TITLE: **THE DIRECT AROMATIZATION OF METHANE**

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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. Thermodynamic calculations have shown that when the reaction is limited to the formation of C_2 to C_{10} products, yields of aromatics can exceed 40% at temperatures of 1200°C. 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 works remains in optimizing the quenching process and this is one of the goals of this program. We are also studying 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.

ACCOMPLISHMENTS AND CONCLUSIONS: During the first two years of this project, a quench reactor system was designed and constructed and a study of the effect of process variables on methane conversion and product selectivities was carried out.

During this last period, significant work has focussed on evaluating the effect of free-radical initiators on methane pyrolysis. Most of the work dealt with a study on the effect of ethane addition on reaction rates and selectivities. Effects of temperature, space velocity, ethane/methane ratio, reaction quenching, quench water flow rates, and reactor configuration were investigated. In addition, studies of initiation of pyrolysis by a solid surface using a variety of catalysts have been started.

Significant reduction in the pyrolysis temperature was observed both in the cases of assisted pyrolysis by the addition of a free-radical initiator, as well as when pyrolysis was initiated on a catalyst surface.

EXPERIMENTAL PROCEDURE

Axial Temperature Profile in the Pyrolysis Reactor

The quench-reactor system designed for this study was described in previous conference proceedings [1]. A new quench reactor has been installed for studying the pyrolysis in presence of a catalyst. 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 flow in the inner tube whereas quench water flows in the annular space between the two tubes. This configuration is more practical than the previous one to load the catalyst into the quench reactor.

The 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 addition of ethane was first studied in the absence of quench water. 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 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/hr 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 ethane-methane ratio and space velocity were also investigated.

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 ($BaMnAl_{11}O_{19}$) 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 latter experiments, the ethane flow rate was maintained between 24-49 cc/min.

RESULTS AND DISCUSSION

Axial Temperature Profile in the Pyrolysis Reactor

(i) Without quench

The heating zone of the furnace 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 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 1 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 loses 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 2 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, water flow rates as low as 250 ml/hr resulted in a substantial decrease in the gas temperature.

Free Radical Initiator Addition

Table 1 summarizes the results on the effect of ethane addition on methane pyrolysis runs conducted without and with quench water. 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. As mentioned earlier, ethane was used as a free radical initiator for the methane pyrolysis reaction. Addition of ethane to the methane feed was first studied in the absence of quench water flow (Runs with prefixes 91 and 92 in Table 1). Some of the runs were repeated for reproducibility checks. Significant methane conversion was observed at temperatures as low as 850°C. At 1100°C the methane conversions were around 40%.

Figure 3 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 4 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 5 shows the effect of temperature on the total carbon (i.e. from methane and ethane) and the product yields.

Runs 87-1, 87-2, 87-3 were performed to evaluate ethane pyrolysis rates and the product distribution 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 reactive 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 ≥ 55%. 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.

The results of the quenched methane pyrolysis experiments conducted with and without ethane addition are also included in Table 1 (Runs with prefixes 95 and 96, respectively). As with the unquenched reaction, methane conversion with quenching was negligible at temperatures below 1100°C (see runs, 93-2, 94-1, 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. 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 $C_2/C_1(x100)$ 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 C_2-C_{10} products in generals was not much affected by changes in space velocity.

Catalytic Pyrolysis

A catalytic pyrolysis process was expected to be initiated by a solid surface at lower temperatures. The preliminary results of pyrolysis in the presence of a variety of catalysts including quartz chips, SiC, α-alumina, and barium manganese hexaaluminate ($BaMnAl_{11}O_{19}$) are summarized in Table 4. 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, α-Al_2O_3, and $BaMnAl_{11}O_{19}$ (BET surface 4.5 m^2/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°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.

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 investigated without reaction quenching. 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.

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. 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 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.

FUTURE PLANS

In the remaining time before the end of this project, 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.

