

Enhanced Ethylene Production via Flash Methanolysis of Coal

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INTRODUCTION

According to a recent report, an estimated 31 billion pounds of ethylene was produced in the U.S. alone (1). Ethylene is an important raw material in the vast plastic and polymer markets. An upward trend in the demand for ethylene has been predicted for the future years. Currently, ethylene is produced mainly through thermal and catalytic hydrocracking of ethane and other hydrocarbons. Although a large amount of work has been performed on the production of gaseous and liquid fuels from coal, much less attention has been focused on the production of ethylene using coal as the raw material. In an on-going pyrolysis research project at the Brookhaven National Laboratory, the methods to increase the yield of ethylene through flash methanolysis of coal is being investigated. Flash methanolysis is defined as pyrolysis of coal under pressure in an atmosphere of methane. This study attempts to identify the influence of important process variables such as reaction temperature, gas pressure, solids residence time, gas/solids ratio etc. on the production characteristics of ethylene and other pyrolysis products.

EXPERIMENTAL

Much of the work discussed in this paper was done using a New Mexico sub-bituminous coal. Other coals of ranks varying from lignite to bituminous were used for comparison purposes. These included North Dakota lignite, Wyodak lignite, Montana Rosebud sub-bituminous and Illinois no. 6 bituminous coals. The proximate and ultimate analyses of these coals are given in Table 1.

The methanolysis experiments were carried out in a highly instrumented down-flow entrained tubular reactor. The reactor, made of Inconel 617 alloy, is heated electrically by four clam-shell type heaters and designed for a maximum pressure of 4000 psi. The detailed description of the design, construction and operation of the reactor has been published (2). The schematic representation of the complete reactor set-up is shown in Figure 1. Coal particles of 150 μm or less in diameter, mixed with 10% by weight of Cab-O-Sil, are fed by gravity at the rate of approximately 500 gm/hour into the top of the 1-in.-i.d. by 8-ft-long reactor. Methane is preheated to 600°C before feeding into the tubular reactor held at isothermal conditions along the length of the reactor at the temperature of interest. The gas samples could be taken from any one of the four sample taps located at 2-ft intervals along the length of the reactor and analyzed via an on-line GC. Products heavier than BTX ($>C_9$) are collected in the water-cooled condensers and analyzed separately. The individual product yields are determined as percent of carbon contained in the feed coal.

RESULTS AND DISCUSSION

Pyrolysis of coal at temperatures higher than 600°C generally results in the formation of light hydrocarbon gases, oxides of carbon, BTX and tar. The product distribution, however, depends on the coal type, the processing conditions, the pyrolysis atmosphere and the method of heating.

A survey of the recent research literature on coal pyrolysis and the composition of various pyrolysis products is available (3). Traditionally, the pyrolysis of coal has been carried out in H₂, He, N₂ or CO atmospheres; Ar, H₂O and CO₂ have also been used in a few instances. Except the previous reports from our laboratory (4), the pyrolysis of coal in an atmosphere of methane, to our knowledge, has not been documented in the literature. The main interest in the use of methane as the pyrolysis medium lies in the fact that for hydrogenation of coal, a large resource of natural gas can be used in the place of hydrogen which has no known natural sources.

The flash methanolysis of New Mexico sub-bituminous coal at temperatures higher than 700°C, produced significant quantities of CO, ethylene, BTX and tar; small amount of CO₂ also was detected. Methane produced due to pyrolysis of coal could not be distinguished from the entraining methane gas. In order to determine the net production or consumption of methane, a calibrated mass flowmeter was placed on the methane inlet to the reactor; the experimental set-up already contained a calibrated positive displacement meter at the reactor outlet. The mole percent of methane in the product-laden gases was determined via GC analysis. The methane and total gas flow data, at steady reactor operating conditions, are shown in Table 2 for several runs. The difference between the methane flows, calculated from the limited data available and shown in the last column of Table 2, indicates a negligible net consumption or production of methane within the limits of combined experimental errors which has been estimated to be approximately ±5%.

