

**APPENDICES**

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## Appendix A. USE OF CODE SYSTEM

A code system is being used in this report and throughout the contract period to identify proprietary data or information which may be the subject of future patents. The code system consists of three classifications, each member of which is assigned a number.

Category A encompasses additives, such as ligands, metal complexes, or salts, which apparently function as catalyst promoters.

Category C consists of catalysts or co-catalysts.

Category S includes solvents for catalytic reactions.

Use of the code system has been approved by the Chief Office of Patent Counsel, U.S. Department of Energy, 9800 South Cass Avenue, Argonne, Illinois 60439.

The following coded information is included in this report:

A16:	A metal-containing catalyst additive
A25:	A catalyst additive
A28:	A catalyst additive
A92:	A catalyst additive
A108-110:	Catalyst additives
C4:	A catalyst precursor
C16:	A catalyst precursor
C23:	A catalyst precursor, possible intermediate

## Appendix B. PROCEDURES FOR CATALYST TESTING

Catalyst tests carried out under this contract are assigned reference ID numbers which identify the appropriate researcher and the notebook reference of the experiment.

### PROCEDURE B(a).

A 100 cc Hastelloy magnedrive autoclave was used for catalyst testing. The cleaned autoclave was purged with nitrogen, charged with the reactants, sealed and pressured to 400 psig with synthesis gas of the desired composition. The reactor was maintained at 400 psig for 10 minutes to check for leaks. The reactor was then heated to the desired temperature and pressured with synthesis gas to 25 psi above the specified pressure. The pressure was maintained within  $\pm 25$  psi of the operating pressure by repressurizing as necessary. After the experiment was completed, the reactor was cooled to 20°C. The gas was vented and the liquid products were collected in a chilled bottle fitted with a septum. The reactor was washed with various solvents until the rinses appeared clean. The reactor was periodically disassembled and cleaned, as required.

### PROCEDURE B(b).

The catalyst, additives, and solvent were charged into a 150 mL Hastelloy C magnedrive autoclave under argon. The reactor was sealed, pressurized with 80 psi of nitrogen, and vented. It was then pressurized to 300 psi with syngas and again vented. This purging was then repeated once more before

the system was pressurized to 1000 psi of syngas. At this point, the system was tested for possible leaks. It was then heated to the specified reaction temperature before being pressurized to the desired level with syngas. The temperature and pressure were then kept constant for the desired reaction time by periodic repressurizations with syngas. The reactor was then rapidly cooled to room temperature by a cool water jacket. The reactor was then slowly vented and the reaction solution was collected and analyzed. The reactor was washed with several solvents, then disassembled and washed manually.

**Procedure B(c).**

A 70 mL stainless steel reactor was used for small scale reactions at pressures up to 1000 psig. The reactor was charged with reactants in a nitrogen filled glove box and then sealed. The reactor was then removed from the drybox and connected to the gas feed lines. The lines were flushed to remove air and the reactor was pressurized to the desired pressure. This pressure was maintained within  $\pm 25$  psi of the operating pressure by repressurizing as necessary. The reactor was heated to reaction temperature by immersion in a previously heated oil bath which could be raised and lowered with a lab jack. Stirring was accomplished with a magnetic stirrer/stir bar. After the experiment was completed the oil bath was lowered, the reactor vented, and the reactor contents analyzed.

**Procedure B(d).**

A 3 oz. glass Fischer-Porter aerosol bottle was used for small scale, low pressure (< 150 psig) reactions. The procedure was identical to that described in B(c).

**PROCEDURE B(a).**

A u-tube micro-reactor system is used for catalyst evaluation. The reactor system contains a manifold in which up to two gas feeds are mixed and then fed to two u-tubes, both of which are maintained at a constant temperature in a common sandbath. The system can be operated at up to 1200 psig, 400°C, and space velocities up to about 1200 l/l/h, and is equipped with an emergency shut-down system for unattended operation. The product analysis consists of collecting a liquid product from the water-cooled condenser, analyzing it on a GC and combining that analysis with on-line gas analyses for hydrocarbons, hydrogen, carbon monoxide, and carbon dioxide.

The standard start-up procedure consists of charging the catalyst to a nitric acid (50/50 acid/water) washed 1/4 inch O.D. 316 stainless steel u-tube and installing it in the high pressure reactor system. The catalyst is charged either as a powder, mixed with twice its volume of 0.5mm glass beads, or as undiluted +10-20 mesh particles. In either case the inlet and outlet of the u-tube is filled with 0.5 mm glass beads and a glass fiber plug is placed in each end. The system is pressurized to the maximum anticipated reaction pressure and the u-tube fittings are tested for leaks with soap solution. The sandbath is then raised around the two u-tubes and the sand is fluidized with air. The sandbath temperature is increased with a temperature controller to the reaction temperature, the pressure is adjusted to the desired reaction pressure and the feed flows are established. The offgas analysis is performed every two hours alternating between the two reactors. The liquid product is collected once a day at approximately 24 hour intervals or twice a day at approximately 8 hour and 16 hour intervals and subsequently analyzed.

Prior to discharging the catalyst, the reactor is cooled to  $\leq 100^{\circ}\text{C}$ , purged with nitrogen, and depressurized.

## Appendix C. PROCEDURES FOR PRODUCT ANALYSIS

### PROCEDURE C(b)

The organic products were analyzed by gas chromatographic methods. The analyses were carried out using a Hewlett-Packard Model HP-5880 equipped with a 10-ft Tenax column. The initial and final temperatures used were 40 and 200°C, respectively. Acetonitrile was used as an internal standard. Gas samples were analyzed using a Carle Analytical Gas Chromatograph, Series S.

### Procedure C(c)

Liquid product analyses were performed on a Hewlett-Packard HP 5890 gas chromatograph equipped with a DB 1701 30m X 0.32mm capillary column attached to a flame ionization detector. The column temperature was held at 35°C for 2 min and then ramped to 200°C at 20°C/min. Product selectivities are based on mole % using experimentally determined response factors.

Gas samples were collected in a septum capped vessel while venting the reactor. The vessel was cooled to -78°C to condense heavy materials. The remaining gases ( $H_2$ , CO,  $CH_4$ ,  $CO_2$ ,  $C_2H_6$ ) were analyzed on a Varian 3700 gas chromatograph equipped with a Carbosieve S-II column and a thermal conductivity detector. The column temperature was held at 225°C and argon was used as the carrier gas. Gas analyses are reported as mole % and were calculated using experimentally determined response factors.

#### PROCEDURE C(d)

Offgas analysis for hydrocarbons was accomplished with a Varian 3700 gas chromatograph equipped with a flame ionization detector and a 3 ft. by 1/8 inch Carbosieve G column. The initial temperature of 70°C was held for 2 minutes, it was then heated at 10°C/min to 200°C where it was held for 32 minutes. The hydrogen, carbon oxides, and nitrogen analysis was done isothermally at 70°C with a Varian 1400 GC with a thermal conductivity detector and a 6 ft by 1/4 inch 2% QF-1 on Burrell Carbon column. Gas standards were used to determine response factors and the gaseous components mole percent concentrations are calculated. The liquid analysis was done on a Varian 3700 GC with a thermal conductivity detector and a 11 ft x 1/8 inch Porapak R column using the same temperature program as for the hydrocarbon analysis. Prior to analysis of the liquid a known weight of ethyl cellosolve is added as an internal standard and liquid standards are periodically run so that weight percents of each component are reported. A Varian 8000 Autosampler was used for liquid sample injection.

The liquid and gas analyses are combined and selectivities in terms of weight percent and carbon molar percent are calculated for all products except CO<sub>2</sub>.