REFERENCES

(1) G. Marcelin, R. Oukaci, and R.A. Migone, "Direct Aromatization of Methane", Proceedings: Coal Liquefaction and Gas Conversion Contractors Review Conference (1994).

Table 1. Effect of Ethane Addition on Methane Pyrolysis with and without Quenching

Run No.	Temp (°C)	Methane		Ethane		Carbon Selectivities (%)		
		Flow (ml/min)	Conv. (%)	Flow (ml/min)	Conv. (%)	Benzene	C_2-C_{10}	"Tar"
87-1	850	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
95-2[2]	1100	"	19	42	99	25.2	60.7	39.3
95-1[2]	1050	"	7.9	"	98	23.0	80.0	20.0
95-4[2]	950	"	2.7	"	94	3.4	79.9	20.3
95-3[2]	850	"	<1	"	42	x	x	x
96-5[2]	1100	"	4	0	-	13.3	88.0	12.0
96-2[2]	1050	"	<1	0	-	x	x	x
96-1[2]	950	"	<1	0	-	x	x	x

[1] He = 500 cc/min; T = Trace amounts; x = Cannot be analyzed accurately

[2] Quenched reaction: Quench water flow rate = 250 ml/hr.

Table 2. Effect of Ethane/Methane Ratio on Methane Pyrolysis[1]

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. 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 Ethane[1]

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. T = 1050°C; Quench water flow rate = 250 ml/hr.
2. Yields are calculated based on total carbon conversion.

Table 4. Effect of Catalyst Surface on (Unquenched) Pyrolysis Initiation

Run No.	Temp. (°C)	Catalyst	Methane		Ethane		Carbon Selectivities (%)		
			Flow (ml/min)	Conv. (%)	Flow (ml/min)	Conv. (%)	Benzene	C_2-C_{10}	"Tar"
79-1	900	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	" *c4a$b100g2P	-	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 4. Effect of Catalyst Surface on (Unquenched) Pyrolysis Initiation (Contd.)

Run No.	Temp. (°C)	Catalyst	Methane		Ethane		Carbon Selectivities (%)		
			Flow (ml/min)	Conv. (%)	Flow (ml/min)	Conv. (%)	Benzene	C_2-C_{10}	"Tar
83-1	900	α-Al_2O_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

