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Title: Slurry Phase Synthesis of Oxygenates with Nanometer Particle Catalysts

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Objective: The purpose of this initiative is to ultimately develop an economically viable route to isobutanol by catalytic conversion of synthesis gas derived from coal or natural gas.

Introduction

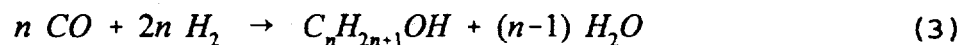Methyl t-butyl ether (MTBE), an oxygenated fuel-additive, is manufactured according to Reaction 1:

$$H_3C-OH + H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 \rightarrow (H_3C)_3C-O-CH_3 \tag{1}$$
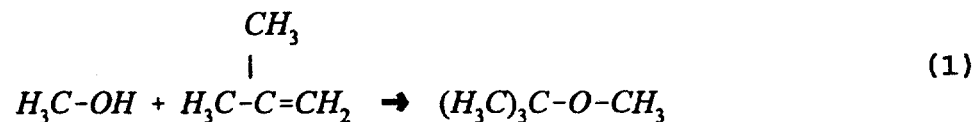
Due to increasing demand, MTBE at 10.9×10^9 Kg and methanol at 4.8×10^9 Kg ranked #9 and #21 in top 50 chemicals produced in the United States in 1993. A shortage of methanol will be met by six natural gas-based plants planned to be built in the next few years. But supply of isobutylene, normally recovered from refineries as a by-product, could become a problem if non-refinery sources are not found or developed. Catalytic transformation of coal or natural gas to isobutanol (dehydration of this molecule produces isobutylene) is a viable option. This approach involves two steps: 1) conversion of coal via gasification and natural gas via steam reforming or partial oxidation (POX) to synthesis gas, 2) catalytic transformation of generated syngas to desired products. The latter step is essentially hydrogenation of carbon monoxide (CO) and both oxygenates as well as hydrocarbons are potential products:

$$CO \xrightarrow[Catalyst]{H_2} Oxygenates \xrightarrow{(H_2?)} Hydrocarbons \tag{2}$$
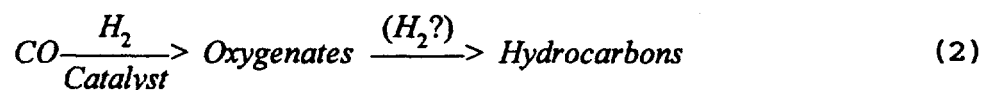
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Thermodynamically, hydrocarbon synthesis being more exothermic is favored but catalytical processes exist to intercept less exothermic oxygenates. Due to higher temperature operation in direct synthesis of higher oxygenates, any improved product selectivity is invariably attained at the expense of hydrocarbon formation. The subject of CO hydrogenation is recently reviewed (1).

For synthesis of higher alcohols, the following reaction stoichiometries are of interest:

$$n \; CO \; + \; 2n \; H_2 \; \rightarrow \; C_n H_{2n+1} OH \; + \; (n-1) \; H_2O \tag{3}$$

$$(2n-1) \; CO \; + \; (n+1) \; H_2 \; \rightarrow \; C_n H_{2n+1} OH \; + \; (n-1) \; CO_2 \tag{4}$$

Except for C_1(MeOH), all alcohols yield H_2O and/or CO_2 as byproducts. Synthesis of higher alcohols, directly from synthesis gas, is favored at higher temperatures but at the expense of selectivity. Approaches used in some of the DOE Indirect Liquefaction programs are covered(2). These and other known catalytic systems include Pd-Li/CeO_2 (3), Rh-Ti/SiO_2 (4), supported NiO (5), MoS_2-based (2), modified Cu (2), Fe-Cu Ruhrchemie catalysts (6), modified CO-Cu IFP (7), and variations thereof (1,2). Specifically, production of isobutylene directly from syngas and isobutanol dehydration to isobutylene have been evaluated (8). Higher alcohol synthesis is typically carried out by either modified Fischer-Trospch (F-T) synthesis or modified methanol synthesis catalysts. The most likely operating mechanisms are as follows:

- Linear alcohols are produced via classical CO insertion mechanisms to form carbon-carbon bond dictated by Anderson-Schulz-Flory (ASF) distribution followed by hydrogenation.

- Isoalcohols are produced via aldol condensation.

