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**LOW TEMPERATURE LIQUID PHASE CATALYTIC SYNTHESIS OF
METHANOL FROM SYNTHESIS GAS**

BNL/AMOCO CRADA #BNL-C-94-01

**Final Report
May 20, 1994 - May 20, 1995**

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September 1995

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ABSTRACT

Innovative routes to liquid fuels are sought to economically transport large reserves of remote and associated gas. A liquid phase low temperature catalyst, developed at Brookhaven National Laboratory (BNL), has been shown to selectively convert natural gas-derived synthesis gas to methanol in unprecedented conversion ($>90\%$) per pass under thermodynamically favorable conditions. To further this unique approach, in May 1994 a one-year Cooperative Research and Development Agreement (CRADA) was signed with Amoco Corporation. Funding for this effort was provided by the Energy Research Laboratory Technology Transfer (ER-LTT) program and Amoco. A preliminary process flow sheet, prepared by Amoco, was utilized to target areas for further investigation. In the just completed work, the impact of typical syngas impurities on catalyst performance was addressed. By manipulating reaction temperature, solvent and metal cocatalyst addition, activation of carbon dioxide was studied. An infrared study to establish catalyst-carbon dioxide interaction was also initiated. Follow-up includes ongoing work on carbon dioxide, effect of other impurities, catalyst life assessment in a mini pilot unit provided by Amoco. The aim is to develop a second-generation low temperature catalyst that will allow development of an atom economical methanol synthesis process for low cost production of methanol.

EXECUTIVE SUMMARY

In May 1994, a one-year Cooperative Research and Development Agreement (CRADA) was signed with Amoco Corporation to further develop the Brookhaven National Laboratory (BNL) Liquid Phase Low Temperature Catalytic Methanol Synthesis Technology. Funding for this CRADA was provided by the Energy Research Laboratory Technology Transfer (ER-LTT) program and Amoco Corporation. A preliminary process economics report on the BNL technology prepared by Amoco provided input in areas of concern to Amoco. This one-year CRADA effort was aimed at reviewing process uncertainties identified by Amoco and initiating a strategy to address these tasks. A follow-up three-year effort was proposed to fully execute the BNL strategy. The follow-up CRADA was awarded and the work began in March 1995. The aim is to clearly demonstrate all the novel features of the BNL technology necessary to realize its commercial potential.

The heart of the BNL Methanol Synthesis Technology is a homogeneous liquid phase catalyst that comprises of a nickel complex and an alkoxide base (typically potassium methoxide) dissolved in methanol (solvent) and glyme (cosolvent) mixture. When balanced synthesis gas ($H_2/CO=2/1$) under pressure $> 1\text{MPa}$ is heated at temperatures between $50\text{-}150^\circ\text{C}$, methanol is synthesized efficiently and selectively. Given below are unique features of this technology:

- A low temperature operation ($T < 150^\circ\text{C}$) thermodynamically allows very high syngas conversion per pass ($> 90\%$) thus eliminating the need for gas recycle.
- A liquid medium allows theoretically maximum gas conversion to be achieved at a given temperature due to uniform heat dissipation.
- A low pressure operation and catalyst inertness to N_2 allows air (instead of O_2) partial oxidation of natural gas.
- The main solvent for the process is the product (MeOH) itself. Glymes/glycols are utilized as cosolvents.
- The homogeneous catalyst formulations renders itself more amenable to mechanistic study for process optimization.

When these features were taken into consideration, a process flow-sheet emerged that indicated substantial cost reduction in methanol production. But to realize full potential of the BNL technology, process uncertainties needed to be addressed were:

- Effect of CO_2 .
- Effect of H_2O .
- Control of $Ni(CO)_4$.
- Catalyst life.

This report summarizes work carried-out during the one-year CRADA (May 20, 1994 - May 20, 1995) and is formatted to satisfy U.S. Department of Energy (DOE) CRADA report requirements.

Significant Accomplishments

The overall strategy is to develop a second generation BNL Methanol Synthesis Catalyst system that can accommodate requirements set-forth above. The initial challenge to execute the conceived work plan was to coordinate tasks for maximum efficiency. During the subject one-year CRADA, notable achievements include:

- Work to assess the effect of CO₂ on catalyst performance was carried-out by studying solution decomposition of potassium methyl carbonate (PMC), the product of potassium methoxide and CO₂ reaction. PMC decomposition was favored by 1) increasing temperature to 140°C, 2) adding Fe(CO)₅ that resulted in 150% increase in rate. Interestingly, CO₂ evolved from solutions containing KOMe/Fe(CO)₅ suggested a non-PMC source of CO₂. Factors affecting this reaction were: 1) presence of CO was necessary, 2) addition of metal carbonyl was necessary, 3) Ru₃(CO)₁₂ was a better catalyst than Fe(CO)₅. These results show that complete PMC decomposition pathway will allow CO₂ to go through the system without adversely affecting the methanol synthesis reaction. Work is underway to establish the non-PMC CO₂ origin.
- Solubility of KOMe in several potential solvents was established. The solubility order was: MeOH > Peg-400 > THF > PolyTHF.
- A colorimetry procedure to quantify Ni was developed.
- An infrared (IR) procedure was developed to establish the fate of Ni(CO)₄ in a dynamic system.
- Ni(CO)₄/CO₂ interaction study was carried-out by subjecting Ni(CO)₄ in triglyme/MeOH solvent under 300 psig syngas (64% H₂/33% CO) containing 3% CO₂. Ni(CO)₄ remained intact after 1) 18 h at R.T., 2) heating at 150°C for 1 hr. This suggested no noticeable detrimental effect of CO₂ on Ni.
- To develop an integrated approach, a literature study yielded two water-soluble ligands of interest. The aim is to develop:
  - A water containing biphasic system.
  - Control of Ni(CO)₄ via ligation.

This task required solubility/miscibility data. It appears that KOH, MeOH, triglyme, 2,2' bipyridyl (bpy) formed a homogeneous solution. An addition of Fe(CO)₅ generated a biphasic system.