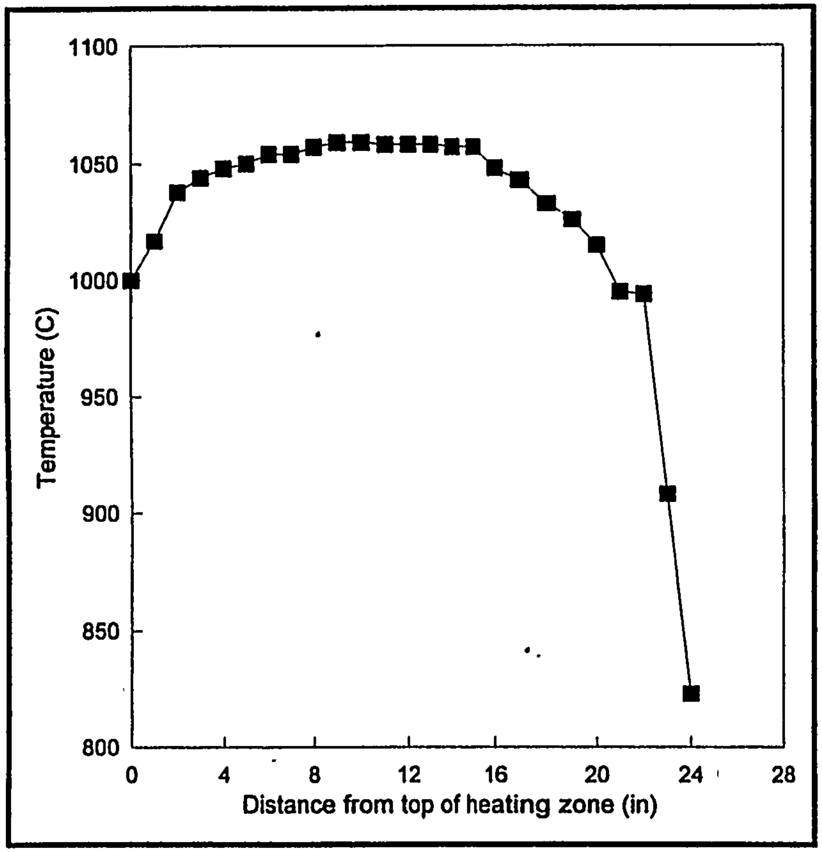

Figure 1. Axial temperature profile in the pyrolysis reactor in the absence of quench water flow (Nitrogen flow = 500 ml/min; Furnace temperature controller setpoint = 1050°C)

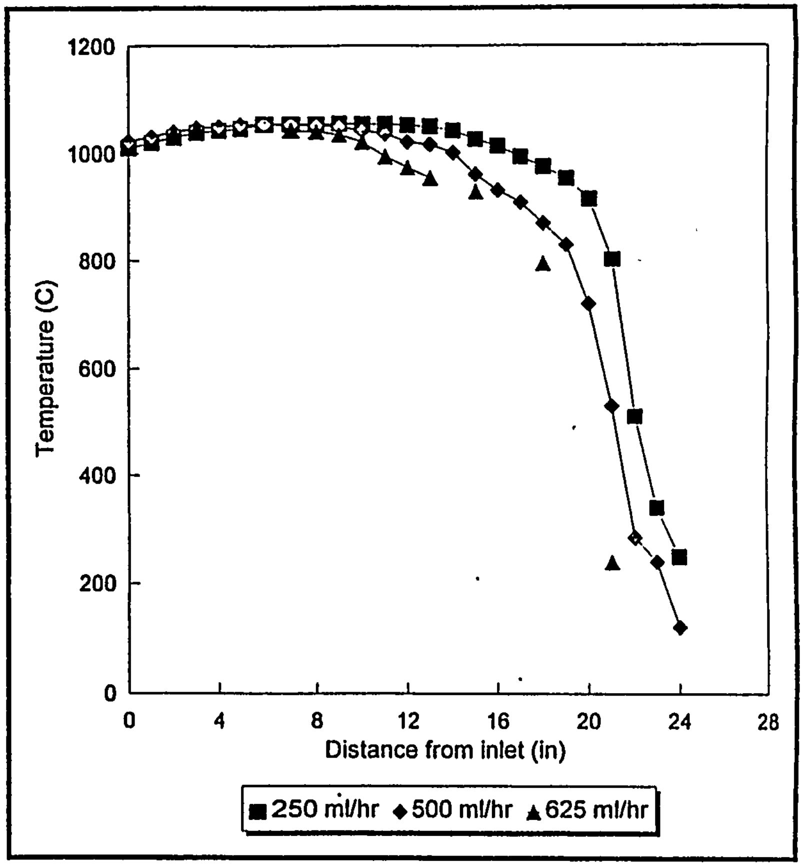

Figure 2. Axial temperature profile in the pyrolysis reactor at different quench water flow rates (Nitrogen flow = 500 ml/min; Water flow = as indicated on the plot; Furnace temperature controller setpoint = 1050°C)

