Flash Pyrolysis of New Mexico Sub-Bituminous Coal in Helium-Methane Gas Mixtures

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ABSTRACT

A New Mexico sub-bituminous coal was flash pyrolyzed in gas mixtures of helium and methane at 1000°C and 50 psi in an 1-in. I.D. entrained down-flow tubular reactor. The mixture contained 0 to 40% helium in methane. Under tested experimental conditions, pyrolysis in gas mixtures resulted in higher yields of ethylene and BTX than in pure methane. For example, under a coal flow rate of 1.0 lb/hr and methane flow rate of 4.0 lb/hr, pyrolysis in pure methane produced 7.7% C_2H_4 and 9.0% BTX on the basis of carbon contained in coal; under similar coal and methane flow rates, as high as 14.8% C_2H_4 and 15.3% BTX were obtained on pyrolysis in 25% He + 75% CH_4 gas mixture. The data show that the coal flow rate and methane flow rate both independently affect the yields of C_2H_4 and BTX. At constant methane flow rate, increase in coal flow rate decreases the yields of C_2H_4 and BTX; at constant coal flow rate, increase in methane flow rate increases the yields of C_2H_4 and BTX.

Keywords: coal; natural gas; pyrolysis; gasification.

INTRODUCTION

The aim of the flash pyrolysis of coal is the production of smaller molecules from it in a shortest possible particle residence time. Therefore, the objective of studying the process chemistry of coal pyrolysis is to investigate the experimental parameters that permit this aim to be achieved and to establish the optimum conditions that produce a favorable product slate. The basic process parameters that influence the product yields during flash pyrolysis of coal are: (1) reaction temperature, (2) gas pressure and (3) residence times of coal particles and ensuing tar vapors. In addition to these major process parameters, product yields can be influenced by other factors such as the nature of the pyrolysis gas and its partial pressure and the gas-to-coal ratio.

Previous work on flash pyrolysis of coal at Brookhaven National Laboratory was performed with inert pyrolysis gases, He, N_2 and Ar, and reactive gas, H_2.[1] Because of its process potential, our recent work has concentrated on the flash pyrolysis of coal with reactive methane gas.

Methane, in the form of natural gas, has become a readily available, low-cost raw material. Utilization and conversion of coal in conjunction with natural gas to produce higher valued fuel and feedstocks, becomes an attractive process proposition.

In general, pyrolysis experiments have been carried out in pure gases, either inert or reactive. In a few instances, mixtures of inert gases e.g. N_2-Ar(2) or reactive gases e.g. H_2-H_2O were used as pyrolysis atmospheres.(3) The potential and usefulness of mixtures of inert and reactive gases towards the selectivity of pyrolysis products, heretofore, has not been investigated.

In order to determine if a relative increase in the heat transfer coefficient of the pyrolyzing gas could be used to increase the yields of ethylene and BTX from coal, a detailed examination of the pyrolysis of a New Mexico sub-bituminous coal was conducted in gas mixtures of helium and methane. The effects of gas mixture composition, coal feed rate and gas feed rate on the yields of ethylene and BTX are reported in this paper.

EXPERIMENTAL

The flash pyrolysis experiments were carried out in a 1-in. diameter-by-8-ft-long downflow entrained tubular reactor, details of which have been reported.(4) The gas mixture consisted of 0-40% helium by volume and the balance methane. Preheated methane or helium-methane gas mixture was fed into the reactor to desired total pressure. The partial pressure of methane was maintained constant at 50 psi in the experiments reported here. A New Mexico sub-bituminous coal, with analysis shown in Table 1, was used in the study. The coal, 150μm or less in size, premixed with 10% by weight of Cab-O-Sil (a fumed silica powder) to prevent agglomeration, was dried in a vacuum oven overnight. The high temperature gas feed is mixed with coal at the top of the reactor causing the pyrolysis reactions to take place. Routine gas analyses were performed with an on-line gas chromatograph. The product yields were determined on the basis of conversion of carbon contained in the coal feed.