- The tedious task of transferring the Amoco AU-96E unit to BNL has been initiated.
- A preliminary BNL process economics report, prepared by Amoco, was received and reviewed.
- A regular exchange of information between BNL and Amoco is critical to the success of this undertaking. To this effect, 1) two review meetings on June 13,

1994 and February 9, 1995 took place at the Amoco facility in Naperville, 2) two interim reports in October 1994 and February 1995 were prepared by the BNL PI and sent to Amoco, 3) per DOE CRADA requirements, two quarterly progress reports were submitted to the BNL Office of Technology Transfer (OTT). All tasks described herein formed the basis for now ongoing three-year CRADA.

Significant Problems

Work is continuing as planned. No unusual problems were encountered.

Industry Benefits Realized

Amoco and its subsidiaries own vast reserves of natural gas in North America and South America. An economical process that allows transport of remote and/or associated gas as a liquid fuel is of obvious interest. Envisioned is a small flexible skid-mounted methanol synthesis unit based on the BNL Methanol Synthesis technology. Development of such a process will find a niche in profitable natural gas market. The economics and engineering input from Amoco reflects their continued involvement that is dictated by world market forces.

Laboratory Benefits Realized

AUI owns title to the subject BNL Methanol Synthesis technology that is covered under U.S. patents and in selective countries. The industrial partner and Electric Power Research Institute (EPRI) is paying annual maintenance fees to keep the patent coverage in force. A successful completion of this ongoing CRADA will benefit BNL multifold: 1) the BNL developed technology will enter the market place, 2) financial reward from royalties to BNL, 3) interaction with industry, 4) ongoing work in the CRADA that may lead to other application of the BNL low temperature concept.

Recommended Follow-up Work

A four-year effort was envisioned when the original work plan, based on the preliminary process flow-sheet economics, was conceived. Before termination of the subject one-year CRADA, the follow-up three-year CRADA went into effect in March 1995. Work is already underway to 1) complete the CO₂ aspect, 2) develop a biphasic system with one phase being aqueous 3) Ni(CO)₄ control through ligation, 4) confirm batch results in the Amoco AU-96E continuous unit. To conduct Task 4), transfer of the Amoco unit to BNL is already nearing completion.

Potential Benefits From Pursuing Follow-up Work

To develop a novel technology of commercial potential, the aforementioned integrated approach is being pursued. A successful execution of the follow-up CRADA will be financially rewarding for Amoco. For BNL, an undertaking of transition from basic research concepts to process development is a challenge.

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A PERSPECTIVE

Since the start of this CRADA last year, the following highlighted relevant information has appeared:

- Between 1992-94, methanol production in the U.S. increased by over 33 % to about 4900×10^6 kg (C&E News, June 1995).
- A continuing demand for methyl t-butyl ether (MTBE), an oxygenated gasoline additive, pushed spot methanol price to \$1.30/gallon in 1994 from a typical \$0.50/gallon range in 1993 (C&E News, October 1994). Methanol is one of the reactants needed to synthesize MTBE.
- Anticipating higher world demand for methanol, Saudi Methanol Co. is building a world-scale plant with a capacity of 0.85×10^9 kg per year. Located on the Persian Gulf coast, the plant is scheduled to be on-line in 1997 (C&E News, April 1995).
- TeraMeth Industries has built the first plant in West Covina, California to produce methanol from landfill gas that is currently flared. At \$4.9 million, the small scale (30 tons/d) plant cost twice that of a typical large scale unit with conventional methanol synthesis technology (Chem. Eng., July 1993).
- Using ICI Katalco's Leading Concept Methanol (LCM) technology, plans are to be build a floating methanol plant to utilize off shore natural gas. The LCM concept involves a higher efficiency natural gas reforming technology but utilizes conventional methanol synthesis technology downstream. The savings are anticipated by sharing natural gas production utilities with the downstream requirements (Chem. Eng., March 1995).
- The U.S. Department of Energy (DOE) will cost share (\$90 million) demonstration of Air Products and Chemicals, Inc. (APCI) liquid-phase methanol (LPMeOH) technology in a 260 tons/day plant at an Eastman Chemical Co. site in Kingsport, Tennessee. This slurry phase methanol process achieves somewhat higher conversion per pass via better heat dissipation, an advantage over conventional packed bed process (Chem. Eng., July 1995).
- Amoco and Hador Topsoe demonstrate dimethyl ether (DME) (dehydration of two molecules of methanol produces DME) as a cleaner diesel fuel (C&E News, May 1995).
- Development of South American natural gas is on a fast track. The economic impact of this initiative is dependent on economical transport of this gas with one of the promising route being via methanol (C&E News, June 1995).

- After 10-year successful operation of the Ruhrchemie/Rhône-Poulenc's environmentally-sound oxo process, homogeneous catalysis in aqueous medium is an area of immense interest (CHEMTECH, January 1995).
- Development of "Atom Economical" reactions is the theme to reduce or eliminate process waste (Angew. Chem. Int. Ed. Engl. 34 259 (1995)).
- Development of "Smart" catalysts that self-assemble and self-repair is underway to eliminate catalyst attrition (Nature 373 324 (1995)).

The foregoing highlights indicate continuing interest in an economical methanol synthesis technology to utilize landfill gas, natural gas especially at remote sites and off-shore gas fields. Also desirable are atom economical reactions and catalysts that can self-repair to reduce process waste and inclusion of aqueous media to eliminate organic solvents. The BNL Methanol Synthesis process essentially incorporates all these features. The development of an optimized sustainable catalyst system forms the basis of this BNL/Amoco CRADA.

BACKGROUND

The utilization of methanol, a key ingredient in production of formaldehyde, acetic acid, chloroalkanes, methyl methacrylate, dimethyl terephthalate, glycol methyl esters, etc., is forecast to increase ~30% by 1997 (1). This projected global production of methanol from 45.6 in 1993 to 58.2 billion pounds in 1997 is the result of the Environmental Protection Agency's (EPA) wintertime oxygenated fuel requirement as specified in the 1990 Amendment to the Clean Air Act. The fuel-additive of choice is methyl t-butyl ether (MTBE) which requires equimolar ratio of methanol and isobutylene for synthesis. In the United States, production of MTBE increased 121% from 10.9 in 1992 to 24.1 billion pounds in 1993 and is projected to increase to 67 billion pounds by year 2000. In 1993, 27% of methanol produced was used for MTBE production. Obviously, chemical companies are scrambling to open or convert existing methanol/ammonia plants to make a hefty profit as spot price for methanol increased from \$.50 per gallon in 1993 to \$1.30 per gallon in October 1994. This upward pressure on methanol price will result in the addition of up to six new world scale plants by 1997.

