Report 1

Development of a Catalytic Process For Alcohol-Based Synthetic Transportation Fuel From Coal-Derived Synthesis Gases

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DEVELOPMENT OF A CATALYTIC PROCESS FOR ALCOHOL-BASED SYNTHETIC TRANSPORTATION FUEL FROM COAL-DERIVED SYNTHESIS GASES

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STATEMENT OF WORK

OBJECTIVES:

1. DEVELOP A CATALYST AND REACTOR SYSTEM FOR CONVERTING COAL-DERIVED SYNTHESIS GASES TO PRIMARILY C_1 - C_4 SATURATED ALCOHOLS.

2. PREPARE A PRELIMINARY PROCESS DESIGN AND EVALUATE ECONOMICS OF PRODUCING ALCOHOL-BASED TRANSPORTATION FUELS IN A COMMERCIAL-SCALE PLANT.

TASK BREAKDOWN STRUCTURE

1. CATALYST FORMULATION AND SCREENING STUDIES*

2. PROCESS VARIABLES STUDIES IN BENCH-SCALE UNIT

3. ENGINEERING AND ECONOMIC ANALYSIS*

4. CATALYST LIFE STUDIES IN PROCESS DEVELOPMENT UNIT

*CURRENTLY IN PROGRESS

SYN GAS CONVERSION ALTERNATIVES FOR INDIRECT COAL LIQUEFACTION

A. $2H_2 + CO \xrightarrow{Cu/Zn} CH_3OH + Q_1$ (4.2)*

B. $2H_2 + CO \xrightarrow[\text{F-T ELEMENTS}]{Cu/Zn +} \begin{cases} CH_3OH \\ C_2H_5OH + H_2O + Q_2 \\ C_3H_7OH \\ C_4H_9OH \end{cases}$ (3.1)*

C. $2H_2 + CO \longrightarrow MeOH \xrightarrow{ZSM\text{-}5} C_8H_{16} + H_2O + Q_3$ (2.0)*

*THEORETICAL YIELD OF LIQUID FUEL, GAL/MSCF

ALKANOL FUELS: WHY?

- VOLATILITY
- SOLUBILITY
- WATER SENSITIVITY
- HEAT OF COMBUSTION/OCTANE

METHYL FUEL VS. ALKANOL FUELS

	PURIFIED METHYL FUEL	SIMULATED ALKANOL FUELS	
		(A) IFP CATALYST	(B) UCI CATALYST
°API	47.2	46.7	46.5
HHV, BTU/GAL	64,386	87,367	73,672
IBP DISTILLATION, °F			
IBP	148	148	141
50% DISTILLED		173	153
99% DISTILLED		250	243
VOLUMETRIC AVERAGE BOILING PT, °F	148	184	159
RESEARCH BLENDING OCTANE NO. (BVON)	135.5	130.5	134.1