Irrespective of the catalyst employed, a highly selective synthesis of isobutanol still remains elusive. Our attempt to design a new catalyst system is based on the following strategy:

1. A successful development of LPMeOH process for synthesis of methanol from synthesis gas (9) demonstrates that slurry phase operation provides an excellent heat management option. A parallel can be drawn with liquid phase homogeneous catalysis where a uniform isothermal operation is routinely achieved.

2. To enhance catalyst lifetime and productivity, dispersed catalysts have been evaluated for direct coal liquefaction(8). A few reports have also appeared in the use of ultra-fine particle (UFP) catalysts for F-T synthesis (10). Our work (11) with a slurried Fe UFP catalyst suggested the following:

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- A commercial Fe UFP catalyst (α-Fe_2O_3 with mean particle diameter (MPD) = 3 nm, and surface area (SA) = 255 $m^2.g^{-1}$) obtained from Mach-1 Inc., was active at 220°C for F-T synthesis. But the reactor was devoid of CO_2 suggesting no water-gas-shift (WGS) activity.

- On volumetric basis, space-time-yield (STY) was higher with Mach-1 compared to that with standard UCI catalyst (MPD = 32.5 μm and SA = 232 $m^2.g^{-1}$).

- EXAFS and Mössbauer characterization of a quenched catalyst sample during the F-T run with Mach-1 at 200°C showed no carbide phase. The phase was found to be 100% magnetite (Fe_3O_4).

- Though oxygenates accounted for only up to 13 wt% of the aqueous phase, linear alcohols (C_1 - C_4) accounted for > 90% of the oxygenated fraction.

3.   The F-T reaction can be effected at a lower temperature with Co based catalyst ([8]). But due to its price, Fe remains the metal of choice. For higher alcohols synthesis, Fe has been evaluated. Razzaghi et al studied Fe/SiO_2 with promoters and obtained selectivity up to 22% to higher linear alcohols ([12]). This yield was too low to be of commercial interest. In another study with an iron catalyst, alcohols yield of 45% (primary aliphatic alcohols) at ~200°C is claimed. The hydrocarbons formed in this reaction were primarily olefins ([13]). Mechanistic studies on Co-Cu or MoS_2 indicate that higher alcohols are formed through the reaction of a C_n hydrocarbon entity with a C_1 oxygenated species (1). In another study synthesis of methanol and higher alcohols by Rh indicated that this system is selective for C_2 oxygenates. Arakawa et al have shown a relationship between turnover (TO) frequency of CO conversion and Rh dispersion with Rh/SiO_2 ([14]).

The aforementioned discussion relevant to slurry phase operation, particle size dependence, C-C bond formation led us to tailor a UFP system capable of enhanced oxygenates synthesis. Our approach to isobutanol synthesis involves the following:

- Initially, Fe UFP (MPD <100 nm) catalyst precursor is to be utilized. Co UFP will follow.
- Slurry phase operation is preferred for heat management and to enhance catalyst/solvent interaction.
- A typical high molecular weight hydrocarbon solvent mixed with a high boiling oxygenated solvent is used as a reaction medium. Ultimately, hydrocarbon solvent will be eliminated. Solvent is to act as an agglomeration inhibitor.
- Slurry-phase operation limits operating temperature to T<280°C. The upper temperature limit drops even further with oxygenated solvent.
- To take advantage of the CO_2 oxidizing atmosphere, runs are to be conducted in the absence of water-gas-shift (WGS) activity. The presence of CO_2 is to be utilized to control Fe oxidation state.
- Base addition is designed to 1) promote C-C coupling to enhance C_4 yield, 2) acts as an agglomeration inhibitor.

- Cocatalysts may be added to promote isomerization and dehydration to produce isobutylene from synthesis gas in one-step.

For this work, the following systems will serve as a guide. It is to be noted that these systems operate in packed-bed reactors.

1. The most studied system is an alkali metal-modified traditional methanol synthesis catalyst. A variation of this catalyst is being evaluated by APCI (8). At P<12Ma, t<310°C with syngas (H_2/CO = 1/4-4/1), maximum rate is 37 and 7 g Kg.h for iBuOH and t-BuOH respectively. It is suggested that favorable conditions for isobutanol synthesis are 1) low H_2/CO ratio, 2) low CO_2, 3) high T.

