DIRECT AROMATIZATION OF METHANE
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ALTAMIRA INSTRUMENTS

149 Delta Drive

Pittsburgh, PA 15238

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EXECUTIVE SUMMARY

Further experiments have been performed on the assisted pyrolysis by the addition of a free-radical initiator, as well as on the initiation of pyrolysis by a solid surface using a variety of catalysts. The reaction has been studied in the temperature range of 850 - 1100°C, methane flow rates of 475 - 1000 Scc/min, and ethane flow rates of 21 - 42 Scc/min. Significant reduction in the pyrolysis temperature was observed in both cases, with measurable amounts of methane being converted at temperatures as low as 850°C. When ethane was added as a free-radical initiator, the major pyrolysis products were ethylene and propylene at temperatures below 950°C. At higher pyrolysis temperatures, the selectivity shifted toward benzene and acetylene which became the main analyzable products at 1050°C and 1100°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 products 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 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

During the ninth quarter of this project, the effect of free radical chain initiators in the methane pyrolysis reaction was further studied. In an attempt to lower the pyrolysis temperature, initiation of pyrolysis by a solid surface was also investigated using a variety of catalysts. A new quench reactor has been installed for studying the pyrolysis in presence of a catalyst.

EXPERIMENTAL

Axial Temperature Profile in the Pyrolysis Reactor

Reactor axial temperature profile has been measured under a 500 Scc/min flow of nitrogen. A movable, high temperature resistant, mineral-insulated, Alloy 6000 thermocouple was used. The thermocouple was placed inside the reactor and displaced over the entire length. Measurements were taken both in the presence and absence of a quench water flow.

Methane Pyrolysis in the Presence of a Free Radical Initiator

Ethane was used as a free radical initiator. The pyrolysis experiments were carried out at temperatures between 800°C and 1100°C. Methane and ethane flow rates of 500 - 1000 Scc/min and 24 - 49 Scc/min were used, respectively. The addition of ethane was studied only in the absence of quench water.

Pyrolysis of Ethane

Since ethane was used as free radical initiator it was of interest to find out its pyrolysis activity and product distribution in the absence of methane. Ethane pyrolysis was therefore investigated under conditions similar to the one used for methane pyrolysis. The reaction was carried out under 42 Scc/min and 500 Scc/min flow of ethane and helium, respectively. Helium flow was used to keep the space velocity of ethane comparable to the experiments where it was added to methane as a free radical initiator.

Catalytic Pyrolysis

Pyrolysis in the presence of a variety of catalysts including quartz chips, SiC, α -alumina, and barium manganese hexaaluminate ($\text{BaMnAl}_{11}\text{O}_{19}$) have been studied. Quartz chips were used to see the effect of an additional inert surface on the methane conversion. The selection of other catalysts was based on the basis of their moderate surface area and structural stability at the temperature of interest, up to 1200°C . Moreover, they are relatively inert to reduction during the methane activation step.

So far, the studies have only been performed using a straight quartz tube, i.e., in the absence of any quench water flow. Catalytic pyrolysis was carried out at temperatures between 800 and 1100°C . Methane flow rates of 500 - 1000 Scc/min, and 0.5 to 1.0 g of catalyst were used. The effect of addition of free radical initiator during catalytic pyrolysis was also studied. In the later experiments, the ethane flow rate was maintained between 24 - 49 cc/min.

For future catalytic pyrolysis experiments, a modified quench tube will be used. As before, this reactor will consist of two concentric tubes. However, as opposed to the quench reactor used in previous studies, in this reactor methane and other gases will flow in the inner tube whereas quench water will flow in the annular space between the two tubes. This will allow us to load the catalyst in the quench reactor which was not possible with the previous configuration.