Table 1

Analysis of New Mexico Sub-bituminous coal (wt%)

Moisture (As Received)	7.8		
<u>Proximate Analysis:</u>		<u>Ultimate Analysis:</u>	(daf)
Dry Ash	22.8	Carbon -	72.4
Dry V.M.	34.9	Hydrogen -	5.6
Dry V.M.	34.9	Nitrogen -	1.4
Dry P.C.	42.4	Oxygen (by diff) -	20.6

RESULTS AND DISCUSSION

Ethylene is an important raw material for the polymer market. Less attention has been focused in the past on the production of ethylene using coal as the raw material.We have shown earlier 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 greter yields of ethylene are obtainable in methane atmosphere when compared to flash pyrolysis in an inert helium atmosphere.(5) The enhancement in the ethylene yield was determined to be due to an interaction between coal and methane at the pyrolysis conditions.(6) Though greater selectivity towards ethylene and BTX production can be achieved by pyrolysis of coal in a methane atmosphere, its relatively low thermal conductivity can limit the total volatiles yield obtainable from coal. Hydrogen is highly reactive and it also has the highest thermal conductivity of all gases; however, it is unsuitable if the aim is to maximize ethylene and BTX yields as they become hydrocracked in the presence of hydrogen. This, then, leads to the possibility of pyrolyzing coal in a mixture of helium with high thermal conductivity and methane with high reactivity.

One of the important process parameters that influenced the ethylene and BTX yields was found to be the methane-to-coal feed ratio. When the gas flow rate was held constant, the yields of C_2H_4 and BTX tend to increase with lower mass loadings of coal. The results of flash pyrolysis of New Mexico sub-bituminous coal in pure methane at 1000°C and a constant methane flow rate of 3.8 lb/hr are shown in Figure 1. The curves for both C_2H_4 and BTX follow the same pattern. The top curves show the total yield of C_2H_4, C_2H_6 and BTX. At the lowest coal flow rate, the ethane yield was 1.0% and no ethane was produced at higher coal flow rates. The decrease in the yields of BTX, C_2H_4 and C_2H_6 at higher coal flow rates can be explained on the basis of accelerated decomposition of the above products on the surface of the hot char particles, the area of which also increases with higher mass loadings of coal. Furthermore, higher mass loadings of coal can also affect the heat transfer between the pyrolyzing gas and the coal particles which, in turn, can reduce the yield of the volatiles from coal. Thus, it becomes necessary to optimize the flow rates of coal and methane in order to maximize the desired product yields.

Table 2 shows the yields of the products obtained when the coal was pyrolyzed in gas mixtures of helium and methane. Three different compositions of gas mixtures were used which contained 6 to 40% He in methane. As shown in Table 2, the partial pressure of methane was constant at 50 psi in all experiments. The coal flow rate ranged from 0.8 to 1.3 lb/hr and the methane flow rate from 2.1 to 4.6 lb/hr. The flow rates shown here were obtained by averaging the flow rates throughout the run which lasted for about an hour. Though instantaneous flow rate of coal is not known, it is not expected to vary because successive gas analyses using on-line GC were consistent for a steady state reaction conditions. The instantaneous flow rate of the pyrolyzing gas which was recorded throughout the run, did not reveal any significant differences.

Table 2

Flash Pyrolysis of New Mexico Sub-bituminous Coal at 1000°C
in Helium-Methane Gas Mixtures
(Partial Pressure of Methane: 50 psi)

Run No.	684	871	868	779	795	766	848	812	849	854	817	837	860	844	841	827
Helium (Vol %)	0	6	6	6	6	6	12	12	12	12	25	25	25	25	40	40
Methane (Vol %)	100	94	94	94	94	94	88	88	88	88	75	75	75	75	60	60
Total Pressure, psi	50	53	53	53	53	53	57	57	57	57	67	67	67	67	83	83
Coal Feed Rate (lb/hr)	1.00	1.22	1.22	0.75	0.81	0.87	1.00	1.18	1.22	1.28	0.97	0.93	0.95	1.01	1.09	1.24
Methane Feed Rate (lb/hr)	4.05	4.13	2.85	4.55	4.92	4.33	3.18	4.60	3.25	1.96	3.98	3.44	2.1	2.69	3.19	3.31
Coal Res. Time (sec)	1.5	1.4	1.9	1.3	1.2	1.3	1.7	1.2	1.7	2.2	1.2	1.3	2.3	1.9	1.6	1.2
Methane/Coal Ratio	4.1	3.4	2.3	6.1	6.1	5.0	3.2	3.9	2.7	1.5	4.1	3.7	2.2	2.7	2.9	2.7
Product Yields, (wt% Coal Carbon Basis)																
C_2H_4	7.7	7.9	4.7	14.1	10.5	6.7	7.6	8.6	6.1	3.3	14.8	10.7	6.1	6.1	7.3	9.3
C_2H_6	0.1	1.5	0.7	1.9	2.2	1.7	1.3	1.6	1.0	0.8	3.0	1.8	1.4	1.4	1.2	1.0
BTX	9.0	10.7	8.8	18.2	14.4	N.D.	11.1	10.2	10.2	7.5	15.3	13.7	10.3	10.5	11.3	10.6
CO	8.0	9.6	6.4	5.3	6.6	5.6	6.3	5.8	5.6	6.8	7.6	7.4	6.2	6.6	6.7	4.6
CO_2	1.7	1.6	1.0	1.8	1.9	1.5	1.5	1.8	1.3	1.6	2.3	1.5	1.5	1.4	1.4	1.3
Total																

N.D. - Not Determined.

