Report 13

KINETIC STUDY USING AN IRON FISCHER-TROPSCH CATALYST

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- OBJECTIVES
- MECHANISM
- EXPERIMENTAL PROGRAM
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OBJECTIVES
(UOP/SDC TASK 15 PHASE-II)

- TO USE A DESIGNED EXPERIMENTAL PROGRAM AND A PROPOSED MECHANISM TO STUDY THE FISCHER-TROPSCH KINETICS WITH IRON CATALYST
- TO USE THE RESULTING KINETICS COUPLED WITH REACTOR MODEL TO EVALUATE VARIOUS REACTOR SYSTEMS FOR INDIRECT LIQUEFACTION VIA CONVENTIONAL FISCHER-TROPSCH CATALYST.
- TO FURTHER USE THE KINETICS AS A FOUNDATION IN THE PRELIMINARY EVALUATION OF A MULTIFUNCTION CATALYST SYSTEM.

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MECHANISM

- PHASE-I
- PHASE-II
- RATE EXPRESSIONS

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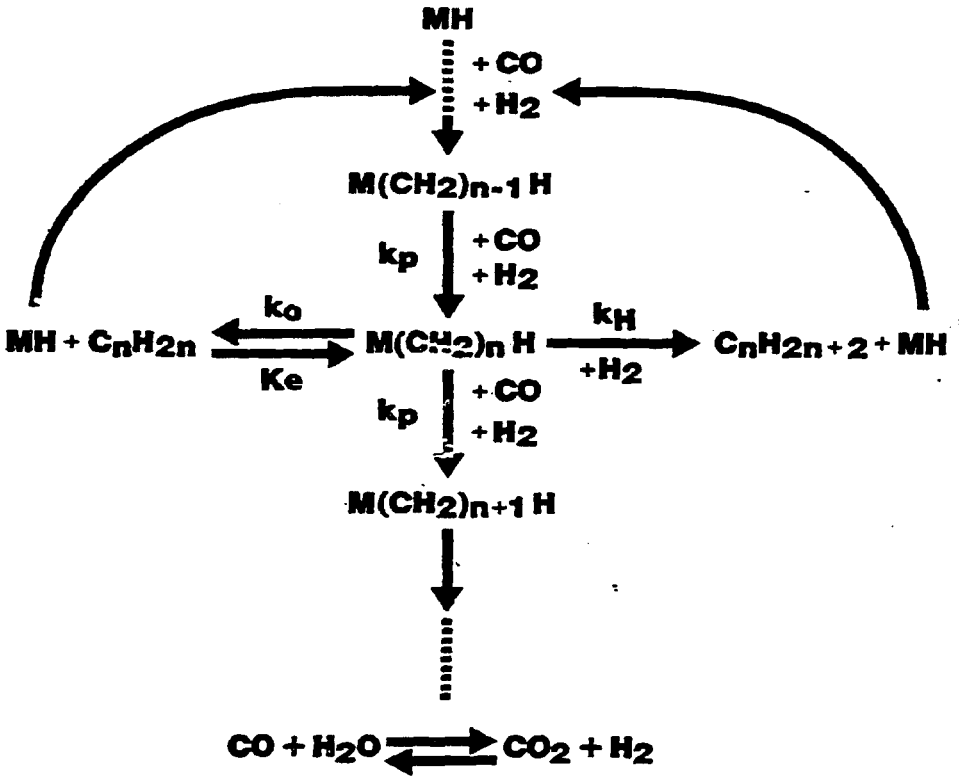
MECHANISM



