Fast Pyrolysis of Cellulose with Reactive Methane Gas in a Single-Pulse Shock Tube

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SYNOPSIS

A shock tube technique was employed to study the fast pyrolysis of cellulose with methane under conditions of high temperature, high heating rate, short reaction time, and rapid quenching. The effects of temperature, methane atmosphere, and reaction time are investigated. Experiments were carried out at temperatures between 700 and 2200°C in 1% methane (diluted in argon), and comparisons in the yields of major gas products are made with the results obtained in pure argon atmosphere. The total gas yield decreased about 25–30% in methane. The principal gas products—carbon monoxide, carbon dioxide, and acetylene, except ethylene—were significantly decreased in methane as compared to the yields in pure argon. An increase of about 25% in ethylene yield in methane over argon was observed. The onset of the decomposition of cellulose and the evolution of major pyrolysis products were changed with the reaction times, which also affected the amplitude and the distribution of the pyrolysis products. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In the two previous works, a shock tube technique was outlined and the results from the fast pyrolysis of cellulose with reactive hydrogen and nonreactive argon was reported.[1,2] This work is also a part of an ongoing research project with the objective of determining the experimental conditions leading to high yields of valuable synthetic gases such as carbon monoxide, hydrogen, and low-molecular-weight hydrocarbons such as methane, ethylene, and acetylene. The results from the previous fast pyrolysis studies indicated that biomass can, indeed, be completely converted to gases under conditions of high temperature, high heating rate, short reaction time, and rapid quenching.[1–5]

In the two previous studies, the effects of temperature, reaction time, and reaction atmosphere on the product yields and distributions were discussed.[1,2] This work presents the results from the thermal decomposition of cellulose with reactive methane and discusses in detail the effects of meth-

ane atmosphere and reaction time on the yields and distributions of the principal pyrolysis products at temperatures of 700–2200°C. Very few researchers have investigated the pyrolysis of cellulose using methane as reaction atmosphere. The literature review in biomass pyrolysis suggests that some synergistic effects might occur when cellulose is pyrolyzed with methane. Steinberg et al.[6] using different biomass and carbonaceous feedstocks carried out experiments in an entrained tubular reactor operating at temperatures between 600 and 1000°C and varied pressures between 20 and 500 psi, using moderate residence times. It was found that pyrolysis with methane enhanced ethylene production. Pyrolysis of cellulose with methane was also conducted in an ultrapyrolysis reactor system at 750 and 850°C with residence times of 100–520 ms.[7] It was found that methane atmosphere (diluted in nitrogen) had no detectable effect on product yields under the conditions investigated.

EXPERIMENTAL

A single-pulse shock tube was used to investigate the fast pyrolysis of cellulose with methane (1% CH$_4$
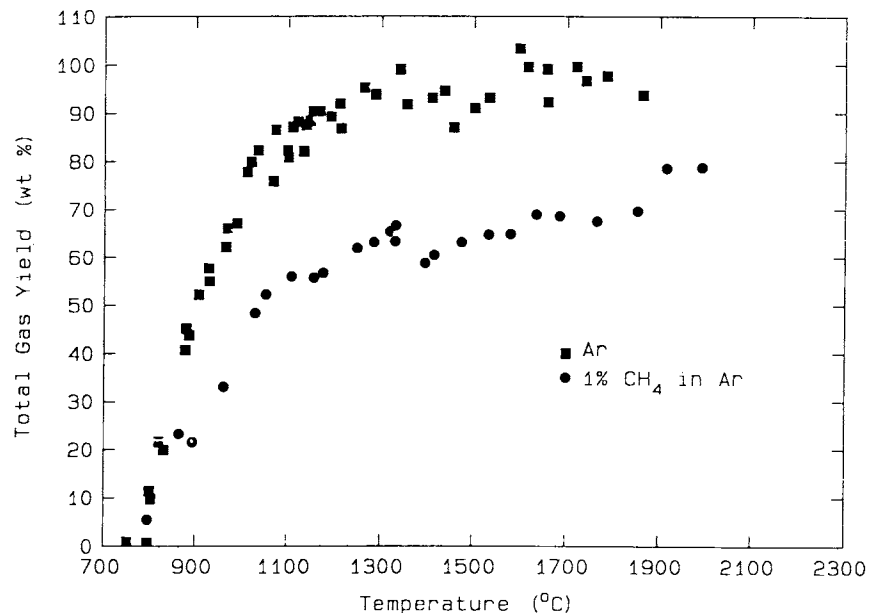

Figure 1   Effect of methane on the total gas yield at reaction times of 2.2–3.0 ms.

diluted in argon). The detailed features of the shock tube, experimental procedure, and the dispersion technique that was utilized in this study have been previously reported elsewhere,[1,8] therefore, only a brief summary of the approach taken will be given here. A preweighed (about 20 mg), powdered sample of cellulose with an average particle size of 20 μm, was placed on a dispersion plate and was shock heated to the desired temperature. Gas samples from

the experimental section of the shock tube were taken and analyzed by gas chromatography.