At 900°C and 50 psi total gas pressure, 21.4% of carbon in the feed coal was converted to products of which approximately half was made up of ethylene. The remaining products were BTX (2.9%C) and CO_x(8.5%C). Table 3 shows that the total carbon conversion tends to increase with pressure up to 200 psi before falling off to a lowest level of 20.0%C at 500 psi. The decrease in total conversion at 500 psi is mainly due to the decrease in the yields of CO and ethylene. There is very little variation in the yield

of CO_2 as a function of pressure. The separate curves for BTX and tar yields, in Figure 2, go through a maximum and minimum respectively at 200 psi. An increase in the methane pressure had an adverse effect on the ethylene yield. At higher pressures, the hydrogenation of ethylene to produce ethane is facilitated.

Table 4 shows the effect of reactor temperature on the methanolysis product distribution and illustrated in Figure 3. There is a marked increase in the total carbon conversion with increasing temperature; this is mainly due to a pronounced increase in the yield of ethylene and BTX. As high as 12.7% carbon was converted to ethylene at 1000°C and approximately 9% was converted to BTX. In contrast, pyrolysis in inert helium atmosphere produced only 2.2% ethylene and 7% BTX under the same conditions. Thus, at 1000°C , 5-6 times greater yield of ethylene is produced during flash methanolysis when compared to helium pyrolysis. When the New Mexico coal was pyrolyzed in the atmospheres of He or N_2 or CO, the maximum yield of ethylene obtainable at 50 psi was approximately 6% and as shown in Figure 4, the maxima occurred around 900°C . A comparison of the maximum yields of ethylene shows that more than twice the amount of ethylene is produced in an atmosphere of methane than any other pyrolysis atmospheres investigated. The ethylene yields from methanolysis experiments were somewhat closer to ethylene yields from pyrolysis in other atmospheres up to 800°C . At temperatures higher than 800°C , only methanolysis experiments recorded a continued increase in the yield of ethylene with increase in the reactor temperature. This clearly indicates the effectiveness of methane atmosphere for enhanced yield of ethylene during pyrolysis of coal. Several blank runs, in the absence of coal, confirmed that reactor walls do not catalyze the decomposition of methane to form products, including ethylene. Blank runs with pyrolysis char, coconut char and Cab-O-Sil additive also showed no formation of ethylene under the same conditions.

In addition to the effect of temperature and pressure, the effect of methane to coal feed ratio on the methanolysis product distribution was investigated. The results are shown in Table 5. In these experiments, the

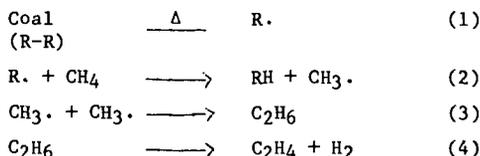
methane feed rate was held almost constant while varying the coal feed rate. This table shows that an increase in the methane to coal feed ratio favors the production of ethylene and BTX as well. However, the ethylene concentration in the product stream follows an opposite trend as seen in Table 5. The maximum concentration of ethylene obtainable, under the conditions investigated, is slightly over 2% and the dependence of ethylene concentration on the coal feed rate, rather than on the methane to coal feed ratio, is apparent.

Using the data in Table 5, a linear regression analysis was made to describe the relation between the individual product yields and the methane/coal feed ratio. The following expressions were obtained:

$$\begin{aligned}
 \%C \text{ C}_2\text{H}_4 &= 2.39 x + 3.11; R^2 = 0.90 \\
 \%C \text{ H.C. Gases} &= 2.57 x + 3.05; R^2 = 0.91 \\
 \%C \text{ BTX} &= 1.89 x + 1.30; R^2 = 0.94 \\
 \%C \text{ Total H.C.} &= 4.46 x + 4.36; R^2 = 0.93 \\
 \%C \text{ CO}_x &= 0.67 x + 3.89; R^2 = 0.63 \\
 \%C \text{ Total Conv.} &= 5.98 x + 6.90; R^2 = 0.90
 \end{aligned}$$

where x = methane/coal feed ratio and R^2 = the correlation coefficient. The rather low correlation coefficient for CO_x is attributed to errors occasionally encountered in the measurement of CO during on-line GC analysis of the product gases.