The described economic picture is obviously of interest to justify methanol as an environmentally-acceptable fuel that will make inroads on the fuel scene in the twenty-first century. At BNL, this scenario was realized in the early 1980's and a strategy was formulated to develop a new methanol synthesis technology. This effort was necessitated by the realization that the two main commercial technologies (ICI and Lurgi) suffered from the following drawbacks.

- Low conversion of syngas per pass (<20% actual) requires a large gas recycle.
- High temperature operation ($\geq 250^{\circ}\text{C}$).
- High pressure operation, typically ≥ 5 MPa.

These factors require world-scale methanol plants (>2000 tons/day) for these commercial technologies to compete economically at >\$.40/gallon methanol price. It is to be noted that all presently planned plants will utilize natural gas feedstock based on known technologies.

To truly address environmental issues, small and remote natural gas fields need to be utilized. To make any economic sense, methanol plants required for these applications will be smaller in size (~100 tons/day). These skid-mounted plants are anticipated to be the wave of the future because any presently known methanol synthesis technology can not compete at this scale. It is earlier suggested that methanol price will remain high (>\$.50/gallon) in the near future. Small plants will remain competitive long after any cyclic downturn in economy will render some world-scale plants uneconomical. It is this prospect that is of interest to BNL. This strategy will be realized based on a low temperature (<150°C) methanol synthesis catalyst that was developed here at BNL. This catalyst can produce methanol with high selectivity and high productivity from syngas and affords unparalleled >90% per pass syngas conversion eliminating the need for a gas recycle. With funding over \$2 Million till 1992 from the Electric Power Research Institute (EPRI), the BNL catalyst was extensively tested. Thereafter, under an EPRI/Amoco agreement, the catalyst was tested and the BNL results were independently confirmed in Amoco laboratories.

In May 1994, a CRADA was initiated with Amoco to further develop the BNL methanol synthesis technology. Funding for this CRADA was provided by the Energy Research Laboratory Technology Transfer (ER-LTT) Program and Amoco Corporation. In an effort to pilot this technology a preliminary economic report prepared by Amoco on the BNL methanol synthesis process provided input in areas of concern to Amoco. A work plan was formulated based on a few process uncertainties that were identified. This report updates the status of this effort.

Realizing that a multi-year effort was necessary to achieve the ultimate goal of this collaboration, a follow-up three-year CRADA was proposed in July 1994. Subsequent to this follow-up CRADA award, the original one-year CRADA Joint Work Statement (JWS) was rearranged to complete all proposed tasks more effectively over the four-year period.

BNL METHANOL SYNTHESIS TECHNOLOGY

The BNL methanol synthesis catalyst consists of a nickel complex activated by an alkoxide base dissolved in a methanol/glyme solvent mixture. The resulting homogeneous liquid medium when heated under syngas at $T < 150^{\circ}\text{C}$, converts syngas into methanol. Typically, the catalyst system consists of the following components:

- Ni complex
- KOMe
- MeOH solvent
- Glyme cosolvent

Some data exist to suggest that methanol synthesis proceeds via an initial interaction of CO with the base:

The methanol formate anion is then hydrogenated to methanol. The following unique features of the BNL methanol synthesis process gives this technology an edge over presently available commercial technologies:

- A low temperature operation ($T < 150^\circ\text{C}$) thermodynamically allows very high syngas conversion per pass ($> 90\%$) thus eliminating the need for gas recycle.
- A liquid medium allows theoretically maximum gas conversion to be achieved at a given temperature due to uniform heat dissipation.
- A low pressure operation and catalyst inertness to N_2 allows air (instead of O_2) partial oxidation of natural gas,
- The main solvent for the process is the product (MeOH) itself. Glymes/glycols are utilized as cosolvents.
- The homogeneous catalyst formulation renders itself more amenable to mechanistic study for process optimization.

PROCESS UNCERTAINTIES

For the BNL technology to fully impact commercially, the following areas of concern are identified:

- At low temperatures of interest, base component of the catalyst system may get tied-up with CO_2 (Reaction 2). This reaction competes with the desired reaction of CO with base (Reaction 1) and inhibits methanol synthesis. Therefore, syngas utilized for methanol synthesis should be CO_2 -free, an added CO_2 clean-up step.

- Syngas contains H_2O to some extent. Since H_2O and CO_2 are tied via water-gas-shift (WGS) reaction, their cumulative effect ($\text{H}_2\text{O}/\text{CO}_2$) needs to be established.
- Irrespective of the source, any starting nickel complex will form nickel tetracarbonyl ($\text{Ni}(\text{CO})_4$) under CO at $T < 150^\circ\text{C}$ in the reactor. The concentration of $\text{Ni}(\text{CO})_4$ formed is a function of p_{CO} and temperature: a lower temperature and higher CO favor $\text{Ni}(\text{CO})_4$ formation. Since OSHA limit of this material is 1 ppb, it needs to be contained and decomposed in a safe manner. The fate of Ni catalyst in the presence of CO_2/CO needs to be established.

All batch data will translate into designing a catalyst system for a longer term testing on the Amoco AU-96E unit that is under transfer to BNL. The ultimate aim is to utilize novel features of the BNL Methanol Synthesis technology to develop a simplified and thus cost effective commercial process. Described below is the status of various completed or ongoing tasks.

TASK DESCRIPTION

Task 1 - BNL Batch Unit

A 0.5L AE Zipperclave reactor unit already in use in the PI's laboratory was readied for operation. The entire batch reactor unit was housed in a fume hood. The reactor system was a 316 SS autoclave stirred via a Dispersimax six-blade impeller mounted on a shaft driven by an AE variable speed motor. Two small holes situated at the top and bottom of the hollow impeller shaft ensured that gas was thoroughly dispersed throughout the liquid. The size of gas bubble entering the liquid phase was controlled by varying the stirring speed. A removal metal ring which fitted stationary inside the reactor vessel acts to suppress vortices that may form due to mixing. A Parr 4831 temperature controller controlled the heating/cooling cycle to achieve and sustain isothermal conditions. Heating was provided by a 500 watt heating mantle (Glass-Col Apparatus Co.) which surrounded the reactor; pressurized air which was introduced via oils positioned around the impeller provides cooling. A thermocouple inside the reactor was used to measure the reactor temperature. Several ports in the reactor head provided inlets and outlets for gases and liquids. The system was capable of operation at pressures up to 3000 psig and temperature up to 350°C. An Omega 2-pen chart recorder was used to record reactor temperature and pressure. A digital pressure readout (Setra Systems, Inc.) capable of monitoring pressure to 1 psi accuracy was also attached to the reactor unit. The unit is rated well above the reaction conditions of interest i.e., <175°C and <1000 psig.

