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DIRECT AROMATIZATION OF METHANE
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ALTAMIRA INSTRUMENTS

149 Delta Drive

Pittsburgh, PA 15238

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EXECUTIVE SUMMARY

Further investigations of assisted pyrolysis by the addition of ethane as a free-radical initiator were carried out during this reporting period . The effects of temperature, space velocity, and ethane/methane ratio, in the presence of quench water, have been addressed. As expected, reaction quenching resulted in lower conversions than without quenching, but also in significantly lower yields of "tar-like" products.

High C_2/C_1 ratios and low space velocities result in significant increases in the "tar-like" product yields. Very low ethane concentrations were required to initiate methane pyrolysis at lower temperatures without a major negative effect on product selectivities.

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 tenth quarter of this project, significant work has focussed on the effect of free radical chain initiators on methane pyrolysis reaction. In particular, the effects of quenching, ethane/methane ratio, and space velocity have been addressed. In addition, the effects of quench water flow rate and of partial reactor shielding on methane pyrolysis in the absence of ethane addition has been investigated with the new reactor configuration.

EXPERIMENTAL

Methane Pyrolysis in the Presence of a Free Radical Initiator

During this reporting period, the assisted pyrolysis by addition of a free-radical initiator was further investigated in the presence of quench water. Ethane was again used as the free-radical initiator. The pyrolysis experiments were carried out at temperatures between 850°C and 1100°C. Methane and ethane flow rates of 200-475 Scc/min and 8-42 Scc/min were used, respectively. The quench water flow rate was maintained at 250 mL/min for all the assisted pyrolysis experiments. In addition to the effect of quench water on methane pyrolysis in the presence of a free-radical initiator, the effects of ethane-methane ratio and space velocity were also investigated.

Effect of Quenching and Shielding on Methane Pyrolysis

The modified quench reactor described in the previous quarterly report was used for all pyrolysis experiments. The effect of quenching and partial shielding of the reactor in order to reduce the length of the reaction zone was also investigated using similar water flow rates to those used for the assisted pyrolysis (i.e., 250 mL/hr). Lower quench water flow rates were also used.

RESULTS AND DISCUSSION

Methane Pyrolysis in the Presence of a Free Radical Initiator

Table 1 summarizes the results of the quenched methane pyrolysis experiments conducted with and without ethane addition. As reported in the previous quarterly reports, methane conversion with or without quenching was negligible at temperatures below 1100°C (see runs 96-1 and 96-2 in Table 1) in the absence of a free radical initiator. The non-assisted methane pyrolysis was measurable only at 1100°C. However, the temperature range of interest was lowered to 850 - 1100°C in the case of ethane addition to the feed (runs 95-1 to 95-4). As expected, the methane conversions were lower at all temperatures than those obtained without reactor quenching at similar temperatures (see previous report). However, the "tar" selectivities and yields were much lower than those obtained without quenching.

Table 2 summarizes the results of the investigation of the effect of ethane-to-methane ratio at relatively low space velocities (runs 96-4 - 102-4). It appears that as the C_2/C_1 ratio was increased, the methane conversion reached a maximum at around $C_2/C_1(\times 100)$ of 4.5. Further increases in ethane flow rate do not seem to improve the methane conversion and may even be having a negative effect. Higher "tar" yields were obtained at the highest C_2/C_1 ratio.

Table 3 illustrates the effect of space velocity on methane conversion and the product selectivity for the methane + ethane pyrolysis at 1050°C and constant C_2/C_1 ratio. Ethane conversion, almost complete at temperatures above 950°C, was unaffected by changes in reaction

conditions. Methane conversion, on the other hand, was very sensitive to changes in space velocity. However, increases in methane pyrolysis rates with decreasing space velocities resulted mainly in increases in "tar" selectivity and yield. The yields of aromatics and C₂-C₁₀ products in general was not much affected by changes in space velocity.

Effect of Quenching and Shielding on Methane Pyrolysis

All the pyrolysis results discussed above were obtained in the modified quench reactor with the lower part shielded as described in the previous quarterly report. The shielding was essential in order to provide an axial temperature gradient, especially during quenching. As indicated by the results in Table 4, without the shield, quench water flow rate changes from 0 and 250 ml/hr had no effect on methane pyrolysis.

Table 5 illustrates the effect of shielding on methane conversion and product selectivities at a fixed quench water flow rate. The presence of the shield resulted in actual quenching of the reaction which resulted itself in significantly lower yields of "tar-like" products, with C₂-C₁₀ yields almost unaffected. Further experiments are required in order to ascertain that the lower "tar" yields are not only the result of lower conversions obtained under the effect of quenching. Pyrolysis experiments at constant conversion will be conducted for this purpose.

Conclusions

Further investigations of assisted pyrolysis by the addition of ethane as a free-radical initiator were carried out during this reporting period . The effects of temperature, space velocity, and ethane/methane ratio, in the presence of quench water, have been addressed. Reaction quenching resulted in lower conversions than without quenching, but also in significantly lower yields of "tar-like" products. However, it is not yet clear whether this decrease in the yield of "tar" is not only a consequence of lower conversions obtained as a result of reaction quenching. Further experiments are necessary to clarify this point.

High C_2/C_1 ratios and low space velocities result in significant increases in the "tar-like" products yields. Very low ethane concentrations were required to initiate methane pyrolysis at lower temperatures without a major negative effect on product selectivities.

The latest experiments with the new reactor configuration demonstrated also that the shielding of the lower part of the reactor was necessary to provide the expected quenching of the reaction.