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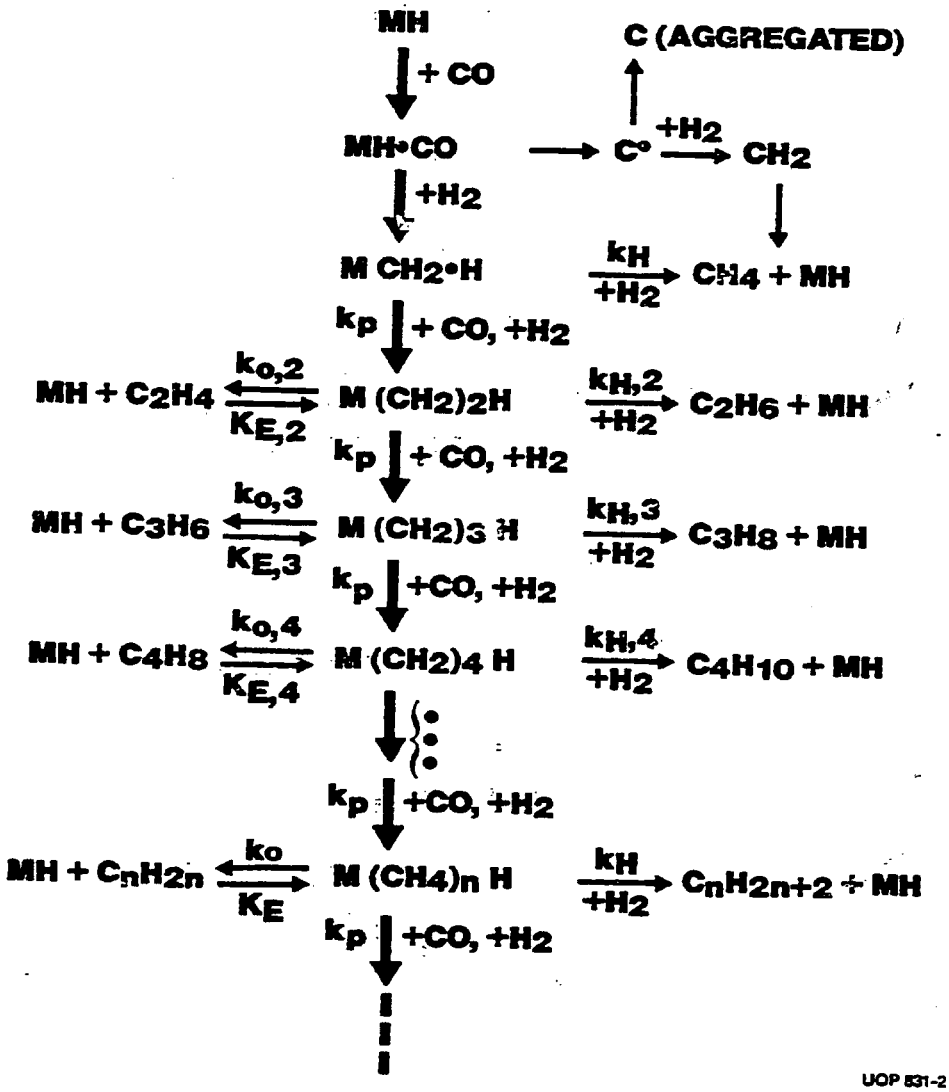
MECHANISM


MH
+ CO
MH•CO
+H2
M CH2•H
kp
+ CO, +H2
MH + C2H4
ko,2
KE,2
M (CH2)2H
kp
+ CO, +H2
MH + C3H6
ko,3
KE,3
M (CH2)3 H
kp
+CO, +H2
MH + C4H8
ko,4
KE,4
M (CH2)4 H
kp
+CO, +H2
MH + CnH2n
ko
KE
M (CH4)n H
kp
+CO, +H2
C (AGGREGATED)
+H2
C°
CH2
kH
+H2
CH4 + MH
kH,2
+H2
C2H6 + MH
kH,3
+H2
C3H8 + MH
kH,4
+H2
C4H10 + MH
kH
+H2
CnH2n+2 + MH
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EXPERIMENTAL PROGRAM