Batch studies involved scoping runs. Since no liquid or gas leaves the reactor during any given run, solvents/reactants/products which are volatile under reaction conditions, can be more easily studied and evaluated. Batch conditions are also favorable since gas residence time is very long compared to that in a continuous system. A major disadvantage is product build-up in the reactor.

Subtask 1.1 - Shake-down Run

A blank run (no catalyst) was conducted to establish baseline measurement error. The measured liquid volume indicated that mass balance within $\pm 5\%$ was attainable (Table 1).

Task 2 Methanol Synthesis -- Process Modification Approach

The BNL catalyst system consists of the following components:

Ni(CO)₄
KOMe

MeOH
Glyme cosolvent

A cumulative effect on these constituents of CO₂ and H₂O that are normally present in syngas needs to be established (see below). A system of interest is to be developed by manipulating reaction parameters (T and P) to allow system constituents to operate and yield desired space-time-yield of methanol.

Subtask 2.1 Effect of CO₂

Syngas, generated from coal or natural gas, invariably contains CO₂. The alkoxide base is an essential component of the BNL catalyst system. Under typical reaction conditions used, the BNL catalyst is somewhat deactivated when methanol synthesis is attempted with CO₂ containing syngas. Since the CO₂ clean up step is expensive, it would be desirable to modify the BNL system so that CO₂ could be tolerated. The preliminary batch data presented in this report show that it may be possible to modify reaction conditions and/or add a cocatalyst to make the BNL catalyst system CO₂ tolerant. The suggested approach involves optimizing reaction conditions that will allow CO₂ in the BNL system without inhibiting methanol synthesis. The reaction of interest is:

This is the reverse of Reaction (2). If this is achieved, CO₂ will essentially pass through the reactor and methanol synthesis will proceed. The identified factors influencing Reaction (3) are:

- temperature
- CO pressure
- addition of a cocatalyst

Subtask 2.1.1 Literature Data - The reaction of an alkali metal alkoxide (AM-OR) with CO₂ is well known and the product is an organic carbonate:

Reaction (4) is exothermic and goes to completion at room temperature. The only complete data available for this reaction in solution are at 0°C (2). For AM = Sodium, and R = Methyl, the values are:

$$k_1 = 5.0 \times 10^5 \text{ M}^{-1} \text{ min}^{-1}$$
$$k_2 = 2.4 \times 10^{-3} \text{ min}^{-1}$$

yielding

$$K_{\text{eq}} \approx 2 \times 10^8 \text{ M}^{-1} \text{ at } 0^\circ\text{C}$$

In literature (3) some data exist on the decomposition of alkyl carbonates but in the solid state. The data are scattered as the extent of thermal decomposition does not seem consistent. Potassium methyl carbonate is thermally stable up to $\sim 100^{\circ}\text{C}$. In terms of solubility, lithium methyl carbonate is extremely soluble in methanol whereas sodium and potassium analogs are sparingly soluble. With these available data as background, a somewhat detailed study of thermal decomposition of alkyl carbonates in solution was undertaken.

An interesting aspect of Reaction 4 is its reversibility in solution. Since methanol synthesis reaction with the new catalyst proceeds well at $< 150^{\circ}\text{C}$, compatible equilibrium rate data for carbonate would be desirable for optimizing the process with minimum carbon dioxide effect. The purpose of the following study was to:

- establish reversible decomposition phenomenon of organic carbonates under different conditions;
- incorporate these results into the methanol synthesis system.

To quantitatively study the carbon dioxide reaction with alkoxides, preparation of product carbonate was desirable. This allowed:

- addition of an exact amount of carbon dioxide;
- decomposition reaction study.

The reversible reaction of carbon dioxide with alcohols (Equation 5) has also been proposed (4). This equilibrium is not expected to appreciably affect the methanol synthesis reaction.

Subtask 2.1.2 Synthesis of Potassium Methyl Carbonate (PMC) - To quantitatively study the decomposition Reaction 3, it was essential to start with potassium methyl carbonate (PMC). A batch of PMC was prepared. Through a known amount of potassium methoxide (50 g) dissolved in 200 mL p-dioxane/methanol (50/50 by volume) carbon dioxide was bubbled until no more gas was absorbed by the solution. A white precipitate, so formed, was filtered under argon, washed with p-dioxane, and dried in vacuo yielding $>90\%$ of potassium methyl carbonate. The carbonate, being hygroscopic, was stored in a glove-box.

Subtask 2.1.3 PMC Decomposition Data Collection - Though it has been previously shown at BNL that Reaction 3 was reversible under certain conditions, true reversibility was to be established. During the present subtask, all products from Reaction 3 will be identified and quantified. The PMC decomposition data were collected in batch mode in a 0.5L AE Zipperclave CSTR shown in Figure 1.

Subtask 2.1.4 PMC Decomposition Reaction - To quantify CO_2 associated with the base, PMC decomposition, according to Reaction 3, was studied. The procedure involved addition of PMC, solvent and/or cosolvent, to the AE batch CSTR (Figure 1). The reactor was sealed,

purged, and pressurized with desired gas. The solution was then heated to different temperatures and the corresponding amount of carbon dioxide released was measured by analyzing the gas phase, at a given temperature, on a gas chromatograph. The mole% decomposition was then calculated as follows:

$$\% \text{ Mole Carbonate Decomposition} = \frac{\text{Moles CO}_2 \text{ Measured}}{\text{Initial Moles of Carbonate}} \times 100 \quad (6)$$

This equation assumes that:

- Every mole of decomposed carbonate produces equal (one) moles of carbon dioxide and alkoxide.
- Solution solubility of carbon dioxide is minimal at decomposition temperature.