2. A multimetal Pd-based catalyst developed in Keim's laboratory at the Technical University of Aachen claims 59 wt% isobutanol selectivity and productivity of 1500 g/Kg h at <450°C and P~10 MPa.

Initially, our emphasis is on maximizing C_1 - C_4 alcohols with an iron catalyst.

Experimental

Two commercially available nanometer size unsupported Fe_2O_3 catalyst precursors were obtained as samples in 1 lb each quantity from the vendors: 1) Mach-1 (MPD=3nm; SA=255 $m^2.g^{-1}$; and 2) BASF (MPD = 20 - 80 nm; SA = 16-20 m^2 .g^{-1} ; density (d) = 0.05 $g.mL^{-1}$; d = 5.25 $g.mL^{-1}$) from BASF. Since Co-based nanometer size catalyst precursors are not readily available, these materials will be generated at BNL via sonolysis of cobalt complexes. The sonication technique will be described in a future publication. Ethylflo-164, a C_{22} hydrocarbon solvent, was obtained from Ethyl Corporation. All chemicals were purchased from Aldrich and premixed syngas of varied composition was purchased from Scott Specialty Gases. All gaseous and liquid reactants and products were analyzed on a PE8500 gas chromatograph in FID and TCD modes. A full mass balance was carried-out on each run. The Fe_2O_3 samples were stored in a glove box to avoid water contamination prior to reduction.

For catalyst screening, a 0.5L AE Zipperclave batch CSTR was modified (Figure 1). The unit is rated at 13 MPa @230°C. For catalyst evaluation, the BNL bench-scale continuous unit fitted with a 1L AE CSTR was modified for oxygenates synthesis (Figure 2). The unit is rated at 40 MPa @340°C.

Results and Discussion

The utilization of both Mach-1 and BASF catalysts in F-T synthesis has been described previously (8, 15). Of interest is the aqueous phase composition of these runs to determine concentration of oxygenates. The total C_1-C_4 values were 5.8, 8.4, 6.0, 13.4, 1.9 wt% respectively for Runs 1-5 as shown in Table 1. These values accounted for >90 wt% of all oxygenates in the aqueous phase. Though the absolute C_1-C_4 values are even smaller with

maximum alcohols produced at 4 wt% with MACH-1, the value was even smaller (0.6 wt%) with BASF. Since our measurements show that MACH-1 is predominately in the Fe_3O_4 phase and preliminary EXAFS and Mössbauer data show quenched BASF catalyst in several mixed phases, our approach to modify Fe oxidation state to maximize alcohols production becomes relevant. To further this concept, catalyst screening was carried-out in the batch reactor. Four runs were completed to establish boundary conditions.

Run OXY #0-Blank: A 10% triglyme/90% Ethylflo-164 solvent mixture (125 mL) was loaded. The reactor was heated under syngas (66% H_2/34% CO) for 2 hours. The reactor was cooled and 124 mL liquid was collected. Mass balance error was set at <∓1%.

Run OXY #1: The desired reaction is intended to be carried-out at a lower temperature. The formation of $Fe(CO)_5$ and thus loss of Fe at lower temperatures (<200°C) is of concern. To address this issue, 5 mmol $KHCO_3$ base and 125 mL 90% Ethylflo-164/10% Triglyme solvent mixture were loaded into the batch reactor. After adding 10 mmol $Fe(CO)_5$ (Fe base = 2/1), the reactor was pressurized with 300 psig syngas (H_2/CO = 66%/34%). In one hour at 170°C and 341 psig, gas analysis showed 5.7 vol % CO_2 (15 mmol). The expected CO_2 from $KHCO_3$ decomposition was 5 mmol. An extra 10 mmol CO_2 needs to be accounted for. The final black slurry (0.7 wt% Fe + base) suggested $Fe(CO)_5$ decomposition at 170°C. Syngas consumed was small at <10 mmol. No further analysis was carried-out. (Table 2).