RESULTS AND DISCUSSION

Problems encountered and remedial measures taken

A series of problems were encountered during the last quarter consuming a lot of time and energy. They are briefly summarized below along with the remedial measures taken:

1. Despite heat tracing the reactor effluent lines, we continued to experience problems related to lines plugging due to the condensation of heavy products. In order to prevent the plugging of the product vent line, we have further modified the system by installing a liquid trap on the line and heat tracing all the lines upstream of the trap. Additionally, the GC sampling valve as well as the sampling loop were further heated by the heat tapes.
2. As a result of the plugging of the sampling loop during one of the runs, an increase in the system pressure (> 30 psig, maximum reading on the pressure gauge) was observed. As a safety measure, a pressure relief valve is now installed at the reactor inlet line (set at 20 psig.).
3. The manual flow controller used to introduce propane as an analytical internal standard broke. Its orifice was found plugged with heavy hydrocarbons. This was probably caused by pressure buildup as a result of the plugging of the sampling loop. Despite all efforts, it could not be fixed and was therefore replaced with a new one which is working satisfactorily.
4. The GC temperature control board malfunctioned, resulting in occasional interruptions of GC operation. This board was replaced with a new one and is now working satisfactorily.

5. As a result of prolonged use and handling of heavy hydrocarbons, the GC column (GS Alumina) lost its separation efficiency. This resulted in broad and tailing peaks, poor resolution, and erroneous peak integration. A new columns was installed, tested, and calibrated.

Axial Temperature Profile in the Pyrolysis Reactor

(i) Without quench

Figure 1 shows the dimensions of the furnace heating zone and other relevant parts. The heating zone is 24 inches long surrounded by the heavy insulated material. The lower 9 inches of the reactor tube inside the heating zone were shielded with the quartz insulation. The thermocouple used for the furnace temperature controller is located in the middle of the furnace (i.e. 12 inches from either end of the heating zone). Figure 2 depicts the axial temperature profile in the quartz tube with 500 Scc/min of nitrogen flow and with the furnace temperature controller set at 1050°C. As a result of heat losses from the top and bottom, there was a slight temperature drop at the ends. The drop was much more significant for the lower three inches of the reactor, possibly because of the small draft of air leaking through the insulation into the furnace from the bottom. The section of the reactor between 4 and 16 inches from the top end of the heating zone was quite uniformly heated and was very close to the furnace temperature controller set point.

(ii) With quench

Figure 3 shows the axial temperature profile in the reactor tube under the various quench water flow rates with the remaining conditions similar to one described above. For all water flows, the temperature profile for the upper half part of the reactor tube was

somewhat similar to the one obtained in the absence of quench. As expected, in the lower half of the furnace, the temperature dropped faster than observed in the absence of quench and decreased more rapidly with increasing water flow. It dropped to even below 100° C (not shown in the Figure) at the outlet of the furnace casing, i.e., at 28 inches from the top. This section of the reactor in the immediate vicinity of the reactor which was not heated previously is now heat wrapped even when not introducing quench water.

Using this reactor configuration, i.e., with the reaction zone in the inner tube and the quench water flowing on the outside, in the annular space between the two tubes, high water flow rates were required in order to observe a substantial decrease in the gas temperature. Even at high water flow rates, the unquenched length remains important. This may explain the high tar contents of the products obtained when this reactor configuration was used.

Pyrolysis Studies

Table 1 summarizes the results of the qualified pyrolysis runs conducted during the ninth quarter of this project. As mentioned in the previous reports only a narrow temperature range was suitable for the production of aromatics, i.e., between 1000 and 1200°C. However, a catalytic pyrolysis process was expected to be initiated by a solid surface at lower temperatures. In the case of ethane addition to the feed ethane was expected to generate free radicals at significantly lower temperatures than methane. The temperature range of interest was lowered to 850 - 1100°C.

Free Radical Initiator Addition

Results for the run 93-1 and 93-2 show the methane conversions for the unquenched pyrolysis in the absence of ethane in the feed at 1100 and 1050°C, respectively. Note that the methane conversions were somewhat lower than reported earlier in quarterly report No. 6, for unquenched methane pyrolysis under similar conditions. The unquenched methane pyrolysis experiments were repeated several times to confirm the results. All the results were found to be reproducible within $\pm 10\%$, ruling out the possibility of experimental error.