- DESIGN OF EXPERIMENTS
- OPERATING CONDITIONS

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PETC/UCP
EXPERIMENTAL PROGRAM

FEED H_2/CO MOLAR RATIO	PRESSURE, psia	ADDITIONAL FEED-COMPONENTS, MOLE-%	OBJECTIVE:
2	315		BASE CONDITIONS
1	315		DETERMINE EFFECTS OF H_2/CO RATIO
4	315		DETERMINE EFFECTS OF H_2/CO RATIO
2	415		DETERMINE PRESSURE EFFECTS
1	115		DETERMINE PRESSURE EFFECTS
2	315	5% CH_4	ASCERTAIN EFFECT OF CH_4
2	315	5% CO_2	DETERMINE EFFECTS OF HIGHER LEVELS OF CO_2
2	415	5% CO_2	DETERMINE COMBINED PRESSURE AND CO_2 EFFECTS
2	315	1% C_2=	DETERMINE OLEFIN ADSORPTION/DESORPTION RATE AND EQUILIBRIUM
2	315	5% C_2=	DETERMINE OLEFIN ADSORPTION/DESORPTION RATE AND EQUILIBRIUM
2	315	5% C_3=	DETERMINE OLEFIN ADSORPTION/DESORPTION RATE AND EQUILIBRIUM
2	315	1.3% l-C_4= + 0.3% l-C_5=	DETERMINE OLEFIN ADSORPTION/DESORPTION RATE AND EQUILIBRIUM
2	415	5% C_2=	DETERMINE EFFECT OF PRESSURE ON OLEFIN ABSORPTION/DESORPTION
2	415	1.3% l-C_4= + 0.3% l-C_5=	DETERMINE EFFECT OF PRESSURE ON OLEFIN ABSORPTION/DESORPTION

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OPERATING CONDITIONS

CATALYST — **FUSED IRON AMMONIA SYNTHESIS CATALYST, 0.8% K_2O**
6~ 8 MESH

REACTOR — **BERTY**

REDUCTION — **1) H_2, 450°C, 300 psig, 2500 HR^{-1}, 72 HRS.**
2) $\frac{2\ H_2}{1\ CO}$, 250°C, 300 psig, 1600 HR^{-1}, 24 HRS.

STANDARD RUN — **1600 HR^{-1}**

275°C
300°C
275°C
325°C
275°C

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DATA INTERPRETATION

- POLYMERIZATION
- WATER-GAS SHIFT REACTION
- OLEFIN FORMATION
- HYDROGENATION
- "EXTRA" METHANE FORMATION

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POLYMERIZATION

$$r_{p,i} = D \bullet [M(CH_2)_i H]$$

IMPROVED RATE EXPRESSION

$$D = \frac{k_p^\circ \bullet [CO] \bullet [H_2]}{[CO] + A \bullet [H_2O]}$$

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INITIATION AND POLYMERIZATION REACTION

TEMPERATURE, °C	$k_p°$	A
275 B	0.258 (10%)	3.64 (21%)
300	0.239 (7.4%)	0.31 (20%)
275 M	0.137 (5.8%)	0.17 (36%)
325	0.330 (8.7%)	0.05 (22%)
275 E	0.140 (3.6%)	0