Run OXY #2: In this run, $Fe(CO)_5$ was replaced with 1g Fe BASF (α-Fe_2O_3) catalyst precursor and slurried with base in the solvent mixture as described in Run OXY #1 (Fe base ~ 1.2). Under 329 psig syngas at 170°C, CO_2 increased to 1.5 vol % in 0.7 hour and the final value in 1.6 hours was 1.7 vol % (4.3 mmol). The measured CO_2 suggested complete $KHCO_3$ decomposition (theoretically maximum CO_2 = 5 mmol). Only ~ 10 mmol syngas was consumed. The initial orange fine powder (α-Fe_2O_3) became slightly darker suggesting incomplete reduction of α-Fe_2O_3 at 170°C (Table 3).

Run OXY#3: A negligible amount of syngas (66% H_2/34% CO) was consumed when 1.0 g α-Fe_2O_3 BASF catalyst and 10 mmol KOMe were slurried in 90% Ethylflo-164/10% Triglyme solvent and heated at 170°C for 1.7 h. Only ~1 mmol CO_2 was measured and the final slurry was dark red suggesting incomplete reduction of the BASF catalyst even with a strong base (Table 4).

The data from Runs OXY#2 and #3 show that base reduction of α-Fe_2O_3 at 170°C is not appropriate to yield reduced Fe catalyst. But this method works well when starting with $Fe(CO)_5$ to generate $Fe^{(0)}$.

Run OXY#4. The strategy is to modify Fe catalyst in a CO_2-rich atmosphere to enhance yield of C_1-C_4 alcohols. To establish a baseline, this run was done in the continuous unit. The run procedure was as follows:

- Reduced catalyst for 24 hours at 280°C under CO.
- Set T = 240°C.

- Added balanced syngas to establish baseline hydrocarbons synthesis.
- Replaced syngas with CO_2-rich syngas.

The BASF catalyst precursor was reduced by slurrying 5 wt% catalyst material in Ethyleflo-164 and heating under 100 psig CO (0.2L/min) to 280°C. The temperature was held at 280°C for 24 hours. At this time, with pressure at 100 psig, the temperature was decreased to 220°C, flow rate was adjusted to 0.7 L/min and syngas (H_2/CO = 66%/34%) was introduced. No conversion was observed in the first 1.5 h. On raising the temperature to 240°C, gas conversion was 8% (at 0.5 L/min flow rate) for 17 h. At 19 h total time, balanced syngas was replaced with CO_2-rich syngas (64%H_2/25%CO)/11%CO_2). Gas conversion initially increased to 16% but then quickly decreased to <5%. The data in Table 5 indicates: 1) The observed 8% conversion at 240°C was far below the previously collected reference F-T data. In the reference run, BASF catalyst (~5 wt%) was reduced under CO at 280°C and its F-T activity was evaluated at 240°C, 100 psig, 0.88 L./min (4.6 $NL.gFe^{-1}.h^{-1}$). Gas conversion peaked at 44% in 24 hours and then slowly decreased to 38% at 144 h. For comparison, the reference F-T run yielded 44% conversion at 19 h whereas gas conversion was 8% in the present run, 2) At 8% conversion, addition of CO_2-rich syngas caused conversion to surge to 16% but value quickly decreased to <5% after 4 h, 3) The aqueous phase contained 7 vol % C_1-C_4 n-alcohols. These alcohols constitute >90 % of all oxygenates produced, 4) Considering that the desired condition likely to enhance oxygenates with CO_2-rich gas is the absence of water-gas-shift (WGS) activity, this condition was not attained in Run OXY#4.

The above observations still failed to explain irreproducibility of gas conversion values. An examination of catalyst reduction procedure revealed that in Run OXY #4, the reactor was pressurized with CO during warm-up (to 280°C) whereas in the reference run (high conversion), N_2 was utilized during reactor warm-up. Instead of further investigating this effect, the original procedure was adopted during subsequent runs. No elaborate higher hydrocarbon analysis was conducted on liquids from Run #4.

Run OXY#5. In this run, BASF catalyst was reduced according to the procedure described for OXY#4 except that during reactor warm up, N_2 was used. At 280°C, N_2 was replaced with CO. The CO_2 value dropped from 10.5 vol % at 0.7 h to 1.2 vol % in 20 h at which time the catalyst was assumed to be >90% reduced.