The purpose was to establish the extent of reversibility of the carbon dioxide/base reaction under feasible methanol synthesis reaction conditions.

Subtask 2.1.5 Base Solubility - The cosolvent solvent plays an important role in maintaining solution homogeneity during methanol synthesis reaction when catalyzed by the BNL catalyst. Though glymes are preferred cosolvents, other alternative solvents are constantly sought. In Table 2, solubility of KOMe in poly THF is compared with that in THF, MeOH, Peg-400. The solubility order is: MeOH > Peg-400 > THF > PolyTHF.

Subtask 2.1.6 PMC Decomposition Runs - The selected run conditions were as follows:

Solvent = 125 mL, Base = 10 mmol, H₂/CO = 2/1
T = 140°C, P = 2 MPa

Run CARB-1. Though KOMe is partially soluble in Poly(THF)-250 at room temperature (Table 1), PMC decomposition was measured in this solvent. This reaction was slow with CO₂ production as follows: 8 mmol (60 min), 9 mmol (50 min).

Run CARB-2. In methanol solvent, CO₂ was measured as follows: 8 mmol (50 min), 9 mmol (105 min). Since KOMe is fairly soluble in MeOH, this may explain faster PMC decomposition in this solvent.

Run CARB-3. In 80% Peg-400/20% MeOH, CO₂ produced was: 9 mmol (45 min), 10.3 mmol (150 min). KOMe is soluble in this solvent mixture.

Run CARB-4. In 90% Triglyme/10% MeOH, CO₂ produced was 6 mmol (40 min), 10 mmol (140 min).

Run CARB-4M. Run CARB-4 was repeated with added 5 mmol $\text{Fe}(\text{CO})_5$. CO_2 values were: 13 mmol (32 min), 17 mmol (60 min). The reaction appeared faster but CO_2 produced was higher than calculated (10 mmol) from the simple Reaction 5.

Run CARB-4R. To mimic the dynamic flow system, Run CARB-4 was repeated. In this run, 5 mmol CO_2 was measured at 31 minutes. At this time, the reactor was depressurized (at 110°C) and the reactor was charged with fresh syngas. In the next 31 minutes, 5 mmol CO_2 was measured and the reactor was again depressurized and then repressurized with fresh syngas. Only <0.5 mmol CO_2 was detected in the next 20 minutes. The total CO_2 produced (10 mmol) corresponded to 100% PMC decomposition.

Run CARB-5 (B1). The solvent mixture, 90% Triglyme/10% MeOH was heated to 140°C under 2 MPA syngas for 30 minutes. The CO_2 measured was 0.12 mmol (BLANK).

Run CARB-6 (B2). The blank Run CARB-5 was repeated with added 5 mmol $\text{Fe}(\text{CO})_5$. The CO_2 yield was 0.14 mmol and the final orange solution was cloudy due to $\text{Fe}(\text{CO})_5$. But $\text{Fe}(\text{CO})_5$ did not seem to interact with the solvent mixture (BLANK).

Run CARB-7 (B3). The blank Run CARB-5 was repeated with added 10 mmol KOMe. 1.3 mmol CO_2 was produced in 90 minutes and the final yellow solution was clear (BLANK).

Run CARB-8. In Runs CARB-6 and 7, it was established that $\text{Fe}(\text{CO})_5$ or KOMe containing solvent mixture produced negligible amount of CO_2 . In this run, when KOMe (10 mmol) and $\text{Fe}(\text{CO})_5$ (5 mmol) were heated at 140°C under 2 MPa syngas, CO_2 measured was 10 mmol in 60 minutes. On further heating, CO_2 increased to 31 mmol in 280 minutes. The origin of this CO_2 is unknown.

Run CARB-9. The CO_2 produced in Run 8 was temperature dependent. At 110°C , only 8 mmol CO_2 was produced in 105 minutes and the final pink solution contained a dark solid.

Run CARB-10. In the absence of CO, CO_2 produced decreased from 8 mmol in Run CARB-9 to 3 mmol in this run. CO appeared to be implicated in the CO_2 producing reaction.

Run CARB-11. The unexpected CO_2 production in the KOMe/90% Triglyme/10% MeOH/CO/ H_2 system observed in Run CARB-9 was not specific to $\text{Fe}(\text{CO})_5$. In the presence of 0.16 mmol $\text{Ru}_3(\text{CO})_{12}$, 13 mmol CO_2 was produced in 105 minutes. The final orange solution was clear.

Run CARB-12. Replacing KOMe with KOCO_2Me in Run CARB-11, CO_2 measured decreased to 6 mmol in 120 minutes. The final red solution was clear.

Run CARB-13. KHCO_3 decomposition should yield CO_2 via Reaction 7:

Replacing KOMe with KHCO_3 in Run CARB-9, CO_2 yield increased from 8 to 13 mmol. The final yellow solution was clear.

The data plots of individual Runs CARB-1 to 13 are shown in the Appendix. Figures 4, 5 and 6 show the effect of temperature, added metal carbonyls and other parameters on CO_2 evolution from solutions containing PMC or KOMe. The following observations were noteworthy:

- CO_2 evolution from PMC was 150% faster at 140°C with added $\text{Fe}(\text{CO})_5$.
- A substantial CO_2 evolution from solutions containing KOMe was observed. CO_2 productions was faster from solution containing KOMe versus PMC.
- CO_2 evolution from KOMe/ $\text{Fe}(\text{CO})_5$ containing solutions was affected by the following:
  - The presence of CO was necessary
  - The addition of metal carbonyl was necessary.
  - $\text{Ru}_3(\text{CO})_{12}$ was a better catalyst than $\text{Fe}(\text{CO})_5$.

The origin of CO_2 from solutions containing no PMC needs to be established. Work is underway to study these observations.

Subtask 2.2 Products Identification

All reaction products are to be identified to establish the mechanism by which CO_2 reversibility is attained. It is known that in the presence of H_2O , alkoxide moiety can hydrolyze to yield an inorganic formate via Reactions 8 and 9:

Interestingly, only when $\text{R}=\text{Me}$, Reaction 8 is reversible. But in the presence of CO, hydroxide anion can further react to yield the formate species. The challenge is to maintain reversibility of Reaction 9 under reaction conditions to make the alkoxide available for methanol synthesis via Reaction 1. Work is now ongoing to identify HCO_2^- , OMe species in solution.