RESULTS AND DISCUSSION

The effects of methane atmosphere and reaction time on the product yields from the fast pyrolysis of cellulose in a single-pulse shock tube have been
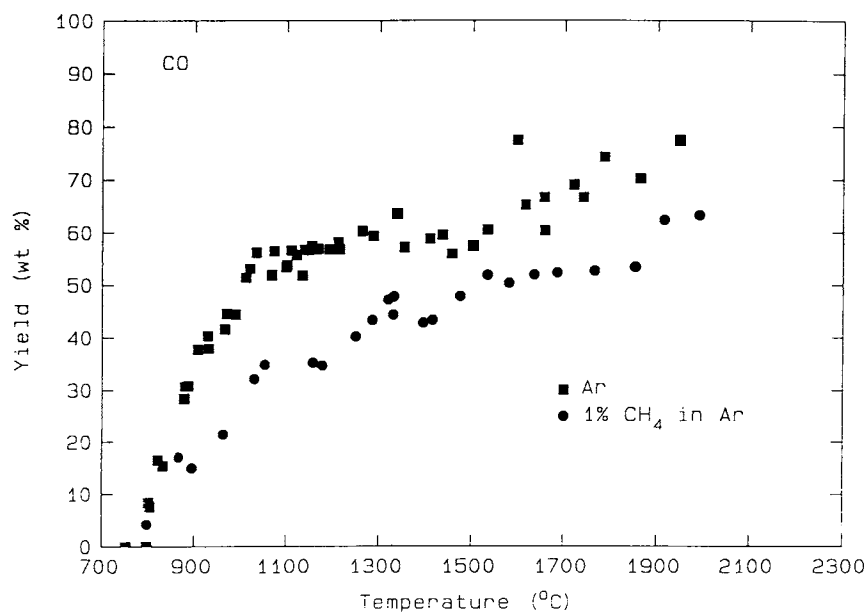

Figure 2   Effect of methane on the carbon monoxide yield at reaction times of 2.2–3.0 ms.
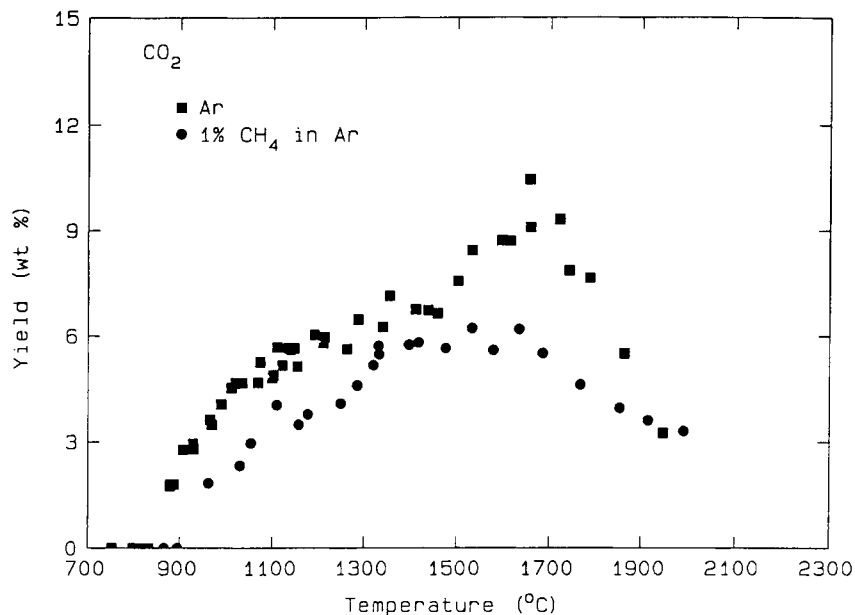
Figure 3   Effect of methane on the carbon dioxide yield at reaction times of 2.2–3.0 ms.

studied at temperatures between 700 and 2200°C. All the gas yields are the weight percent of cellulose samples, and the temperatures refer to the gas temperatures. No tar and char were observed, however, some soot apparently from the decomposition of methane itself was seen during the course of this investigation. It should be noted that no soot was seen from the decomposition of cellulose in hydrogen and argon. Some unreacted cellulose powder was also observed, as was the case in pyrolysis with hydrogen

and argon, at temperatures below 900°C for long (2.2–3.0 ms) reaction times.