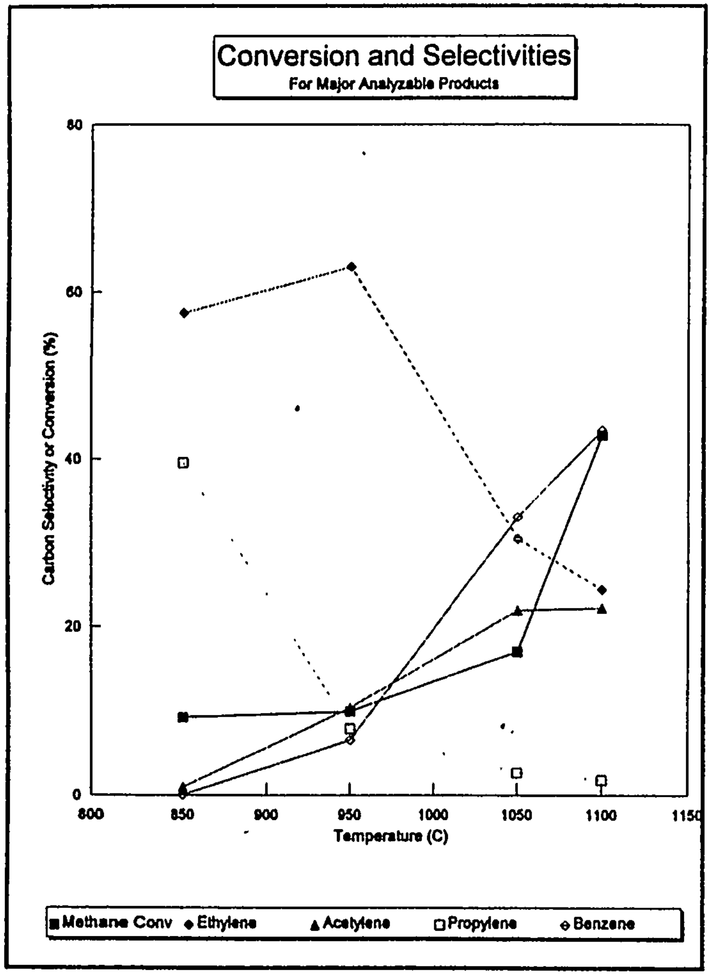

Figure 3. Effect of temperature on methane conversion and selectivities for major analyzable products of methane + ethane unquenched pyrolysis. (Methane flow = 475 ml/min, Ethane flow = 42 ml/min)

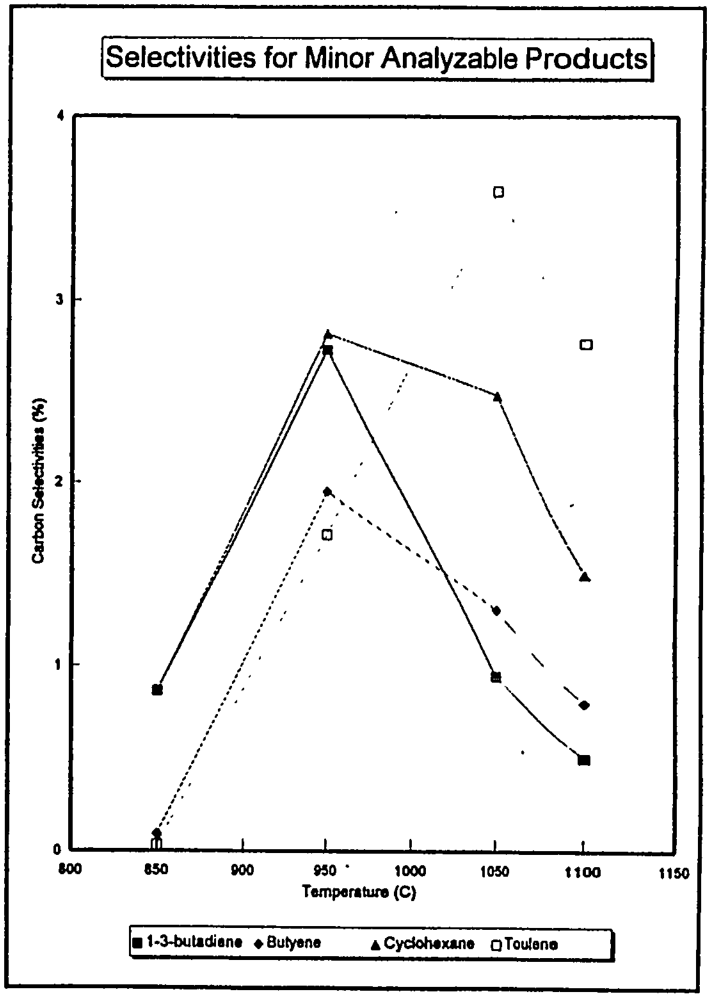

Figure 4. Effect of temperature on selectivities for minor analyzable products of methane + ethane unquenched pyrolysis. (Methane flow = 475 ml/min, Ethane flow = 42 ml/min)

