0
5
10
15
20
25
30
Carbon Number

THE PRODUCT DISTRIBUTION FROM THE CONVERSION OF 1:1 H_2:CO SYNGAS TO HYDROCARBONS USING COBALT AND UCC-101 AS THE CATALYST




SCHULZ-FLORY
Plot of the Hydrocarbon
Product Distribution
from Co + UCC-101
Ln (Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Catalyst	Ref. Iron	Fe + UCC-101	Fe/K + UCC-101	Modified Fe/K + UCC-101	Fe/K + UCC-104
$C_1 - C_2$	15	19.4	19.7	16.9	22.8
$C_3 - C_4$	18	25.5	24.0	23.2	26.7
Gasoline	42	50.1	42.8	42.3	41.5
Diesel Oil	18	4.9	11.3	14.4	7.8
Heavies	9	0.2	2.3	3.2	1.2
Total Motor Fuel	**59**	**54.9**	**54.1**	**56.7**	**49.3**

Catalyst	Co + UCC-101	Modified Co + UCC-101	Modified Co + UCC-108
$C_1 - C_2$	16.0	16.9	17.2
$C_3 - C_4$	7.9	13.2	10.3
Gasoline	44.4	50.9	46.8
Diesel Oil	24.5	16.3	23.4
Heavies	7.2	2.7	2.3
Total Motor Fuel	**68.9**	**67.2**	**70.2**

THE RESULTS OF AN EXTENDED TEST OF IRON-UCC-103 FOR FISCHER-TROPSCH SYNTHESIS IN A PLUG FLOW REACTOR

Days on Stream	27	44	47	57	69	85
Temperature	310	310	310	310	340	340
H_2 : CO	1.6	0.8	0.8	1.6	1.6	1.6
H_2 + CO Conv.	52.5	57.6	62.1	51.3	55.7	56.1
Selectivity						
C_1	10.8	12.2	12.1	20.7	34.7	28.9
C_2-C_4	43.9	32.9	34.0	35.3	42.3	37.5
C_5^+	45.3	54.9	53.9	44.0	22.0	33.6

CONCLUSIONS

- Catalysts comprising F-T metal catalysts and UCC molecular sieves show high total motor fuel yields due to the cutoff of high boiling hydrocarbons by the molecular sieve. These catalysts produce a wax-free liquid product.
- Catalysts containing selected molecular sieves show excellent durability indicating practical lifetimes.