The enhanced yield of ethylene in flash methanolysis experiments probably has a free radical origin. An abundance of thermal free radicals from coal at elevated temperatures facilitates the decomposition of methane to produce methyl radicals which can lead to the formation of ethylene, probably with an ethane intermediate, as follows:



High temperatures favor reaction (4) in the forward direction as written. Other free radical reactions, leading to the formation of higher hydrocarbons and heavy materials are also possible which might explain the increased liquid product yields in these experiments. Since no net consumption of methane was noticed, it is reasonable to assume that (1) a part of ethylene comes from coal due to thermal effects as in the case of straight inert helium gas pyrolysis and (2) the remaining ethylene comes from the methyl radicals generated from coal which would have been converted to methane in helium pyrolysis via autohydrogenation effect. In other words, methane, at high concentrations, causes part of the coal radicals to form ethylene instead of methane. The methane formed from coal appears to be in balance with the reacted methane gas. For example, at 1000°C and 50 psi helium pressure, the total hydrocarbon gases yield was 10.9% (5.5% CH₄ + 5.4% ethylene) which compares well with 12.1% total hydrocarbon gases (12.0% C₂H₄ + 0.1% C₂H₆) in Table 5 under an identical gas to coal feed ratio. Thus it is seen that methane acts as a shuttler in methanolysis experiments.

Table 6 summarizes the results of flash methanolysis of other coals under identical temperature and pressure conditions. Difficulties were encountered in closely controlling the coal feed rates during some experiments as a result of which the methane to coal feed ratios could not be kept uniform in all cases. At this time, it is not known whether the effect of methane to coal feed ratio on the methanolysis product distribution from these coals is similar to what was seen in the case of New Mexico sub-bituminous coal. Apparently, there is no clear trend in the yields of ethylene or BTX with respect to the coal rank. Correlation of the data with volatile matter content, fixed carbon or ash content also did not reveal any trend. For example, a comparison of the data from the two lignites, obtained under similar reaction conditions, in Table 6, shows a wide variation in the producer yields despite the fact that the proximate and ultimate analyses of these coals, in Table 1, do not show any remarkable difference between them. The change in the product distribution

between different coals might then be due to important structural differences among the coals. This is supported by the recent findings of Calkins who was able to correlate the pyrolysis ethylene yields to polymethylene contents of coals successfully (5).

CONCLUSIONS

We have shown that there are definite advantages in the use of methane as an atmosphere in the flash pyrolysis of coal. At temperatures higher than 800°C, 2 - 5 times greater yields of ethylene is obtainable in methane atmosphere when compared to flash pyrolysis in an inert helium atmosphere. An enhancement in the yield of ethylene and BTX is seen at a lower coal feed rate. Since ethylene and BTX are important raw materials in the vast polymer and plastic markets, flash methanolysis of coal has potential process applications.

ACKNOWLEDGEMENT

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Table 2
Mass Flowmeter Data

Run No.	Pressure (psi)	Temp. (°C)	Feed Methane- In (SCF/Min) ¹	Total Gases Out (SCF/Min)	% Methane in the exit gases	Methane- out (SCF/Min)	% Difference in CH ₄ Flow
643(2)	20	1000	0.88	1.06	82	0.87	-1.1
644(2)	50	1000	0.93	1.06	88	0.93	0
650(3)	50	900	1.00	1.10	88	0.97	3.0

- 1) SCF= Standard Cubic Feet at 15°C and 1 atm.
 2) New Mexico sub-bituminous coal
 3) Montana Rosebud sub-bituminous coal