Subtask 2.3 Ni(CO)₄/CO₂ Interaction

As discussed in Subtasks 2.1 and 2.2, the interaction of CO₂ with base study is underway. But the interaction of Ni with CO₂ also needs to be established. Since Ni(CO)₄ can be easily followed via IR, this complex was chosen for this study.

Subtask 2.3.1 Nickel Analysis Procedure - Here, the UV/VIS technique was applied. The chemical quantification involves analyzing Ni in gas (Ni(CO)₄) and liquid phases. After careful analysis, a standard procedure was developed. Two important considerations were:

- Ni(CO)₄ being heavier settled at the bottom of the reactor. Before taking a Ni sample, reactor contents were stirred to ensure uniform mixing. Otherwise, liquid Ni(CO)₄ concentration appeared higher and gas Ni(CO)₄ concentration was lower.
- For Ni analysis, 12M HNO₃ was required to ensure complete instant Ni(CO)₄ decomposition. 6M HNO₃ may not be strong enough and will lead to a lower Ni value.

The developed procedure involved the following steps:

1. Zml liquid sample (or 5 mL gas sample) + (1-Z)mL 12M HNO₃. Shake vigorously.
2. 3 mL H₂O
3. 1 mL Br₂ water. Warm with hot tap water and shake well.
4. 3 mL aqueous NH₃ to form a colorless solution.
5. Cool in ice water.
6. 2 mL dimethylglyoxime (DMG) (1 wt% in EtOH).
7. Wait 2 minutes and run a visible spectrum. A Perkin-Elmer Lambda 4B UV/VIS spectrophotometer is available.
8. The λ_{max} is ~443 nm. Note absorbance at this wavelength.

A standard 0.01 M Ni(OAc)₂·4H₂O solution in 6M HNO₃ was prepared. The above procedure was followed to measure absorbance of the standard solution at initial concentrations of 0.010, 0.015, 0.020 M. A plot of these data in Figure 2 shows a linear correlation ($A = ECl$ where A =absorbance, C is concentration(M), l =cell path length (cm) and E is a constant). From this plot unknown reactor Ni concentration was calculated once the absorbance was measured.

Subtask 2.3.2 Qualitative Identification of Ni(CO)₄ - A simpler method to identify Ni(CO)₄ is to follow Ni(CO)₄ in the infrared region where this species has a sharp peak at 2040 cm⁻¹. A typical procedure involves taking a gaseous sample from the reactor. A special gas cell of 1" pathlength and fitted with NaCl windows is filled with the gas sample at ambient pressure. The spectrum is scanned on a Perkin-Elmer 1330 Infrared spectrometer. The transmittance value can be converted to absorbance if necessary.

Subtask 2.3.3 Ni(CO)₄/CO₂ Reaction - This study was carried-out in the AE batch unit. 125 mL of 80% Triglyme/20% MeOH solvent was loaded and the reactor was sealed and purged twice with 50 psi syngas (H₂/CO = 66%/34%). 4.2 mmol liquid Ni(CO)₄ was dispersed into the solvent via a special syringe and the reactor was pressurized to 311 psig with syngas. The following samples were taken for IR analysis:

- #1. Blank before adding Ni(CO)₄
- #2. 1" cell after adding Ni(CO)₄ and 66% H₂/34% CO at R.T.
- #3. After 18h at R.T.

These baseline data suggest no Ni(CO)₄ decomposition under H₂/CO at room temperature. The reactor was then heated to 150°C then cooled to room temperature after 1 hour.

- #4. After heating under 66%H₂/34% CO at 150°C.

The reactor was depressurized and then pressurized with 300 psig H₂/CO/CO₂. This translated into 24 mmol CO₂ that was about 5 times the concentration of Ni(CO)₄. The solution was heated to 150°C for 1h and then cooled.

- #5. Ni(CO)₄ under 33%CO/64%H₂/3%CO₂ at R.T.
- #6. After heating at 150°C for 1h.

After the infrared study, the contents of the reactor were subjected to the UV/VIS method for Ni mass balance. Using Figure 2, Ni was calculated to be 0.91 mmol and 3.1 mmol in gas and liquid phases respectively. This corresponded to 4.01 mmol Ni versus 4.2 mmol Ni(CO)₄ added yielding 95% accountability.

The actual infrared data is shown in Figure 3. It appears that presence of 3% CO₂ in syngas does not affect Ni(CO)₄. This preliminary study is now being extended to design a system for further testing.

Task 3 Alternate Approaches

Though beyond the scope of this phase, other approaches need to be considered if the present effort does not produce acceptable economics. These are:

- a. Other Parameters
  - 1. Role methanol
  - 2. Role of cosolvent
  - 3. Optimization of Base/MeOH ratio.

b. Cocatalyst for Water Gas Shift (WGS) Activity: The BNL system avoids the otherwise inevitable WGS reaction by operating at a lower temperature. But if the syngas feed contains H_2O and CO_2 , the options are:

1. Remove $\text{CO}_2/\text{H}_2\text{O}$ before methanol synthesis.
2. After methanol synthesis:
  - a. CO_2 /Base separation
  - b. $\text{H}_2\text{O}/\text{MeOH}$ separation

The original design was based on (1) and accounts for an additional 10% of the total cost, an expensive step. If the present work is successful, (2) needs to be considered. Task 3 forms the basis of the now ongoing follow-up multi-year CRADA that was initiated in March 1995. The necessary background will be covered in a later report. For now, it is suffice to mention two approaches:

- A biphasic system with one of the phases being aqueous.
- Control of $\text{Ni}(\text{CO})_4$ through ligation.

To design such a system requires solubility/miscibility data. These data were compiled and are shown in Table 3. Note that KOH , MeOH , triglyme, 2, 2' bipyridyl (bpy) ligand, formed a single phase. The system became biphasic when $\text{Fe}(\text{CO})_5$ was added (for simplicity, $\text{Fe}(\text{CO})_5$ was substituted for $\text{Ni}(\text{CO})_4$). The implication of these data will be discussed in a follow-up report under the now ongoing CRADA.

A literature data base is being built to study the $\text{H}_2\text{O}/\text{CO}_2$ combination effect.

