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**DIRECT AROMATIZATION OF METHANE
QUARTERLY TECHNICAL PROGRESS REPORT No. 2**

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

by

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Date of Report: June 30, 1993
Date of Contract: September 26, 1992
Anticipated Completion: May 25, 1995

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Reporting Period: 1-1-93 to 3-31-93

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ABSTRACT

The design of the quench reactor has been completed. A high temperature furnace, capable of reaching 1540°C has been ordered.

Thermodynamic equilibrium calculations were carried out in order to determine the maximum possible yields of various products from methane pyrolysis, assuming that the reaction could be quenched at C₁₀ aromatics. Acetylene, benzene and naphthalene were identified as the major products of such a process. Ethylene, propylene, cyclopentadiene, methylnaphthalene and toluene, vinylacetylene, butadiene, and propadiene were identified as minor products. The yields of benzene and naphthalene are highest in the temperature range between 1350 - 1550 K, with a maximum aromatic yield of ca. 45% (benzene + naphthalene) expected at about 1475 K (ca. 1200°C).

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.

TECHNICAL REPORT

Introduction

Work this quarter concentrated on three activities:

- 1) Construction of the quench-reactor;
- 2) Development of technique for quantitative analysis of the expected products;
and
- 3) Thermodynamic calculations of the product concentrations for quenched pyrolysis.

Status of the Construction of Quench-Reactor

The construction of the quench-reactor is proceeding on schedule. An existing control cabinet has been adapted for housing the mass-flow controllers, water pump, and electronics. The choice of furnace and temperature controller was carefully investigated. Both conventional resistively-heated, as well as infrared furnaces were evaluated. Based on performance and price, a furnace incorporating silicon carbide elements was chosen. This furnace has a single-zone construction, 24-in. heated length and is rated for a maximum temperature of 1540°C. Delivery is expected in April.

A number of other minor components, including the quartz reactor tubes, have been ordered. Once all the necessary components are received the reactor will be assembled.

Analytical Procedures

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 along with aromatics such as benzene, toluene, xylenes, ethylbenzene, and naphthalene. An Alumina-GS microbore capillary column gave a good separation for the lighter hydrocarbons, although it overloaded for the higher aromatics. Development of the analytical procedure is continuing.

Thermodynamic Calculations on the Quenched-Pyrolysis of Methane

The thermal reactions of methane can be considered to follow mainly a stepwise dehydrogenation sequence, viz.:

C₂ hydrocarbons are readily attacked by CH₃ radicals formed in the decomposition of methane forming higher hydrocarbon products. However, each of the four dehydrogenation steps indicated above is complex, involving a variety of free-radical and molecular intermediates. The final step from acetylene to carbon is believed to proceed through the formation of polyunsaturated and polyaromatic hydrocarbons followed by polymerization and loss of hydrogen. The hydrocarbon products which have been detected and identified in other studies are highly unsaturated and included ethylene, acetylene, propylene, propyne, butadiene, vinylacetylene, cyclopentadiene, benzene, toluene, naphthalene,

methylnaphthalene, biphenyl, cyclopentadiene, biphenylene, and other less significant compounds such as styrene, indene, phenylacetylene.

Thermodynamic equilibrium calculations were carried out using PROCESS™ Simulation Program in order to determine the maximum possible yields of various products from methane pyrolysis, assuming that the reaction could be quenched at C₁₀ aromatics. Although all the products listed above were included in the thermodynamic calculation, the results revealed that only a limited number of products could be formed, at least in the range of temperature studied. The major products are: acetylene, benzene and naphthalene. The minor products are: ethylene, propylene, cyclopentadiene, methylnaphthalene and toluene. Vinylacetylene, butadiene, propadiene were formed in minute quantities.

The results of these thermodynamic equilibrium calculations are presented in Table 1 and Figures 1-5. Table 1 lists the equilibrium distribution of all the products as a function of temperature. Figure 1 gives the wt% methane conversion to all these products. Figure 2-4 illustrates how the product distributions vary with temperature. Finally, Figure 5 represents the yields of the major products as a function of temperature. The yields of benzene and naphthalene are highest in the temperature range between 1350 - 1550 K, with a maximum aromatic yield of ca. 45% (benzene + naphthalene) expected at about 1475 K (ca. 1200°C). Naphthalene is the most thermodynamically favored and stable hydrocarbon at these temperatures, while at much higher temperatures acetylene is the most favored product.