Since the ultimate goal is to drive the reaction at the lowest possible temperature, the data were collected at 240, 220, 200°C. Initially, the temperature was reduced to 240°C, CO was replaced with balanced syngas (H_2/CO = 66%/34%) and flow rate was adjusted to 0.6 L/min to establish a baseline. At 1 h, gas conversion was 4% that steadily increased to 14% in 4 h at which time flow was decreased to 0.4 L/min. Gas conversion increased to 45% in 29 h. At 29.2 h, CO_2-rich gas was introduced. The conversion was 40% at 47 h (a steady-decrease in 18 h) and CO_2 in the exit gas increased from 12% at 29 h (with 66% H_2/34% CO syngas) to 22.2% at 47 h (with 64% H_2/25% CO/11% CO_2). The temperature was further reduced to 220°C at 48 h. Gas conversion remained stable at ~28% (28-30.5%) in the 26 h run time at 220°C. The only parameter varied during this period was stirring speed (500 rpm

between 52 to 70 h). At 70 h, the reactor was pressurized to 510 psig and operated in batch mode. The pressure decreased from 510 to 318 psig in 0.6 h. The reactor was left in batch mode for 73 h with pressure dropping to 185 psig. On repressurization to 510 psig, the pressure dropped to 325 psig in 18.5 h. The temperature was further decreased to 200°C and in continuous-mode operation at 100 psig, 8% conversion was recorded at 170 h (including 91.5 h batch-mode operation). The reactor was cooled to room temperature after 170 h. The data are shown in Table 6.

The data in Table 6 indicate that CO conversion was 40%, ~30%, and 8% respectively at 240, 220, and 200°C with the BASF catalyst. At these temperatures, CH_4 values were: 2.6%. 0.6%, 0.03%. CO_2 was 12% (240°C at 29 h) with 0%CO_2 incoming syngas), 22.2% (240°C at 47 h) with 11% CO_2 containing syngas (assuming 11.2% was a contribution from WGS reaction), 13.7% (220°C at 70 h) with only 2.7% from WGS activity). Since the last value of 21.2% at 170 h was taken after only 3.5 h at 200°C after the run was in batch-mode from 91.5 h this value may be high. The net 2.7% CO_2 value at 70 h shows some WGS activity at 220°C and the true intended conditions were not attained.

The collected hydrocarbons and aqueous phases were 23 mL and 72 mL respectively. Since the aim of this project is to enhance oxygenates production, the aqueous phase was analyzed to yield the following: MeOH (0.5 mL), EtOH (3.4 mL), PrOH (0.9 mL) and BuOH (0.3 mL) with C_1-C_4 alcohols at 5.9 vol % accounting for >90% of all oxygenates produced. The overall selectivity to alcohols was 18 vol % corresponding to the alcohols/hydrocarbon ratio of about 1/6. This value is higher than that reported earlier from our laboratory with balanced syngas. Considering that the ultimate catalyst system is yet to be formulated, our approach to synthesize alcohols with Fe-based catalyst appears promising.

Accomplishments and Conclusions

From the runs completed so far the following conclusions are noteworthy:

- Since thermodynamic equilibrium conditions are normally not attained during planned runs, a 0.5L AE batch CSTR (T < 230°C; P < 13 MPa) was selected for catalyst screening. This has now been replaced with a 0.3L Parr batch CSTR (T<350°C P < 13 MPa). This method is quick, inexpensive and very efficient. The selected catalyst can be then fully evaluated in the continuous unit.

- Two commercially available nanometer scale catalysts were selected (Mach-1 and BASF). All Co-based catalysts will be generated via sonolysis.

- To set boundary limits several batch runs were conducted:

  - The formation of $Fe(CO)_5$ and thus loss of Fe is of concern at intended lower temperatures of operation. The data from Run OXY#1 suggest that $Fe(CO)_5$ fully decomposed even under syngas (66% H_2/34% CO) at 170°C to form a dispersed black slurry.

- A slurried BASF α-Fe_2O_3 did not fully reduce with $KHCO_3$ at 170 °C. Even with a stronger base KOMe, the reduction was incomplete. A slow syngas consumption was noted in both cases.

- A baseline run (Run OXY#4) conducted with reduced BASF catalyst in continuous mode showed somewhat enhanced gas consumption with CO_2-rich syngas. The problem with attaining baseline catalytic activity (gas conversion: 44% for reference versus 8% attained in this run) made added CO_2 effect unclear (Run OXY#4).