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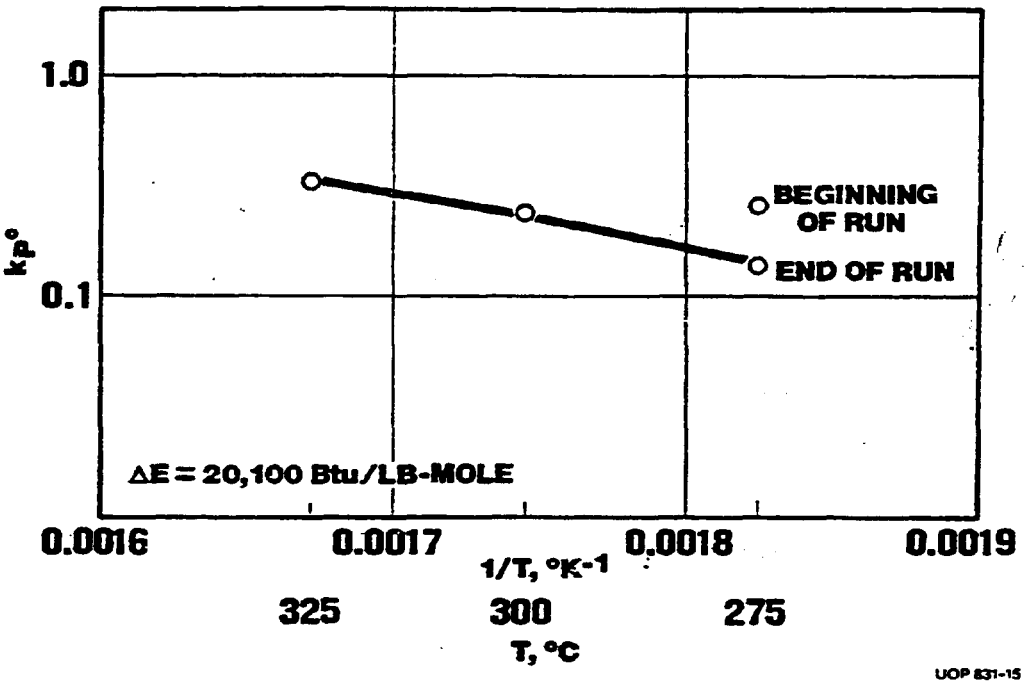
ARREHNIUS PLOT OF $k_p°$



WHEN THE CATALYST STABILIZES:

$$r_{p,i} = k_p^{\circ} \bullet [H_2] \bullet [M(CH_2)i]$$

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WATER-GAS SHIFT REACTION

IMPROVEMENT OF RATE EXPRESSION:

$$r_{CO_2} = \frac{k_{WG} K_{CO} K_{H_2O} \left([CO][H_2O] - [CO_2][H_2]/K_E \right)}{\left(1 + K_{CO}[CO] + K_{H_2O}[H_2O] + K_{CO_2}[CO_2] + K_{H_2}[H_2] \right)^2}$$

REDUCED TO:

$$r_{CO_2} = \frac{k_{WG} A \left([CO][H_2O] - [CO_2][H_2]/K_E \right)}{\left([CO] + A[H_2O] + B[H_2] \right)^2}$$

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WATER-GAS SHIFT REACTION

T, °C	K_{WGC}	A	B
275 S	0.0144 (35%)	4.10 (48%)	0.185 (59%)
300	0.0145 (38%)	1.31 (34%)	0
275 M	0.0108 (30%)	1.95 (20%)	0.018 (278%)
325	0.0257 (60%)	0.33 (44%)	0
275 E	0.0125 (38%)	1.52 (17%)	0

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AT END OF RUN:

$$r_{CO_2} = \frac{k_{WG} \cdot A \cdot \left([CO] \cdot [H_2O] - [CO_2]\,[H_2]/K_E\right)}{\left([CO] + A \cdot [H_2O]\right)^2}$$

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CONCLUSIONS

IT HAS BEEN DEMONSTRATED IN THIS WORK THAT SOME INSIGHTS OF FISCHER-TROPSCH REACTIONS CAN BE GAINED THROUGH THE USE OF A KINETIC MODEL COMBINED WITH A DESIGN EXPERIMENTAL PROGRAM.

IN THIS CASE:

- **THE CHANGING PROPERTIES WITH RESPECT TO TIME ARE CLEARLY REVEALED.**
- **HYDROGEN CONCENTRATION IS THE MAJOR FACTOR IN DETERMINING CONVERSION OF A GIVEN CATALYST AT A GIVEN TEMPERATURE.**

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