TABLE 1. EQUILIBRIUM PRODUCT DISTRIBUTION (Including Methane)

PRODUCTS \ TEMPERATURE (K)	900	1000	1100	1150	1200	1250	1300	1325	1350	1375	1400
METHANE	93.1	85.11	72.9	65.48	57.57	49.56	41.85	38.21	34.75	31.5	28.46
ACETYLENE	0	0	0.02	0.05	0.14	0.35	0.78	1.13	1.62	2.29	3.19
ETHYLENE	0.05	0.18	0.47	0.69	0.96	1.26	1.58	1.74	1.9	2.05	2.2
PROPYLENE	0.15	0.44	0.97	1.31	1.65	1.96	2.21	2.31	2.38	2.44	2.46
PROPADIENE	0	0	0	0	0	0	0.01	0.01	0.01	0.02	0.02
1-3-BUTADIENE	0	0	0	0	0	0	0	0	0	0	0.01
VINYLAETHYLENE	0	0	0	0	0	0	0	0	0	0	0.01
1-3-CYCLOPENTADIENE	0	0.01	0.06	0.1	0.17	0.28	0.42	0.5	0.6	0.7	0.81
BENZENE	1.93	3.93	6.73	8.29	9.83	11.25	12.43	12.91	13.3	13.59	13.79
TOLUENE	0.1	0.18	0.26	0.29	0.31	0.32	0.32	0.31	0.29	0.28	0.28
NAPHTHALENE	3.15	6.94	12.89	16.59	20.6	24.69	28.58	30.35	31.95	33.33	34.45
1-METHYLNAPHTHALENE	0.07	0.13	0.2	0.23	0.25	0.27	0.28	0.28	0.28	0.27	0.26
2-METHYLNAPHTHALENE	0.11	0.2	0.3	0.34	0.38	0.4	0.41	0.41	0.41	0.4	0.39
HYDROGEN	1.34	2.87	5.21	6.62	8.13	9.66	11.13	11.83	12.49	13.1	13.68
TOTAL (KG/HR)	100	100	100	100	100	100	100	100	100	100	100
METHANE CONVERSION (WT%)	6.9	14.89	27.1	34.52	42.43	50.44	58.15	61.79	65.25	68.5	71.54
PRODUCTS \ TEMPERATURE (K)	1425	1450	1475	1500	1525	1550	1575	1600	1700	1750	1800
METHANE	25.64	23.04	20.65	18.46	16.46	14.63	12.96	11.44	6.76	4.85	3.45
ACETYLENE	4.38	5.92	7.9	10.41	13.54	17.39	22.05	27.56	62.5	70.27	74.58
ETHYLENE	2.34	2.46	2.57	2.67	2.74	2.8	2.83	2.83	2.68	2.08	1.57
PROPYLENE	2.47	2.45	2.42	2.36	2.27	2.17	2.05	1.91	1.33	0.81	0.48
PROPADIENE	0.03	0.04	0.05	0.06	0.07	0.08	0.1	0.11	0.18	0.16	0.13
1-3-BUTADIENE	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0
VINYLAETHYLENE	0.01	0.02	0.02	0.03	0.04	0.06	0.07	0.09	0.22	0.2	0.17
1-3-CYCLOPENTADIENE	0.93	1.05	1.17	1.28	1.39	1.49	1.56	1.6	1.65	0.92	0.48
BENZENE	13.87	13.84	13.68	13.38	12.93	12.34	11.58	10.65	7.32	2.96	1.1
TOLUENE	0.26	0.25	0.23	0.21	0.19	0.17	0.15	0.13	0.07	0.02	0.01
NAPHTHALENE	35.23	35.64	35.61	35.07	33.99	32.23	29.78	26.64	0.01	0.01	0
1-METHYLNAPHTHALENE	0.25	0.24	0.22	0.21	0.19	0.17	0.14	0.12	0	0	0
2-METHYLNAPHTHALENE	0.38	0.36	0.34	0.31	0.28	0.25	0.21	0.18	0	0	0
HYDROGEN	14.21	14.7	15.14	15.54	15.9	16.22	16.5	16.75	17.26	17.71	18.04
TOTAL (KG/HR)	100	100	100	100	100	100	100	100	100	100	100
METHANE CONVERSION (WT%)	74.36	76.96	79.35	81.54	83.54	85.37	87.04	88.56	93.24	95.15	96.55

Figure 1. Equilibrium Methane Conversion

**Figure 2. Equilibrium Product Distribution
(Excluding Hydrogen)**

**Figure 3. Equilibrium Product Distribution
(Minor Products)**

Figure 4. Equilibrium Product Distribution
(Including Hydrogen)

Figure 5. Rate of Formation of Major Products
(Inlet CH_4 = 100 kg/hr)

CURRENT STATUS

Project is proceeding on schedule.

WORK PLANNED FOR NEXT QUARTER

Work for next quarter will concentrate on two specific activities:

- finalize construction and testing of the quench reactor;
- initiate runs on the aromatization of methane using the quenched-pyrolysis.

**DATE
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END