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DIRECT AROMATIZATION OF METHANE

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by

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EXECUTIVE SUMMARY

During the eleventh quarter of this project, significant time was spent in reinstalling the reactor system in Altamira's new location. In addition, the experimental system was modified in order to include a shorter furnace, 8-inch heated length compared to the original 24-inch heated length. With the shorter reactor, contact times in the order of milliseconds can be achieved. Following the physical modification, a number of gas phase experiments were conducted in order to verify the operation of the system. As expected, conversions were typically lower in the shorter furnace. Preliminary investigations of the initiation of pyrolysis by a solid surface using $\alpha\text{-Al}_2\text{O}_3$ were also carried out during this reporting period .

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 eleventh quarter of this project, most of the time was spent in dismantling and reassembling the reactor system in Altamira's new location. In addition, the experimental system was modified in order to include a shorter furnace, 8-inch heated length compared to the original 24-inch heated length. Following the physical modification, a number of gas phase experiments, with and without addition of a free radical initiator, were conducted in order to verify the operation of the

system. Preliminary investigations of the initiation of pyrolysis by a solid surface using $\alpha\text{-Al}_2\text{O}_3$ were also carried out during this reporting period .

EXPERIMENTAL

System Modification

The preliminary experiments on catalytic pyrolysis of methane (reported in quarterly report No. 9) were carried out in an unquenched 24 in. long reactor. The results have shown that in the presence of a catalyst, most of the methane converted formed mainly tar products. In addition, it was not possible to segregate between the effect of the catalyst and the gas phase reaction. These results suggested that shorter contact times may be necessary for optimum production of C₂-C₁₀ hydrocarbons. To minimize the effect of gas phase reaction during catalytic pyrolysis and to achieve shorter contact times, the original system was modified by replacing the original furnace with a shorter furnace, 8-inch heated length compared to the original 24-inch heated length. The modified reactor has a similar diameter to the one used in previous studies. Contact times in the order of milliseconds can be achieved with this new system.

Methane Pyrolysis in the Blank Reactor in the Absence and Presence of Free Radical Initiator

Following the physical modification of the system, a number of gas phase pyrolysis experiments were conducted. The purpose of these experiments was to verify the operation of the system and to obtain base line values for activity and product selectivities in the absence of a catalyst. for comparison with results of catalytic pyrolysis. Experiments without and with addition of ethane,

the free radical initiator, were carried out. A fixed methane flow of 200 Scc/min was used. For the pyrolysis studies in the presence of the free radical initiator, ethane flow rates of ca. 6 Scc/min were used while keeping the methane flow rate constant. In both cases, the reaction temperature was varied from 850 to 1100°C.

Catalytic Pyrolysis

Following the blank tests, some methane pyrolysis experiments were carried out in the presence of a catalyst, α -Al₂O₃. The catalytic pyrolysis was carried out at temperatures between 850 and 1100°C. A methane flow rate of 200 Scc/min and 0.5 g of catalyst were used.

Prior to the pyrolysis reaction, the catalyst was calcined in-situ under flowing air at 1100°C for approximately 16 hours. Following pretreatment, the catalyst sample was brought to reaction temperature under nitrogen flow. The flow was then switched to methane and a GC sample was taken after 1.5 min of reaction. In subsequent runs, any coke formed on the catalyst was burned off by flowing air for 30 min at 700°C. This practice has ensured that the catalyst surface was coke free for the subsequent reaction carried out at a different temperature.

RESULTS AND DISCUSSION

Tables 1 and 2 summarize the results of the methane pyrolysis experiments conducted with and without ethane addition, respectively. As reported in the previous quarterly reports, methane conversion was negligible at temperatures below 1100 °C in the absence of a free radical initiator (Table 1). When ethane was added, higher conversions of methane were observed even at the lower

temperatures (Table 2). As expected, the methane conversions in all cases were lower at all temperatures than those obtained with the longer reactor. However, the product selectivities were comparable with high levels of tar being produced when ethane was added.

Table 3 summarizes the results of the preliminary investigation of pyrolysis initiation by a solid surface using α -Al₂O₃. The results indicate significant methane conversions at temperatures as low as 950 °C. However, the selectivity towards "tar" was significant under the conditions used. The reaction conditions may still need to be optimized in order to improve the selectivities towards valuable products.

CURRENT STATUS

The project is within schedule and running within the proposed costs.

WORK PLANNED FOR THE NEXT QUARTER

In the next quarter, we expect to complete the experimental part of this project with further investigations of the initiation of pyrolysis by a solid surface using a variety of catalysts. A series of catalysts including SiC, α -Al₂O₃, and hexaaluminates with various surface areas and composition have been selected for this purpose.

Table 1

Summary of results of methane pyrolysis without ethane addition

Run No.	Temp. (°C)	Catalyst	Methane		Ethane		Carbon Selectivities (%)			
			Flow (ml/min)	Conv. (%)	Flow (ml/min)	Conv. (%)	C ₂	Aromt	C ₂ -C ₁₀	"Tar"
116-2	950	-	200	<1	0	-	x	x	x	x
122-2	"	-	"	<1	"	-	x	x	x	x
116-5	1050	-	"	<1	"	-	x	x	x	x
119-5	"	-	"	1.5	"	-	x	x	x	x
122-1	"	-	"	1.5	"	-	x	x	x	x
119-3	1100	-	"	8.0	"	-	34.0	25.4	77.0	23.0
125-1	"	-	"	8.4	"	-	29.5	20.0	66.4	33.6

x Cannot be analyzed accurately
 * Short Reactor

Table 2

Summary of results of methane pyrolysis with ethane addition

Run No.	Temp. (°C)	Catalyst	Methane		Ethane		Carbon Selectivities (%)			
			Flow (ml/min)	Conv. (%)	Flow (ml/min)	Conv. (%)	C ₂	Aromt	C ₂ -C ₁₀	"Tar"
119-5	950	-	200	1.5	6.2	83.8	x	x	x	x
125-4	"	-	"	1.7	"	80.2	x	x	x	x
119-1	1050	-	"	9.7	"	95.9	20.7	26.0	60.7	39.3
125-3	"	-	"	6.0?	"	57.2	?	?	?	?
119-5	1100	-	"	21.6	"	97.7	12.5	25.4	43.6	56.4
125-2	"	-	"	20.9	"	99.2	21.8	24.5	56.6	47.4

x Cannot be analyzed accurately
 * Short Reactor

Table 3

Summary of results of methane pyrolysis in the presence of a catalyst

Run No.	Temp. (°C)	Catalyst	Methane		Ethane		Carbon Selectivities (%)			
			Flow (ml/min)	Conv. (%)	Flow (ml/min)	Conv. (%)	C ₂	Aromt	C ₂ -C ₁₀	"Tar"
118-1	850	α -Al ₂ O ₃	200	0	0	-	0	0	0	0
120-1	950	"	"	4.5	"	-	1.7	0	8.7	91.4
120-2	1050	"	"	8.5	"	-	6.7	0.2	14.1	85.9
121-1	"	"	"	6.6	"	-	6.6	4.5	14.8	85.2
121-3	"	"	"	6.1	"	-	10.3	0.6	22.2	77.8
118-4	1100	"	"	20.2	"	-	NA			
120-3	"	"	"	17.8	"	-	4.2	0.4	11.8	88.2
120-4	"	"	"	16.9	"	-	11.6	4.9	19.9	80.1

1 Approx. 0.5 g of catalyst used
 x Cannot be analyzed accurately
 * Short Reactor