- The data from Run OXY#5 indicate that the catalyst reduction procedure is critical to achieving baseline activity. The adopted procedure involves slurrying BASF material in Ethylfo-164 solvent, heating to 280°C for 24 h before starting the actual run. Just by substituting CO with N_2 during warm-up, conversion dropped from 45% to 8% at 240°C (Runs OXY #4 and #5).

- With syngas containing 11%CO_2, conversion was 40% in 18 h at 240°C. A 5% drop (from 45 to 40%) during this period was not conclusively attributed to added CO_2.

- The measured CO_2 was 13.7% at 220°C. Considering syngas at the inlet contained 11% CO_2, a net 2.7 % is attributed to WGS reaction. Obviously, a desired condition of no WGS activity was close but not met.

- The oxygenates constituted 5.9 vol % of the aqueous phase. The selectivity to C_1-C_4 alcohols was 18 vol %. This is promising considering that all the intended modifications to the Fe catalyst system have not been implemented.

Future Direction

The selected approach utilizes 1) nanometer particles of Fe or Co in a slurry-phase, 2) CO_2-rich syngas, 3) added compatible base to enhance yield of oxygenates and effect the reaction at a lower temperature of T < 240°C.

The selected Fe catalyst is unusual in that it is unsupported. Considering that Fe_3O_4 is anticipated to be the predominant phase, the addition of an oxygenated solvent becomes important to avoid agglomeration. If this system is successful, these and other features of the working system may find application in Fischer-Tropsch catalysis. As for enhancing alcohols yield. several baseline runs are now underway to establish the fate of added C_1-C_4 alcohols under reaction conditions to eliminate the possibility of secondary reactions. The target is to first match and then exceed the reported 45 wt% C_1-C_4 alcohols yield with a base modified Fe catalyst. This will be the subject of a forthcoming publication. These planned runs are intended to achieve our goal of enhancing C_1-C_4 alcohols yield with an Fe catalyst. This will be followed by enhancement of C-C bond formation to increase yield of C_4 alcohols.