Table 1
Analyses (Wt%) of Coals Used

	Wyodak Sub-bit.	North Dakota Lignite	Ill. No. 6 Bit.	New Mexico Sub-bit.	Montana Rosebud Sub-bit.
Moisture*	3.0	9.6	6.83	7.8	9.1
<u>Proximate Analysis</u>					
Dry Ash	10.0	10.0	12.4	22.8	11.8
Dry V.M.	43.8	46.2	38.5	34.9	46.8
Dry FC	46.2	43.8	49.1	42.4	41.4
<u>Ultimate Analysis</u>					
Carbon	55.3	59.0	68.8	55.9	67.7
Hydrogen	4.1	4.0	5.0	4.3	4.8
Nitrogen	0.9	0.9	1.2	1.1	0.9
Sulfur	0.9	0.5	3.4	1.0	2.2
Oxygen**	28.8	25.6	9.2	14.9	12.6

* As received; ** By difference.

Table 4

Flash Pyrolysis of New Mexico Sub-Bituminous Coal with Methane
Effect of Reactor Temperature

Run No.	685	683	683	683	692	692	692	684
Reactor Temperature (°C)	800	800	850	900	900	950	1000	1000
Reactor Pressure (psi)	50	50	50	50	50	50	50	50
Coal Feed Rate (lb/hr)	1.01	0.99	0.99	0.99	0.90	0.90	0.90	1.00
Methane Feed Rate (lb/hr)	4.1	4.05	4.05	4.05	4.15	4.15	4.15	4.05
Coal Particle Residence Time (sec)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.4
Methane/Coal Ratio	4.1	4.1	4.1	4.1	4.6	4.6	4.6	4.6
X Carbon Converted to Product								
C ₂ H ₄	6.1	5.1	10.2	10.0	8.9	12.6	12.7	12.0
C ₂ H ₆	0.5	0	0	0	1.1	1.1	1.2	0.1
BTX	0.6	0.8	2.1	2.9	3.1	4.2	8.8	9.0
CO	5.2	5.2	5.7	6.8	3.8	4.2	5.4	8.0
CO ₂	1.4	1.5	1.8	1.7	1.3	1.3	1.2	1.7

Table 3

Flash Pyrolysis of New Mexico Sub-Bituminous Coal with Methane
Effect of Gas Pressure

Run No.	683	454	451	424
Reactor Temperature (°C)	900	900	900	900
Reactor Pressure (psi)	50	100	200	500
Coal Feed Rate (lb/hr)	0.99	1.22	0.85	1.05
Methane Feed Rate (lb/hr)	4.05	3.5	4.0	5.6
Coal Particle Residence Time (sec)	1.5	1.8	2.7	3.0
Methane/Coal Ratio	4.1	2.9	4.7	5.3
X Carbon Converted to Product				
C ₂ H ₄	10.0	8.3	7.1	4.3
C ₂ H ₆	0.0	1.4	3.9	3.5
C ₃ H ₈	0.0	0.9	0	0
Total Gaseous H.C.	10.0	10.6	11.0	7.8
BTX	2.9	3.4	6.5	3.6
>C ₉	ND	6.9	5.2	7.1
Total Liquid H.C.		10.3	11.7	10.7
CO	6.8	4.6	5.5	0
CO ₂	1.7	1.7	2.2	1.5
Total CO _x	8.5	6.3	7.7	1.5
Subtotal	21.4	27.2	30.4	20.0
Char	ND	ND	ND	58.7
Total				78.7