TYPICAL ALCOHOL COMPOSITIONS

(A) 20 WT % C_1; 40% C_2; 20% N-C_3; 20% N-C_4

(B) 70 WT % C_1; 10% C_2; 10% N-C_3; 10% N-C_4

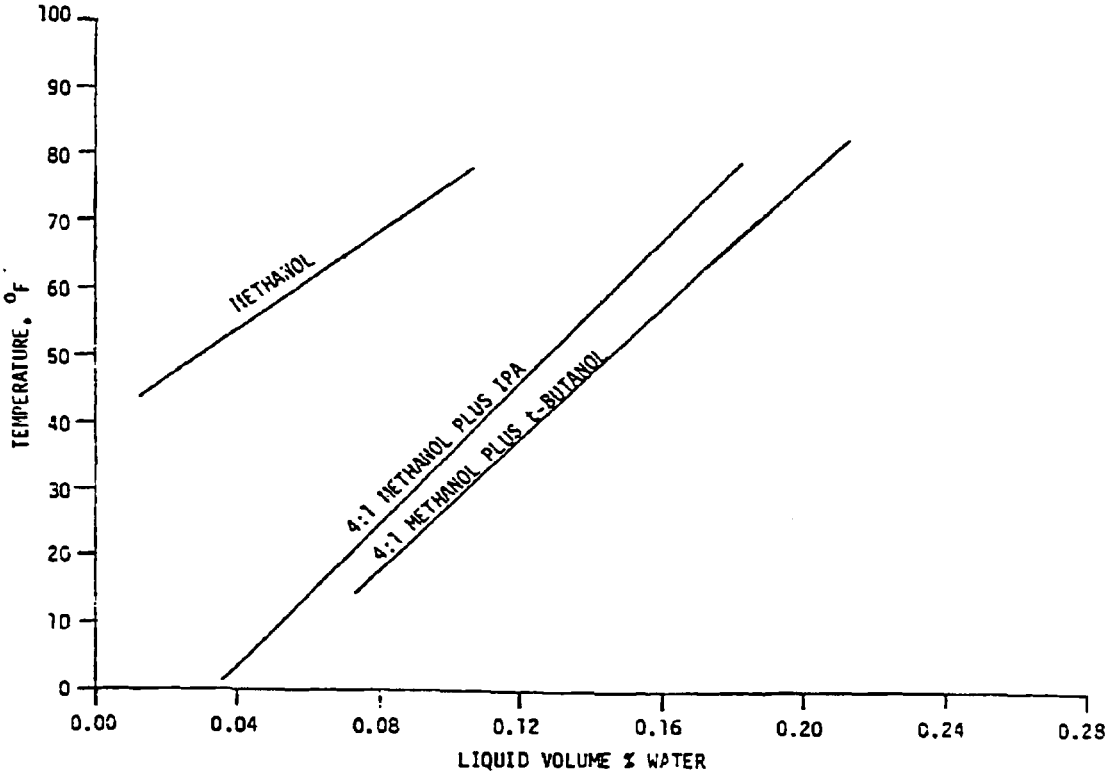
EFFECT OF ALKANOLS ADDITION ON METHANOL SOLUBILITY

	HYDROCARBON COMPOSITION		CLOUD PT FOR 10% ALCOHOL IN HYDROCARBONS, °F		
TEST #	% SATURATES*	% AROMATICS*	1% MeOH	80% MeOH, 20% TBA	80% MeOH, 20%IPA
1	100	0	+80	+68	+72
2	65	21	+44	+14	+4
3	43	2	+20	-38	-38
4	20	78	+4	-30	-42

*IN HYDROCARBONS, BALANCE BEING OLEFINS
SOURCE: CROWLEY, FEB 1975

EFFECT OF *ALKANOL* COMPONENT ADDITION TO 10% ALCOHOL-GASOLINE BLENDS ON WATER TOLERANCE

SOURCE: A. W. Crowley, 1975



CATALYST COMPOSITION CLASSIFICATION

GROUP I: CATALYSTS CONTAINING Cu, Zn, Co, Cr AND ALKALI

GROUP II: CATALYSTS OF GROUP I WITHOUT Zn, Co, OR Cr

GROUP III: MODIFIED METHANOL SYNTHESIS CATALYSTS OF Cu-Zn-Al FAMILY

GROUP IV: CATALYSTS OF GROUP I WHERE Cr IS SUBSTITUTED BY TRANSITION METAL(S) SUCH AS Fe, Mn, Ti, Th, ETC.

GROUP V: CATALYSTS OF GROUPS I, II OR IV SUPPORTED ON INERT OXIDES SUCH AS SiO_2, TiO_2 OR MnO

GROUP VI: COBALT CARBONYL AND POTASSIUM-IMPREGNATED METHANOL SYNTHESIS CATALYSTS

GROUP VII: TERNARY CATALYSTS CONTAINING Cu, Co, AND K

GROUP VIII: BINARY CATALYSTS CONTAINING Cu OR Co AND K

TARGETS FOR CANDIDATE CATALYST

1. >10% CO CONVERSION/PASS
2. 80-90% SELECTIVITY TO OXYGENATES
3. SPACE TIME YIELD GREATER THAN 3-5 MOL/HR/KGM

COMPARISON OF CATALYST PERFORMANCE

CATALYST DEVELOPER	IFP	UCI	CHEM SYSTEMS	
ATOMIC FORMULA	$Cu_xCo_yCr_zK_v$	L1132 PROPRIETARY	$CuZn_{.1}CoTh_{.5}Fe_{.1}K_{.1}$	$CoK_{.1}Ru_{.02}/\alpha\text{-}Al_2O_3$
% CO CONVERSION/PASS	12.5(A)	27(B)	13.1(C)	31.8(D)
SELECTIVITY, %(CO_2-FREE BASIS)				
CH_3OH	30.4	51.2	13.4	0.7
C_2-C_6 ALCOHOLS	67.0	17.7	35.4	33.6
HYDROCARBONS	2.6	31.1	51.2	65.7
ALCOHOLS SPACE TIME YIELD, MOL/HR/KG11	6.5	3.5	0.5	10.8

(A) 270°C, 60 ATM, 4000 VHSV, 1.9 H_2/CO
(B) 353°C, 100 ATM, 2100 VHSV, $2H_2/CO$
(C) 260°C, 60 ATM, 1000 VHSV, $2H_2/CO$
(D) 295°C, 60 ATM, 13000 VHSV, $2H_2/CO$