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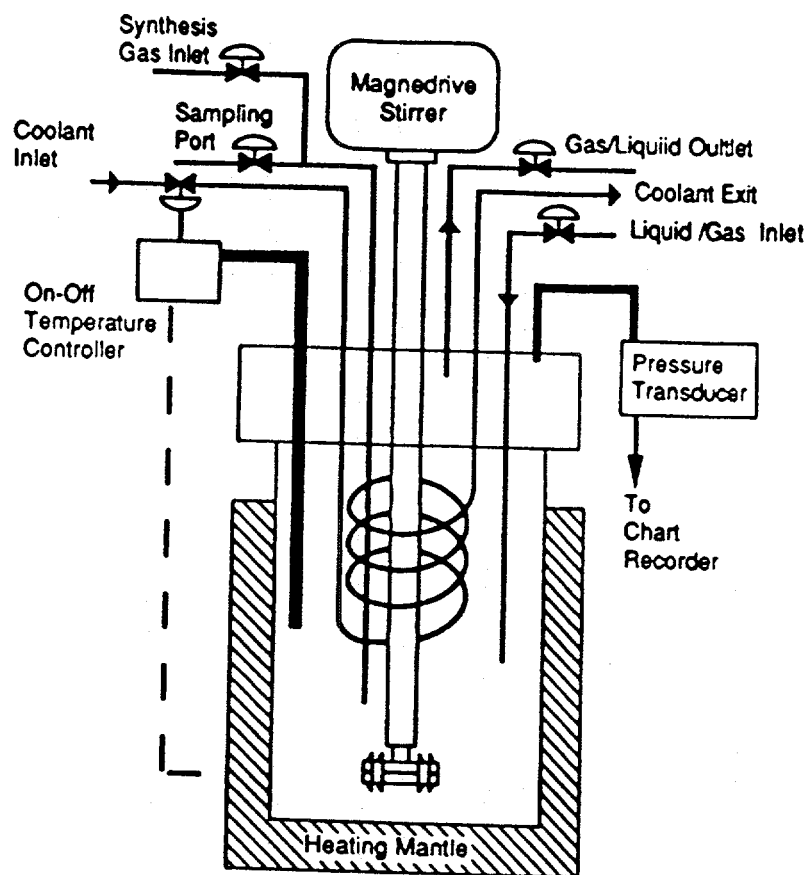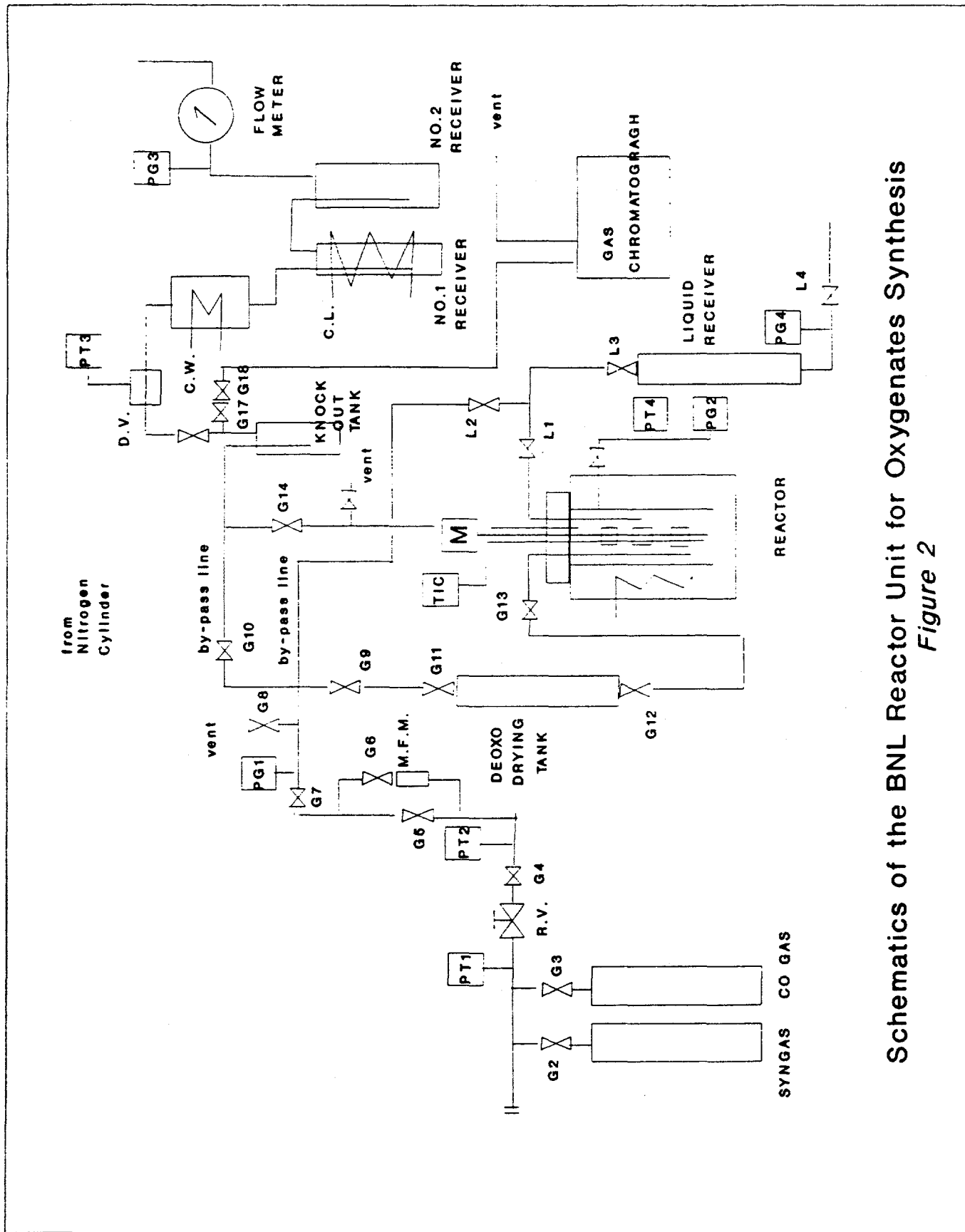
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Figure   1.   AE Zipperclave Reactor used in Batch Studies

Schematics of the BNL Reactor Unit for Oxygenates Synthesis
Figure 2

Table 1
Alcohols Composition in Aqueous Phase[a]

Run	Catalyst	T,°C	% Aqueous Phase	ROH, wt%			
				C_1	C_2	C_3	C_4
1	Mach-1	220	56	0.9	2.0	2.3	0.6
2	Mach-1	240	47	1.9	3.8	1.9	0.8
3	Mach-1	260	36	1.1	2.4	2.0	0.5
4[b]	Mach-1	220/260	32	3.2	4.8	3.8	1.6
5	BASF	240	29	0.3	1.1	0.3	0.2

[a] Data from reference F-T runs.
[b] Syngas: $H_2/CO = 1/1$, in this run. In all other runs, 2/1 gas was used.