This discrepancy in methane conversion is due to the use of new straight tube reactor which resulted in a different space velocity for the same flow rate used for the previous reactions. In the old quenched tube reactor, methane pyrolysis took place in the annular space between inner quench water and the outer tubes. Considering the entire length of the tube in the heating zone (24 in.) as a reaction zone, for the old quenched tube, the actual volume in which pyrolysis took place was 59.2 % higher than the volume of the straight tube reactor. This results in significant difference in the methane space velocity for the same inlet flow rate. For example, the methane space velocity for 475 ml/min flow through the straight tube reactor was 24.6 min^{-1} . In order to keep the same space velocity, the flow of methane for the quenched tube reactor should be 755 ml/min.

As mentioned earlier, ethane was used as a free radical initiator for the methane pyrolysis reaction. Addition of ethane to the methane feed was studied in the absence of quench water flow (Runs with prefixes 91 and 92 in Table 1). Some of the runs were repeated to see the reproducibility. Significant methane conversion was observed at

temperatures as low as 850°C. At 1100°C the methane conversions were around 40%.

Figure 4 shows the effect of temperature on methane conversion and the product selectivity for major analyzable products for the methane + ethane pyrolysis. At temperatures below 950°C, the major pyrolysis products were ethylene and propylene. With an increase in pyrolysis temperature the selectivity was somewhat shifted toward benzene and acetylene. At 1050°C and 1100°C, benzene and ethylene were the main analyzable product. Figure 5 shows a similar plot for the minor analyzable products. Apparently, with an increase in the pyrolysis temperature, the product selectivity for all of the minor products passed through a maxima. Figure 6 shows the effect of temperature on the total carbon (i.e. from methane and ethane) and the products yield.

Runs 87-1, 87-2, 87-4 were performed to find out the pyrolysis activity and the product distribution of ethane under similar conditions used for unquenched methane pyrolysis. To maintain the ethane space velocity in the reactor close to the one used when it was added to the methane feed, 42 ml/min of ethane feed were mixed with He flowing at 500 ml/min. It is evident from the results that, as compared to methane, ethane is far more active for pyrolysis since, even at 850°C, 91% of it was converted. The selectivity for "tar" was relatively higher and at all temperatures it was $\geq 55\%$. Table 2 shows the typical product distribution of ethane pyrolysis. Only a very small fraction of ethane had cracked to methane. Most of it was dehydrogenated to ethylene, acetylene or converted into "tar". Benzene was formed only in trace amounts.

Catalytic Pyrolysis

Pyrolysis in the presence of a variety of catalysts including quartz chips, SiC, α -alumina, and barium manganese hexaaluminate ($\text{BaMnAl}_{11}\text{O}_{19}$) have been carried out. Before testing solids which were expected to have some catalytic activity, the very first few runs were performed to find out the effect of an additional inert surface on the pyrolysis activity. Runs 79-1, 79-2, 79-3, and 80-1 showed the effect of temperature on unquenched pyrolysis of methane in the presence of quartz chips in the reactor. The result indicate that the additional surface from the quartz chips did not have any positive effect on the pyrolysis activity. At temperatures below 1050°C , there was almost no methane conversion. Similar observations were made in the absence of quartz chips, thus indicating that their presence did not modify the pyrolysis process.

Runs 81-1, 81-2 and 81-3 showed the effect of addition of ethane (a free-radical initiator) on the pyrolysis of methane in the presence of quartz chips. The runs were performed at 950°C and under different methane and ethane flows. In all cases a measurable amount of methane was converted, but the conversions were very low and did not change significantly with the amount of ethane in the feed. In all cases, the selectivity towards "tar" was significant.