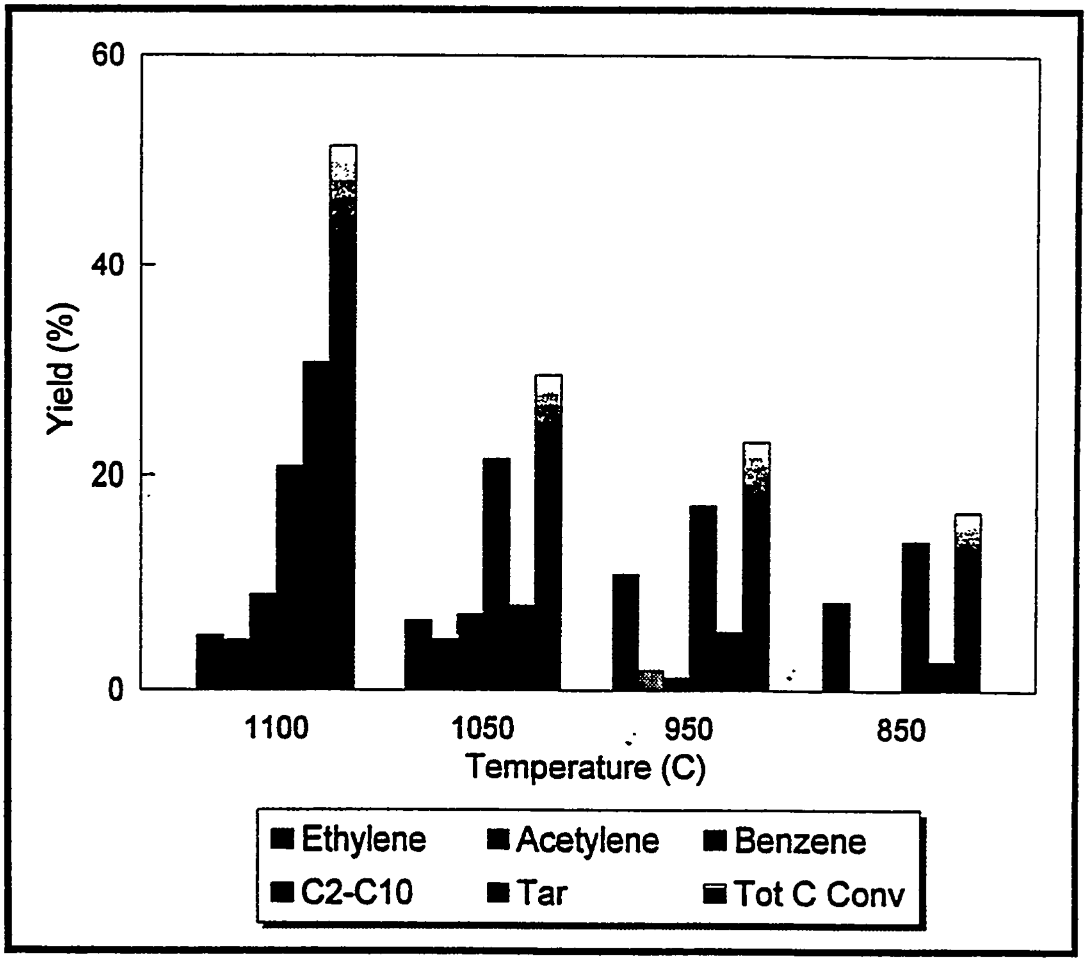

Figure 5: Effect of temperature on the product yield for the unquenched pyrolysis of methane + ethane (Methane flow = 475 ml/min, Ethane flow = 42 ml/min)