Table 2
Run OXY #1 in Batch Mode

Run Conditions

Catalyst precursor: $Fe(CO)_5$ = 10 mmol
Solvent: 90% Ethylflo-164/10% Triglyme = 125 mL
Base: $KHCO_3$ = 5 mmol
Syngas: 66% H_2/34% CO
T: 170°C
P: 341 psig @ T
On-line time: 1.0 h

Data

Initial Solution = yellow homogeneous
Final Solution = Black slurry
CO_2 = 15 mmol
Syngas Consumed = 10 mmol

Table 3
Run OXY #2 in Batch Mode

Run Conditions

Catalyst precusor: BASF (α-Fe$_2$O$_3$) = 1.0 g
Solvent: 90% Ethylflo-164/10% Triglyme = 125 mL
Base: KHCO$_3$ = 5 mmol
Syngas: 66% H$_2$/34% CO
T: 170°C
P: 341 psig @ T
On-line time: 1.6 h

Data

Slurry: Initial = Reddish
               Final = Dark red

CO$_2$ = 5 mmol
Syngas consumed $\approx$ 10 mmol

Table 4
Run OXY #3 in Batch Mode

Run Conditions

Catalyst precursor: BASF (α-Fe$_2$O$_3$) = 1.0 g
Solvent: 90% Ethylflo-164/10% Triglyme = 125 mL
Base: KOMe = 10 mmol
Syngas: 66% H$_2$/34% CO
T: 170°C
P: 303 psig @ T
On-line time: 1.7 h

Data

Initial/Final solution: Dark red slurry
CO$_2$ $\approx$ 1 mmol
Syngas consumed: negligible

Table 5
Data Summary of Run OXY#4

Run Conditions and Data

    Catalyst: Reduced BASF Fe
    Stirring Speed = 250 rpm

Time h	T °C	P psig	Flow Rate L/min	Initial Syngas			Final Gas				Gas Conv. %
				$\%H_2$	$\%CO$	$\%CO_2$	$\%H_2$	$\%CO$	$\%CO_2$	$\%CH_4$	
1.5	220	100	0.7	66	34	0	64.6	36.4	0.4	0.04	0
19	240		0.5				62.2	31.9	1.3	0.4	8
23				64	25	11	64	22.5	10.2	0.5	16
24		300	0.4				62.3	21.7	12.3	0.5	20
41							63.5	20.5	13.9	0.4	<5

Mass Balance

    Initial Slurry Weight = 310g
    Final Slurry Collected - 307g
    Liquid Collected in Tank #1 = 39g = 42 mL
    Hydrocarbons = 6.5 mL
    Aqueous = 35.5 mL

Aqueous Analysis (35.5 mL)

    MeOH = 1%
    EtOH = 4%
    n-ProH = 1.2%
    n-BuOH = 1%

Table 6
Data Summary of Run OXY#5

<u>Run Conditions</u>

    Catalyst: Reduced BASF
    Stirring Speed: 250 rpm

Time h	T °C	P psig	Flow Rate L/min	Initial Syngas			Final Gas				Gas Conv. %
				$\%H_2$	%CO	$\%CO_2$	$\%H_2$	%CO	$\%CO_2$	$\%CH_4$	
1	240	100	0.6	66	34	0					4
4			0.4				62.7	28.8	1	0.7	14
21							65.2	17.7	11.7	2.7	39
21.5											42
29							64.6	16.5	12.0	2.6	45
29.2				64	25	11					
47							62.1	10.6	22.2	2.1	40
48.5	220										
52[a]											28
70[a]							63.5	17.6	13.7	0.6	29
75[a]		500									31
166.5[b]	200	100									
170							56.8	22.8	21.2	0.03	8

[a]Stirring speed was 500 rpm
[b]Reactor in batch mode for 68 h under 500 psi which dropped to 185 psig. See text.