Table 6

Flash Pyrolysis of Coals with Methane
Effect of Coal Type

Run No.	Wyodak Lignite			North Dakota Lignite			Illinois No. 6 Bituminous			Montana Rosebud Sub-Bituminous		
	722	722	722	731	731	731	720	720	720	708	708	708
Reactor Temperature (°C)	900	950	1000	900	950	1000	900	950	1000	900	950	1000
Reactor Pressure (psi)	50	50	50	50	50	50	50	50	50	50	50	50
Coal Feed Rate (lb/hr)	0.93	0.93	0.93	1.00	1.00	1.00	0.60	0.60	0.60	1.45	1.45	1.45
Methane Feed Rate (lb/hr)	3.85	3.85	3.85	4.1	4.1	4.1	3.88	3.88	3.88	3.81	3.81	3.81
Coal Particle Residence Time (sec)	1.6	1.5	1.5	1.6	1.6	1.5	1.6	1.5	1.5	1.5	1.5	1.3
Methane/Coal Ratio	4.14	4.14	4.14	4.1	4.1	4.1	6.5	6.5	6.5	2.6	2.6	2.6
§ Carbon Converted to Product												
C ₂ H ₄	7.6	8.9	11.0	4.0	4.5	5.1	4.5	7.0	11.1	4.5	4.9	6.2
BTX	4.6	6.6	9.9	1.7	2.4	3.9	2.2	6.0	12.8	1.7	2.6	3.9
Total H.C.	12.2	15.5	20.9	5.7	6.9	9.0	6.7	13.0	23.9	6.0	7.5	10.1
CO	7.0	9.1	8.0	5.7	8.6	9.6	2.2	2.5	3.4	4.0	5.1	6.3
CO ₂	5.0	4.7	3.0	4.9	3.9	5.2	0.8	0.8	0.9	2.6	2.5	2.5
Total CO _x	12.0	13.8	11.0	10.6	14.5	14.8	3.0	3.3	4.3	6.6	7.6	8.8

Table 5

Flash Pyrolysis of New Mexico Sub-bituminous Coal with Methane
Effect of Methane/Coal Ratio

Run No.	684	692	703	704	705	706
Reactor Temperature (°C)	1000	1000	1000	1000	1000	1000
Reactor Pressure (psi)	50	50	50	50	50	50
Coal Feed Rate (lb/hr)	1.0	0.90	1.89	1.9	2.77	5.08
Methane Feed Rate (lb/hr)	4.05	4.15	3.79	3.77	3.77	3.75
Coal Particle Residence Time (sec)	1.5	1.5	1.5	1.5	1.5	1.5
Methane/Coal Ratio	4.05	4.61	2.01	1.98	1.36	0.74
X Carbon Converted to Product						
C ₂ H ₄	12.0	12.7	9.0	10.4	8.3	4.6
C ₂ H ₆	0.1	1.2	1.0	0.0	0.0	0.0
Total Gas H.C.	12.1	13.9	10.0	10.4	8.3	4.6
BTX	9.0	8.8	7.2	5.7	4.1	2.2
Total H.C.	21.1	22.7	17.2	16.1	12.4	6.8
CO	8.0	5.4	6.0	ND	5.1	2.2
CO ₂	1.7	1.2	2.0	1.5	1.8	0.9
Total CO _x	9.7	6.6	8.0	1.5+	6.9	3.1
Total	30.8	29.3	25.2	18.0+	17.3	9.9
Methane Concentration (X)	93	94	87	84	83	81
Methane Partial Pressure (psi)	46.5	47	43.5	42	41.5	40.5
Ethylene Concentration (Vol%)	1.1	1.1	1.7	1.9	2.3	2.3

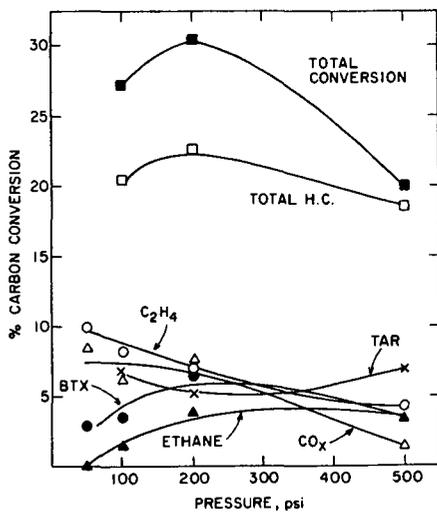


FIGURE 2. EFFECT OF PRESSURE ON PRODUCT DISTRIBUTION.