ANALYSIS OF LIQUID PRODUCT

BASIS: UCI CATALYST L-1123
353°C; 1500 PSIG; 2/1 H_2/CO; 2000-3000 VHSV
172 HOURS ON-STREAM

WT % DISTRIBUTION (H_2O-FREE BASIS)

MeOH	85.4
EtOH	3.0
n-PrOH	4.8
i-BuOH	3.0
C_4H_{10}	0.6
C_5H_{12}	0.7
C_6H_{14}	0.6
C_7H_{16}	0.1
C_8H_{18}	0.8
OTHERS (ALDEHYDES, ETC)	1.0

EFFECT OF MAXIMUM REDUCTION TEMPERATURE
AT 350 C, 1500 PSIG, 3000 VHSV, 2/1 H_2CO

BASIS: UCI CATALYST L-1123

MAX. REDUCTION TEMP., °C	240	350	450
% CO CONVERSION	23.5	13.7	14.3
SPACE TIME YIELD TO OXYGENATES, MOL/HR/KGM	9.1	3.4	3.1
% SELECTIVITY			
MeOH	67.6	53.0	64.0
C_2+ ALCOHOLS	10.3	11.2	7.6
C_4-C_9 HYDROCARBONS	4.4	5.3	3.5
C_1-C_3 HYDROCARBONS	6.7	15.9	13.7
CO_2	11.0	14.6	11.2
CALCULATED COMPOSITION OF ALKANOLS, WT%			
MeOH	82.0	76.1	84.9
C_2 + ALCOHOLS	12.6	16.3	10.4
C_4-C_9 H.C.	5.4	7.6	4.7

HIGHER ALCOHOL/HYDROCARBON BLENDS*

METHANOL	19.4 WT%	
ETHANOL	28.5	
N-PROPANOL	13.7	
N-BUTANOL	6.2	
N-PENTANOL	3.6	
		71.4
N-PENTANE	21.9	
N-HEXANE	3.3	
N-HEPTANE	1.9	
N-OCTANE	1.1	
N-NONANE	0.4	
		28.6
RESEARCH OCTANE	102	
MOTOR OCTANE	86.6	
ROAD OCTANE $\frac{R+M}{2}$	94.3	
CALCULATED $\frac{R+M}{2}$ USING BVON'S 77		

*PRODUCED WITH $CuZn_{.125}Co\ Fe_{0.1}Th_{0.5}K_{0.11}$ CATALYST

COMMERCIAL REACTOR DESIGN STUDY

DESIGN BASIS

2500 STPD ALKANOL FUEL (18,000 BPD)
250°C SYNTHESIS TEMPERATURE
4500 HR^{-1} SPACE VELOCITY
97% SELECTIVITY TO C_1 - C_6 ALCOHOLS
WATER-GAS SHIFT EQUILIBRIUM

REACTOR TYPE

1. LIQUID-FLUIDIZED BED
2. ADIABATIC FIXED-BED
3. MULTI-TUBE, JACKETED FIXED-BED

PARAMETERS STUDIED

	CASE I	CASE II
SYNTHESIS PRESSURE	60 ATM	120 ATM
H_2/CO RATIO	1.8	2.5
% CO CONVERSION/PASS	30.8	61.6

COMPARATIVE INCREMENTAL PROCESSING COSTS*

COST	1	2	3	4
REACTOR TYPE	LIQUID-FLUIDIZED	MULTI-TUBE	LIQUID-FLUIDIZED	MULTI-TUBE
PRESSURE, ATM	120	120	60	60
TOTAL CAPITAL COSTS, $MM	60.4	81.2	49.5	78.3
RELATIVE FEED GAS REQUIREMENTS	1.0	1.0	1.23	1.23
UTILITY REQUIREMENTS, M LB/HR STEAM	(365.7)	(385.0)	(499.1)	(522.0)
TOTAL INCREMENTAL COST, $/BBL ALKANOL	0.76	1.49	(0.69)	0.43

*EXCLUDING RAW MATERIAL COSTS (COAL, CATALYSTS, ETC.), PURGE GAS CREDITS.

FURTHER POTENTIAL ADVANTAGES OF LIQUID-ENTRAINED (SLURRY) REACTOR DESIGN

1. SMALLER REACTOR VOLUME DUE TO INCREASED CATALYST PRODUCTIVITY (MOL/HR ALKANOL/KGM CATALYST)

2. REDUCED TEMPERATURE RISE BY INCREASED INERT OIL CIRCULATION RESULTING IN RECOVERY OF MORE, HIGHER LEVEL REACTION HEAT

3. MINIMIZES CATALYST ATTRITION PROBLEMS