Similar studies were performed using the three other catalysts including SiC, $\alpha\text{-Al}_2\text{O}_3$, and $\text{BaMnAl}_{11}\text{O}_{19}$ (BET surface $4.5\text{ m}^2/\text{g}$) characterized by the run numbers with prefixes 82, 83, and 84, respectively. The results for all three catalysts were quite similar. In the absence of ethane in the feed, at temperatures $\leq 950^{\circ}\text{C}$, the methane conversion was $< 1\%$ in all the cases, except for Run No. 82-1. At 1050°C , the methane conversion for the three

catalysts varied between 6-10% and the selectivity toward "tar" was > 35 %. In Run No. 82-1, even at 900°C a methane conversion of 21.3 % was observed. It is possible that SiC was very active even at 850°C and deactivated after the first run. This could explain why its higher activity was not evident in the subsequent higher temperature runs. This experiment will have to be repeated to confirm the results.

Conclusions

Assisted pyrolysis has been performed by the addition of ethane as a free-radical initiator. The effects of temperature and methane and ethane flow rates has been addressed during this reporting period. Measurable amounts of methane were converted at temperatures as low as 850°C, and the major pyrolysis products were ethylene and propylene at temperatures below 950°C. At higher pyrolysis temperatures, the selectivity shifted toward benzene and acetylene. Other reaction conditions will have to be studied in order to evaluate fully the effect of adding free radical initiators. More specifically, the effect of water quenching, ethane-methane ratio, and space velocity will have to be investigated.

The initiation of pyrolysis by a solid surface using a variety of catalysts has also been investigated. The preliminary results indicate that a significant reduction in the pyrolysis temperature may be obtained in the presence of some catalysts. However, the selectivity towards "tar" was significant in most cases. The reaction conditions have to be optimized in order to improve the selectivities towards valuable products.

CURRENT STATUS

The project is approximately three months behind schedule and running within the proposed costs.

WORK PLANNED FOR THE NEXT QUARTER

In the next quarter, we expect to conclude the experimental work on the assisted pyrolysis by addition of a free-radical initiator. We will also continue the investigation of the initiation of pyrolysis by a solid surface using a variety of catalysts.

Figure 1: Schematic of the furnace used for pyrolysis studies

Figure 2: Axial temperature profile in the pyrolysis reactor in the absence of a quench water flow.

Nitrogen flow = 500 ml/min

Furnace temperature controller setpoint = 1050°C

Figure 3: Axial temperature profile in the pyrolysis reactor at different quench water flow rates.

Nitrogen flow = 500 ml/min

Water flow = as indicated in the plot

Furnace temperature controller setpoint = 1050°C

Figure 4: Effect of temperature on methane conversion and selectivities for major analyzable products of methane + ethane unquenched pyrolysis.

Methane flow = 475 ml/min, Ethane flow = 42 ml/min

Figure 5: Effect of temperature on selectivities for minor analyzable products of methane + ethane unquenched pyrolysis.

Methane flow = 475 ml/min, Ethane flow = 42 ml/min

Figure 6: Effect of temperature on the product yield for the unquenched pyrolysis of methane + ethane.

Methane flow = 475 ml/min, Ethane flow = 42 ml/min

Table 1

Summary of Qualified Experimental Runs Performed During Reporting Period

Run No.	Temp. (°C)	Water flow (ml/hr)	Catalyst	Methane		Ethane		Carbon Selectivities (%)		
				Flow (ml/min)	Conv. (%)	Flow (ml/min)	Conv. (%)	Benzene	C ₂ C ₁₀	"Tar"
79-1	900	0	quartz ¹	1000	<1	0	-	x	x	x
80-1	950	"	"	"	<1	"	-	x	x	x
79-2	1000	"	"	"	<1	"	-	x	x	x
79-3	1050	"	"	"	3.7	"	-	1.3	30.7	68.0
81-1	950	"	"	"	1.7	42	100	1.3	57.0	43.0
81-2	"	"	"	475	4.4	42	"	8.2	62.4	37.6
81-3	"	"	"	"	5.1	21	"	5.1	54.1	45.9
82-1	900	"	SiC ¹	"	21.3	0	-	0	0	100
82-2	950	"	"	"	<1	"	-	x	x	x
82-3	1000	"	"	"	1.1	"	-	0	59.2	40.8
82-4	1050	"	"	"	6.21	"	-	9.3	47.1	52.9
82-5	950	"	"	"	4.25	42	100	7.2	48.3	51.7

1. Approx. 1 g
 x Cannot be accurately analyzed

Table 1 (Cont.)

