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**DIRECT AROMATIZATION OF METHANE
QUARTERLY TECHNICAL PROGRESS REPORT No. 3**

Prepared for the U.S. Department of Energy Under
Contract No. DE-AC22-92PC92109

by

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Date of Report: July 20, 1993
Date of Contract: September 26, 1992
Anticipated Completion: May 25, 1995
Total Government Award: \$340,930
Program Manager: George Marcelin
COR: Arun C. Bose
Reporting Period: 4-1-93 to 6-30-93

ABSTRACT

The construction of the quench-reactor has been completed. Gaseous reactants are fed in a downward flow and the quenching medium (water) pumped upward into a concentric reactor housed in a high temperature (1540°C) furnace. The furnace has a 24 inch, resistively-heated zone, with an overall length of 38 inches. The gaseous effluent is sampled directly into a gas chromatograph via a sampling valve.

A gas chromatographic procedure for the analysis of the expected products is being developed. Several chromatographic columns have been tested for the separation of a standard mixture of C₁ - C₉ aliphatic hydrocarbons and aromatics such as benzene, toluene, xylenes, ethylbenzene, and naphthalene. An Alumina-GS microbore capillary column had been found to provide the necessary separation, but with poor peak shape. Modification of the injector system are planned and development of the analytical procedure is continuing.

In anticipation of Task 4, in which catalysts will be employed to reduce the temperature of the pyrolysis, a preliminary search of the literature has identified several alumina-based materials that may be suitable for high temperature operation and will prove to have some catalytic activity. The preliminary synthesis and characterization of potentially useful materials have been started.

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1. OBJECTIVE

The thermal decomposition of methane shows significant potential as a process for the production of higher unsaturated and aromatic hydrocarbons when the extent of the reaction is limited. Preliminary experiments have shown that cooling the product and reacting gases as the reaction proceeds can significantly reduce or eliminate the formation of solid carbon and heavier (C_{10+}) materials. Much work remains in optimizing the quenching process and this is one of the goals of this program. We will also study means to lower the temperature of the reaction as this will result in a more feasible commercial process due to savings realized in energy and material of construction costs. The use of free-radical generators and catalysts will be investigated as a means of lowering the reaction temperature thus allowing faster quenching. It is highly likely that such studies will lead to a successful direct methane to higher hydrocarbon process.

2. TECHNICAL REPORT

2.1 Introduction

Work this quarter concentrated primarily on three activities:

- 1) Construction of the quench-reactor;
- 2) Development of a technique for the quantitative analysis of the expected products; and
- 3) Preliminary investigation into catalytic materials stable at the temperatures of interest ($< 1400^{\circ}\text{C}$).

2.2 Status of the Construction of Quench-Reactor

The construction of the quench-reactor has been completed. A schematic of the final system is shown in Figure 1. A control cabinet houses two mass-flow controllers for delivery of methane and inert, respectively, a pump for delivery of the water, and various other heater controls and electronics. The furnace has a 24 inch, resistively-heated zone, with an overall length of 38 inches. It is vertically mounted on a separate rack. The furnace is capable of achieving 1540°C and has been tested and tuned to 1400°C .

Figure 1. Simplified schematic of quench reactor system.

Gaseous reactants are fed in a downward flow and the quenching medium (water) is flowed upward. The gaseous effluent is sampled directly into a Varian 3400 gas chromatograph via a sampling valve. Analysis is recorded using a Spectraphysics integrator.

2.3 Analytical Procedure

A gas chromatographic procedure for the analysis of the expected products is being developed. Several chromatographic columns have been tested for the separation of a standard mixture of $C_1 - C_9$ aliphatic hydrocarbons and aromatics such as benzene, toluene, xylenes, ethylbenzene, and naphthalene. An Alumina-GS microbore capillary column had been found to provide the necessary separation, but with poor peak shape for the aromatics. Modification of the injector system improved the peak shape somewhat but not sufficiently for proper analysis. Further modifications are planned and development of the analytical procedure is continuing.

2.4 Catalytic Materials Stable at High Temperatures

2.4.1 Background

In anticipation of Task 4, in which catalysts will be employed to reduce the temperature of the pyrolysis, a preliminary search of the literature has been conducted to identify materials that will be suitable for high temperature operation and will prove to have some catalytic activity.

Few solid materials are structurally or texturally stable at the desired temperatures and those that are stable may possess too low a surface area to serve as useful catalysts. Alumina is widely used as a catalyst and catalyst support and is generally considered to be a "refractory" oxide, that is, one capable of withstanding high temperature conditions without changes in its structure. In fact, alumina undergoes many phase transformations with temperature ultimately leading to the formation of α -alumina, a low surface area material, at temperatures around 1100°C.

A number of reports have detailed the thermal stabilization of alumina by addition of other components. The addition of such components can serve a dual purpose in

catalytic combustion. Firstly, they can help stabilize the alumina and assist in maintaining a high surface area at elevated temperatures. Secondly, the additives may impart some catalytic activity. Two types of alumina-based catalysts have been identified in the literature as potentially useful in this work, hexaaluminates and blocked aluminas.

Arai and coworkers have reported on cation substituted hexaaluminates (Machida 1987a & b; 1988; 1989; 1990). Hexaaluminates consist of alumina lattices to which small amounts of other cations, specifically barium, have been added. The addition of barium leads to the formation of the compound $\text{BaO} \cdot \text{Al}_2\text{O}_3$ which has a unique layered structure stable at elevated temperatures. For example, with the system $\text{BaO} \cdot 6\text{Al}_2\text{O}_3$, specific surface areas of up to $14 \text{ m}^2/\text{g}$ have been reported after calcination to 1600°C ! (Machida 1988). This represents at least a 10-fold improvement on surface area from a similarly heat-treated alumina.

Various additives can retard the formation of $\alpha\text{-Al}_2\text{O}_3$ and the reduction in surface area that accompanies its formation. Amato et al. (1975) suggested that these additives are effective in suppressing the enlargement of the micropore structure in the precursor and thus maintaining the surface area. Additives that can block (hence the term "blocked" aluminas) the formation of $\alpha\text{-Al}_2\text{O}_3$ include La_2O_3 (Matsuda 1984), SiO_2 (Amato 1975), B_2O_3 (Peil 1988; 1989), and the alkaline earths (Machida 1987).

2.4.2 Preliminary Experiments

A Ba-hexaaluminate has been synthesized following the recipe of Machida et al. The hexaaluminate structure was confirmed by powder X-ray diffraction. After calcination to 1400°C , the material retained a surface area of *ca.* $2 \text{ m}^2/\text{g}$ and showed no loss of the hexaaluminate structure. This is a significant surface area for such high temperature treatment; it is, however, below values reported in the literature of *ca.* $15 \text{ m}^2/\text{g}$.

Other alumina materials have been prepared containing Ca, Pd, and Co. These are yet to be calcined at high temperature and have their surface area measured.

2.5 **References**

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3. **CURRENT STATUS**

Project is proceeding approximately one month behind schedule. The development of an analytical technique has taken considerably more time than was originally estimated.

4. **WORK PLANNED FOR NEXT QUARTER**

Next quarter we will begin experimental runs on the aromatization of methane by quenched-pyrolysis. The initial work will concentrate in a study of the influence of the various experimental parameters on conversions and selectivities.

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