Task 4 Transfer of Amoco AU-96E Unit

This is a tedious task and is the subject Task 1 of the multi-year follow-up CRADA. Realizing that this task was a time consuming process, discussion to form a strategy for successful transfer was initiated earlier this year. Work is almost nearing completion.

Task 5 Economics

A preliminary BNL process economics report prepared by Amoco has been obtained. The ongoing and proposed tasks reflect the input from this report. As work progresses, this report will be updated.

Task 6 Information Exchange And Reports

The BNL/Amoco information exchange is an important aspect of this effort. To this effect, in addition to routine information exchange, two review meetings were held at the Amoco research facility in Naperville, Illinois. An informal briefing was also held in Pittsburgh on September 7, 1994.

Review Meeting #1 - This meeting between a twelve-member team headed by Dr. Theo Fleisch and the BNL Principal Investigator (PI) took place on June 13, 1994. The purpose was to initiate the one-year approved CRADA and discuss proposed multi-year effort necessary to pilot this technology. The BNL presentation titled "BNL Methanol Synthesis Technology Development -- Approaches to Process Uncertainties" outlined strategy to implement the project. Presented below is the summary of the PI's presentation.

Summary of the PI's Presentation during the BNL/Amoco Meeting on June 13, 1994 at Amoco

BNL MeOH Synthesis Technology

Present Assumptions

Syngas via POX
T = 130°C
P_T = 450 psig (40% N₂) = 270 psig (syngas only)
CO conversion per pass = 95 %
Preclean-up of CO₂
Reactor size large based on the Amoco data.
Ni(CO)₄ containment cost.

Result

Low value process waste heat. At 95% CO conversion, the 5% residual syngas is supplemented by natural gas burning to generate enough heat for the integrated process.

*Present process economics (Amoco Study).

Proposed Approach

T raised to 140-170°C
Water-gas-shift (WGS) reaction to be introduced by Ni or by adding a known homogeneous WGS catalyst.
Cosolvent changed from Triglyme to Glycols or poly-THF to solubilize carbonate and increase alkoxide solubility.

Bidentate phosphine or water-soluble phosphine ligand added to stabilize Ni(Ni-P complexes).

Result

T = 140 - 170°C

P = fixed at 450 psig

Base poisoning reversed at higher T. CO₂-resistant catalyst. No preclean-up of CO₂ needed. H₂O tolerated.

Solution homogeneity maintained.

Ni(CO)₄ controlled.

CO conversion decreased to 85 % (Theoretical maximum at 150°C = 90%).

At 3 % CO₂ in syngas, effective syngas pressure decreases by 3%.

The quality of process waste heat improved at higher T. Lower CO conversion (85%) increases tail gas to 15%. Supplemental natural gas burning requirement decreased or eliminated.

*Modified economics with proposed catalyst modifications.

This presentation and the associated discussion resulted in the multi-year CRADA proposal.

Review Meeting #2 - This meeting took place on February 9, 1995 at Amoco in Naperville subsequent to submission of a technical report (Report #1) to Amoco by the BNL PI. A briefing was prepared by the PI but the Amoco unit transfer (see below) was the main topic of the meeting agenda. Priorities were redefined to efficiently carry-out the proposed work. A state-of-the-art continuous bench-scale unit was built at Amoco to evaluate the BNL technology. Under the BNL/Amoco CRADA Agreement, this unit will be transferred to BNL to facilitate catalyst evaluation. Since the unit is intricate, this transfer is a tedious task. For this reason, the unit transfer task is being given a top priority and this task was high on the agenda during the BNL PI's recent visit to Amoco. A successful execution of this task will require the following (as agreed upon by both BNL and Amoco):

Amoco

- Amoco AU-96E unit disassembly.
- Crating
- Shipping to BNL
- Assistance in unit assembly at BNL.

BNL

A laboratory is to be renovated at BNL to house the unit.

The progress to date is as follows:

- Laboratory 253 in Building 555A has been assigned for this project.
- The schematics as well as pictures of the unit were received in early February.
- A request has been submitted to provide adequate hoods in Laboratory 253.

All modified catalyst formulations are to be tested in this unit if batch-mode data look promising.

Interim Report #1 A detailed report covering the period from May through September 1994 was prepared and sent to Amoco in October 1994. This report mainly highlighted overall approaches to the project and emphasized data related to the CO₂ aspect.

Interim Report #2 A second report covering the period between October 1994 and February 1995 was prepared and sent to Amoco. This report mainly described coordination of the Amoco AU-96E unit transfer to BNL.

DOE Progress Reports As per CRADA requirements, the following Quarterly Progress Reports were submitted to the BNL OTT:

1. Period covering May 20 - June 30, 1994.
2. Period covering July 1 - September 30, 1994
3. Final Report - May 20, 1994 - May 20, 1995 (this document)

FUTURE DIRECTION

This report describes progress made so far to further develop the BNL Methanol Synthesis Technology. Soon after this completed one-year CRADA was initiated, it was realized that a multi-year effort was necessary to achieve the ultimate goal of this collaboration. A follow-up three-year CRADA was proposed in July 1994. In October, the follow-up CRADA award was recommended with cost-sharing between Amoco and the U.S. Department of Energy (DOE). The DOE part of funding is being provided by the ER/LTT Program. Work on the three-year follow-up CRADA started in March 1995. The major themes of this work are:

- Development of a second generation BNL Methanol Synthesis Catalyst to address identified process uncertainties.
  - Specifically, accommodate CO₂ and H₂O in the system.
  - Biphasic system with one of the phases being aqueous.
  - Ni(CO)₄ control through ligation or other approaches.
- Screen and optimize catalyst in batch mode.
- Catalysis performance in the Amoco AU-96E continuous unit to establish catalyst life and space-time-yield (STY).
- Update economics to reflect process improvements.

The BNL/Amoco team is striving to achieve these goals and design a system for scale-up in the specific period. A combination of novel catalytic chemistry and simplified process considerations are expected to result in development of a new methanol synthesis process based on the BNL technology.