Summary of Qualified Experimental Runs Performed During Reporting Period

Run No.	Temp. (°C)	Water flow (ml/hr)	Catalyst	Methane		Ethane		Carbon Selectivities (%)		
				Flow (ml/min)	Conv. (%)	Flow (ml/min)	Conv. (%)	Benzene	C ₂ -C ₁₀	"Tar"
83-1	900	0	α -Al ₂ O ₃ ¹	475	<1	0	-	x	x	x
83-2	950	"	"	"	<1	"	-	x	x	x
83-3	1000	"	"	"	1.0	"	-	x	x	x
83-4	1050	"	"	"	5.7	"	-	11.7	67.9	32.1
83-5	950	"	"	"	7.0	42	100.0	9.6	61.3	38.7
83-6	800	"	"	"	2.7	"	29.8	0	55.2	44.8
83-7	850	"	"	"	4.3	"	66.8	0.3	44.3	55.7
84-1	850	"	BaMnAl ₁₁ O ₁₉ ²	"	<1	0	-	x	x	x
84-2	950	"	"	"	<1	"	-	x	x	x
84-3	1050	"	"	"	9.6	"	-	10.2	45.3	54.7
84-4	950	"	"	"	6.1	42	100.0	0.5	34.2	65.8
84-5	850	"	"	"	6.0	"	73.9	10.1	60.4	39.6

1. Approx. 1.0 gm
 2. Approx. 0.5 gm
- x Cannot be analyzed accurately

Table 1 (Cont.)

Summary of Qualified Experimental Runs Performed During Reporting Period

Run No.	Temp. (°C)	Water flow (ml/hr)	Catalyst	Methane		Ethane		Carbon Selectivities (%)		
				Flow (ml/min)	Conv. (%)	Flow (ml/min)	Conv. (%)	Benzene	C ₂ C ₁₀	"Tar"
87-1	850	0	-	0 ¹	-	42	91.0	T	41.2	58.8
87-2	950	"	-	"	-	"	99.3	2.2	45.0	55.0
87-3	1100	"	-	"	-	"	100.0	0.6	39.2	60.8
91-4	850	"	-	475	9.2	"	61.5	0.1	84.5	15.5
91-3	950	"	-	"	9.9	"	96.8	5.0	76.5	23.5
91-1	1050	"	-	"	17.1	"	98.6	24.1	72.8	27.1
91-2	1100	"	-	"	42.9	"	99.1	17.6	40.4	59.6
92-1	1050	"	-	"	24.1	"	98.9	21.5	61.4	38.6
92-2	1100	"	-	"	39.1	"	99.3	14.9	33.3	66.7
93-1	1100	"	-	"	13.7	0	-	22.1	70.6	29.4
93-2	1050	"	-	"	< 2	"	-	x	x	x
94-1	1050	"	-	"	< 1	"	-	x	x	x

1 He = 500 cc/min, T In trace amounts, x Cannot be analyzed accurately

Table 2

Typical Product Distribution of Unquenched Ethane Pyrolysis in the Presence of Helium

Run No.	87-1	87-4
Temperature (°C)	850	1100
C ₂ Total Conversion (%)	91.0	100.0
C ₂ Conversion to Analyzable Products (C %)	37.5	39.2
C ₂ Conversion to "Tar" (C %)	53.5	60.8
Product Distribution (C %)		
CH ₄	1.2	0.8
C ₂ H ₄	27.7	23.3
C ₂ H ₂	2.8	9.1
Butyne	0.1	0.2
Unsaturated Hydrocarbons	3.5	0.4
Benzene	T*	0.6
Toluene	T*	T*
Naphthalene	T*	T*
Tar	58.8	61.8
C ₂ -C ₁₀	41.2	38.2

Ethane = 42 Scc/min, Helium = 500 Scc/min

No Quench Water Flow

* = In trace amounts