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. Controlled experiments at constant conversion with and without quenching or without the partial reactor shield will also be conducted in order to evaluate the true effect of reaction quenching on selectivity.

Table 1. Effect of Ethane Addition on Methane Pyrolysis¹

Run No.	95-2	95-1	95-4	95-3	96-5	96-2	96-1
Temp (°C)	1100	1050	950	850	1100	1050	950
Methane Flow (ml/min)	475	475	475	475	475	475	475
Methane Conv. (%)	19	7.9	2.7	<1	4	<1	<1
Ethane Flow (ml/min)	42	42	42	42	0	0	0
Ethane Conv. (%)	99	98	94	42	-	-	-
Total C Conv. (%)	32	22	17	<1	4	<1	<1
Selectivities							
Ethylene	15.7	27.8	58.6	x	36.4	x	x
Acetylene	14.5	18.5	5.7	x	10.4	x	x
Aromatics	26.9	23.4	4.1	x	16.7	x	x
C ₂ -C ₁₀	60.7	80.0	79.9	x	88.0	x	x
Tar	39.3	20.0	20.3	x	12.0	x	x
Yields ²							
Ethylene	6.1	5.0	10.0	x	1.5	x	x
Acetylene	4.1	4.6	1.0	x	0.4	x	x
Aromatics	8.5	5.2	0.7	x	0.7	x	x
C ₂ -C ₁₀	19.3	17.7	13.6	x	3.5	x	x
Tar	12.5	4.4	3.4	x	0.5	x	x

1. New reactor configuration; Lower 9 inches of the reactor shielded; Quench water flow rate = 250 ml/hr.
 2. Yields in the presence of ethane are calculated based on total carbon conversion.
- x Cannot be analyzed accurately.

Table 2

Effect of Ethane/Methane Ratio on Methane Pyrolysis¹

Run No.	96-4	102-4	102-1	102-2
Methane Flow (ml/min)	200	200	200	200
Ethane Flow (ml/min)	0	9	18	36
C_2/C_1 (x100)	0	4.5	9	18
Methane Conv. (%)	1.4	17	16	13
Ethane Conv. (%)	-	98	99	99
Total C Conv. (%)	1.4	24	29	39
Selectivities				
Ethylene	x	14.1	14.7	13.7
Acetylene	x	8.1	9.4	7.5
Aromatics	x	23.9	24.3	22.9
C_2-C_{10}	x	51.0	54	47.5
Tar	x	49.0	46	52.5
Yields ¹				
Ethylene	x	3.4	4.3	5.3
Acetylene	x	2.0	2.8	2.9
Aromatics	x	5.8	7.1	8.9
C_2-C_{10}	x	12.3	15.9	18.5
Tar	x	11.9	13.5	20.5

1. New reactor configuration; Lower 9 inches of the reactor shielded; T = 1050°C; Quench water flow rate = 250 ml/hr.
 2. Yields are calculated based on total carbon conversion.
- x Cannot be analyzed accurately.

Table 3

Effect of Space Velocity on Methane Pyrolysis
in the Presence of Ethane¹

Run No.	95-1	102-3	102-1
Methane Flow (ml/min)	475	300	200
Ethane Flow (ml/min)	42	26	18
C_2/C_1 (x100)	8.8	8.7	9.0
Methane Conv. (%)	8	13	16
Ethane Conv. (%)	98	99	99
Total C Conv. (%)	22	27	29
Selectivities			
Ethylene	27.7	17.7	14.7
Acetylene	18.5	11.2	9.4
Aromatics	23.4	25.4	24.3
C_2-C_{10}	80.0	59.8	54
Tar	20.0	40.2	46
Yields ²			
Ethylene	6.1	4.7	4.3
Acetylene	4.1	3.0	2.8
Aromatics	5.2	6.8	7.1
C_2-C_{10}	17.7	16.0	15.9
Tar	4.4	10.8	13.5

1. New reactor configuration; Lower 9 inches of the reactor shielded; T = 1050°C; Quench water flow rate = 250 ml/hr.
2. Yields are calculated based on total carbon conversion.

Table 4

Effect of Quench Water Flow Rate on Methane Pyrolysis¹

Run No.	96-6	99-5	97-2
Methane Flow (ml/min)	200	200	200
Quench Water Flow (ml/hr)	250	125	0
Methane Conv. (%)	32	31	31
Selectivities			
Ethylene	16.3	36.4	11.0
Acetylene	9.4	10.4	8.2
Aromatics	20.3	20.4	21.5
C ₇ -C ₁₀	43.8	45.1	44.1
Tar	56.2	54.9	55.9
Yields			
Ethylene	3.4	4.0	3.5
Acetylene	2.0	1.5	2.5
Aromatics	6.4	6.3	6.7
C ₂ -C ₁₀	13.9	13.9	13.8
Tar	17.8	16.9	17.4

1. New reactor configuration; No reactor shielding; T = 1100°C.

Table 5

Effect of Shielding on Product Selectivity

Run No.	99-6	96-3
Temp (°C)	1100	1100
Reactor Shielding	N	Y
Methane Flow (ml/min)	200	200
Quench Water Flow (ml/hr)	250	250
Methane Conv. (%)	32	21
Selectivities		
Ethylene	11.2	16.3
Acetylene	9.1	9.4
Aromatics	20.3	27.3
C2-C10	43.8	67.0
Tar	56.2	41.5
Yields		
Ethylene	3.5	3.4
Acetylene	2.9	2.0
Aromatics	6.4	6.1
C2-C10	13.9	12.1
Tar	17.8	8.6