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Table 1
Shake-down Run in Batch Mode

Run Conditions

Catalyst precursor: --
Solvent: 80% Triglyme/20% MeOH = 125 mL
Base: --
Syngas: 66% H₂/34% CO/0% CO₂
T: 150°C
P: 293 psig (524 psig @ T)

Data

On-line time: 1.7 h
Final P = 288 psig
H₂ = 66%
CO = 33%
CO₂ = <0.05%
Final Volume = 121 mL
Syngas consumed < 5 mmol

Table 2
Solubility of KOMe in Different Solvents

KOMe = 5 mmol (0.35g)

Solvent = 5 ml

Solution = 1M

Solvent	Solution State ¹ in 3 min/2h
PolyTHF	Light orange, partially dissolved
THF	Colorless, partially dissolved
MeOH	Colorless, dissolved
Peg-400	Amber, partially dissolved

¹ Stirred at room temperature.

Table 3
Solubility/Miscibility of Various Components

T = 25 °C

Solvent	Additive	<u>Solution</u>	
		Color	State
H ₂ O	KOH	Colorless	Homogeneous
H ₂ O/MeOH	KOH	Colorless	Homogeneous
MeOH	bpy*	Colorless	Homogeneous
H ₂ O/MeOH	KOH/bpy*	Colorless	Homogeneous
H ₂ O/MeOH/Triglyme	KOH/bpy*	Colorless	Homogeneous
H ₂ O/MeOH/Triglyme	KOH/bpy*/Fe(CO) ₅	Yellow	Biphasic

* 2,2'-bipyridyl

Figure 1. AE Zipperclave Reactor used in Batch Studies

Fig. 2. Plot of [Ni] vs. Absorbance

Wavenumber, cm^{-1}

Figure 3. Infrared spectra of 0.034M Ni(CO)_4 in 80% Triglyme/20% MeOH. Gas samples were taken from the reactor under 300 psig. 1) Blank 1 cm gas cell with NaCl windows, 2) 1" cell was used for the study under 66% H_2 /34% CO at R.T., 3) Solution after 18 h, 4) After heating at 150°C for 1h and then at R.T., 5) Solution under 64% H_2 /33% CO/3% CO_2 at R.T., 6) After 1h at 150°C and then at R.T. For 4), 5), and 6), the baseline was moved for clarity.

Fig. 4. CO₂ Evolution from Solution containing KOMe / Fe(CO)₅

P=300 psig; Solvent:90% Triglyme/10% MeOH; T=140° C; H₂/CO= 2/1

Fig. 5. Effect of Added $\text{Fe}(\text{CO})_5$ on PMC Decomposition

P=300 psig; Solvent:90% Triglyme/10% MeOH; T=140° C; $\text{H}_2/\text{CO}=2/1$

Fig. 6. CO₂ Evolution from PMC and KOMe with Metal Carbonyls

APPENDIX

This section contains 17 pages.

Table A-1. Standard Nickel vs. Absorbance Data

Standard: $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in 6M HNO_3 = 0.01

T = 25 °C

Run #	Standard, mL	λ , nm	$[\text{Ni}]^*$, M	Absorbance
----	0	----	0	0
N-5	0.10	442.6	0.00010	1.264
N-4	0.10	442.2	0.00010	1.278
N-6	0.15	443.2	0.00015	1.912
N-7	0.20	444.3	0.00020	2.567
N-8	0.20	444.6	0.00020	2.577

* The final diluted volume was 10 mL

Run CARB-1
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KOCO₂Me
Solvent: Poly(THF)250
Syngas: H₂/CO = 2/1; T = 140 C; P = 2 MPa

Run CARB-2
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KOCO₂Me
Solvent: MeOH
Syngas: H₂/CO = 2/1; T = 140 C; P = 2 MPa

Run CARB-3
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KOCO₂Me
Solvent: 80% PEG-400 / 20% MeOH
Syngas: H₂/CO = 2/1; T = 140 C; P = 2 MPa

Run CARB-4
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KOCO₂Me
Solvent: 90% Triglyme / 10%MeOH
Syngas: H₂/CO= 2/1; T= 140 C; P= 2 MPa

Run CARB-4M
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KOCO₂Me; Fe(CO)₅ = 5 mmol
Solvent: 90% Triglyme / 10% MeOH
Syngas: H₂/CO = 2/1; T = 140 C; P = 2 MPa

Run CARB-4R
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KOCO₂Me, 10 mmol
Solvent: 90% Triglyme / 10% MeOH, 125 ml
Syngas: H₂/CO = 2/1; T = 110 C; P = 2 MPa

Run CARB-5(B1)
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: NO
Solvent: 90%Triglyme / 10%MeOH
Syngas: H₂/CO= 2/1; T= 140 C; P= 2 MPa

Run CARB-6(B2)
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: NO; Fe(CO)₅ = 5 mmol
Solvent: 90% Triglyme / 10% MeOH
Syngas: H₂/CO = 2/1; T = 140 C; P = 2 MPa

Run CARB-7
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KOMe
Solvent: 90% Triglyme / 10% MeOH
Syngas: H₂/CO = 2/1; T = 140 °C; P = 2 MPa

Run CARB-8
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KOMe; Fe(CO)₅ = 5 mmol
Solvent: 90% Triglyme / 10% MeOH
Syngas: H₂/CO = 2/1; T = 140 C; P = 2 MPa

Run CARB-9
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KOMe; Fe(CO)₅ = 5 mmol
Solvent: 90% Triglyme / 10% MeOH
Syngas: H₂/CO = 2/1; T = 110 °C; P = 2 MPa

Run CARB-10
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KOMe; Fe(CO)₅ = 5 mmol
Solvent: 90% Triglyme / 10% MeOH
Syngas: H₂/CO = 2/1; T = 110 C; P = 2 MPa

Run CARB-11
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KOMe; Ru₃(CO)₁₂ = 0.16 mmol
Solvent: 90% Triglyme / 10% MeOH
Syngas: H₂/CO = 2/1; T = 110 C; P = 2 MPa

Run CARB-12
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KOCO₂Me; Ru₃(CO)₁₂ = 0.16 mmol
Solvent: 90% Triglyme / 10% MeOH
Syngas: H₂/CO = 2/1; T = 110 °C; P = 2 MPa

Run CARB-13
Time Profile of CO₂ Evolution
0.5 L AE batch reactor; Solvent = 125 ml; Base = 10 mmol

Base: KHCO₃; Fe(CO)₅ = 5 mmol
Solvent: 90% Triglyme / 10% MeOH
Syngas: H₂/CO = 2/1; T = 110 °C; P = 2 MPa