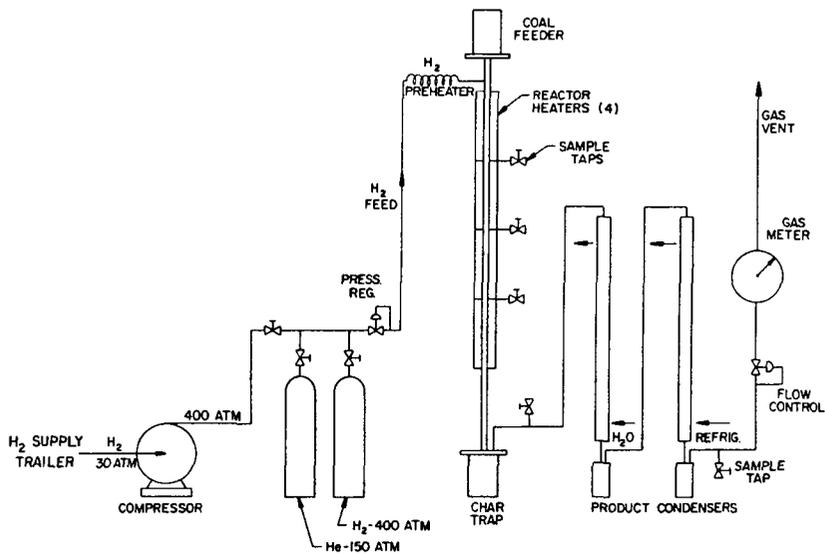


FIGURE 1. Schematic representation of the pyrolysis reactor.

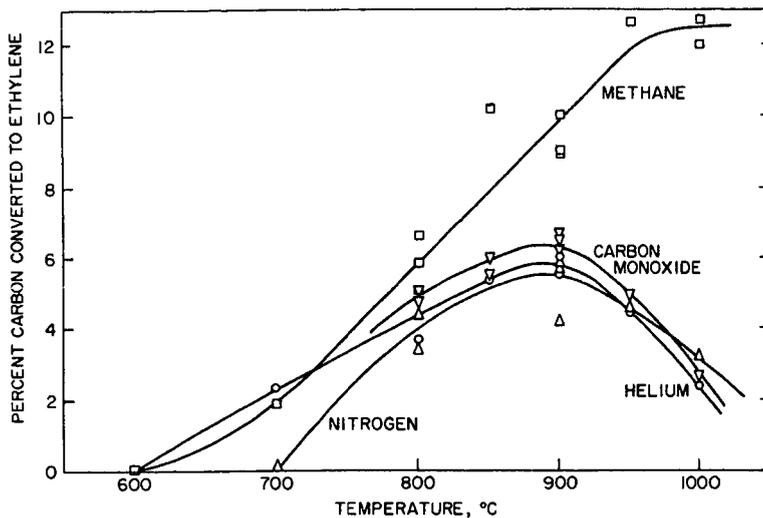


Figure 4. Effect of Temperature and Pyrolysis Atmosphere on Ethylene Yield.

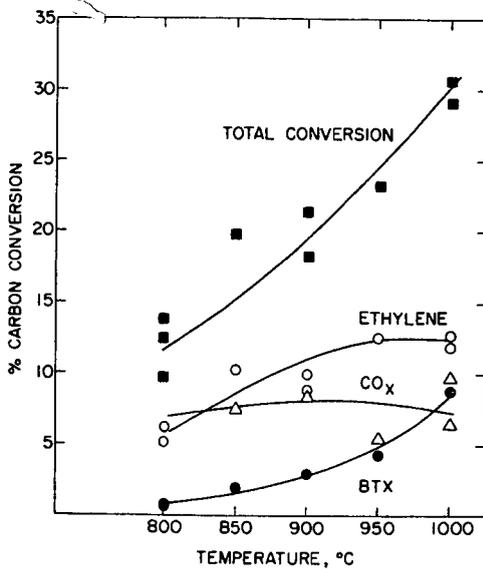


FIGURE 3. EFFECT OF TEMPERATURE ON PRODUCT DISTRIBUTION.