Figure 2 shows the yields of ethylene and BTX as a function of volume percent helium in the pyrolyzing helium-methane gas mixture at methane-to-coal ratio of 3.9 to 4.1 and coal particle residence time of 1.2-1.5 sec. Both curves show that, under the conditions investigated, the yields of C_2H_4 and BTX increase with the amount of helium in the gas mixture. It also appears that the yields of C_2H_4 and BTX will be going through a maximum, since the yields with pure helium are much lower than with the mixtures of CH_4 and He. The data in Table 2 indicate that the effect of the helium concentration in the gas mixture on C_2H_4 and BTX yields is more pronounced at high methane-to-coal ratios than at low methane-to-coal ratios.

Figure 3 shows the effect of the methane flow rate on the yield of ethylene at a constant coal flow rate of 1.0-1.2 lb/hr. The curves for the three different gas mixtures used in our experiments, which contained 6, 12 and 25% helium by volume, all follow similar trends. For all gas mixtures, C_2H_4 yield increased with the flow rate of methane. It is seen from Figure 3 that for a given methane flow rate, the yield of C_2H_4 increased with the helium content of the gas mixture. If the increased ethylene yield came from the pyrolysis of methane alone, i.e., if the ethylene yields were additive, an effect opposite to this would have been noticed. A similar trend is noted in Table 3 with respect to BTX yield. Thus, there is greater selectivity in the production of ethylene and BTX in the presence of He/CH_4 than in the presence of either pure He or pure CH_4. This indicates an attractive process application for the production of ethylene and BTX from coal via Flash Methanolysis.

ACKNOWLEDGEMENT

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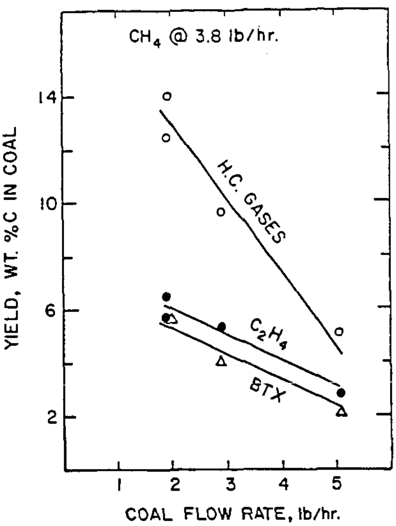
Figure 1



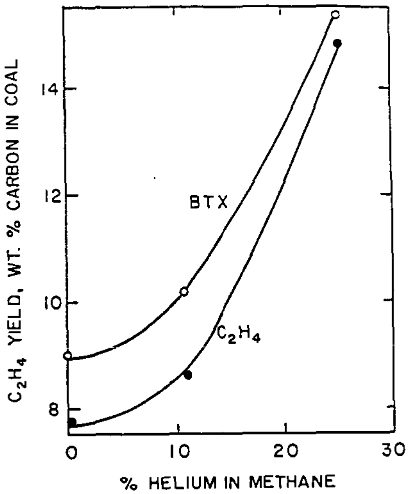
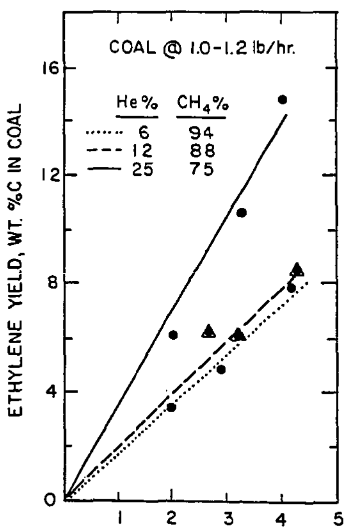


Figure 2



Methane Flow Rate, lb/hr

Figure 3

Figure 1. Effect of Coal Flow Rate on C_2H_4 and BTX yield

Figure 2. Effect of Helium Concentration in Methane on C_2H_4 yield

Figure 3. Effect of Gas Composition and Methane Flow Rate on C_2H_4 yield