Effect of Methane

It is known from studies of the thermal decomposition of methane in inert atmospheres that cracking of methane takes place at temperatures exceeding 1000°C. Since the experiments in this study were carried out above 1000°C, the decomposition of
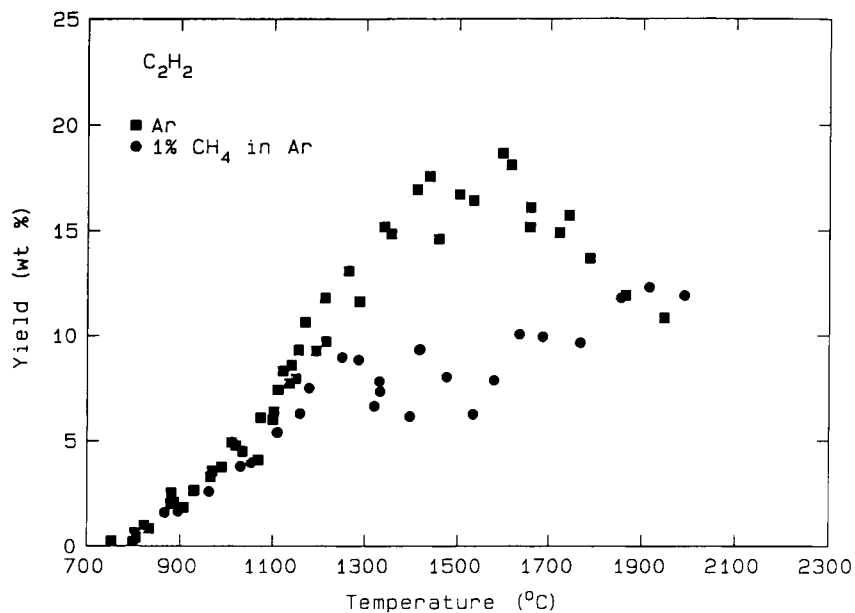

Figure 4   Effect of methane on the acetylene yield at reaction times of 2.2–3.0 ms.
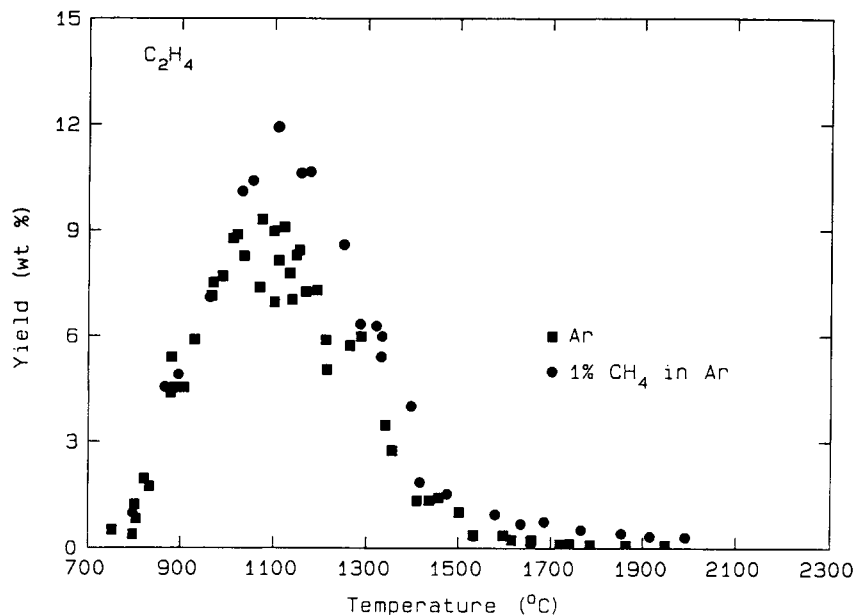
Figure 5   Effect of methane on the ethylene yield at reaction times of 2.2–3.0 ms.

methane will occur. In order to determine the effect of methane on the product yields from the cellulose pyrolysis, methane (1% CH$_4$ diluted in argon) was pyrolyzed independently and together with cellulose for the same temperature and reaction time range, and gas samples were independently analyzed by gas chromatography. The yields from the pyrolysis of cellulose with methane were then subtracted from the yields obtained from the pyrolysis of methane. The yields of total gas and major gas products

as a function of temperature are presented in Figures 1–5.

The total gas yield, as seen from Figure 1, significantly decreased about 25–30% in methane as compared to pure argon, however, it should be noted that the total gas yield excludes the possible methane formation from the decomposition of cellulose because it was not possible to accurately separate it from large amounts of methane in the driven gas.
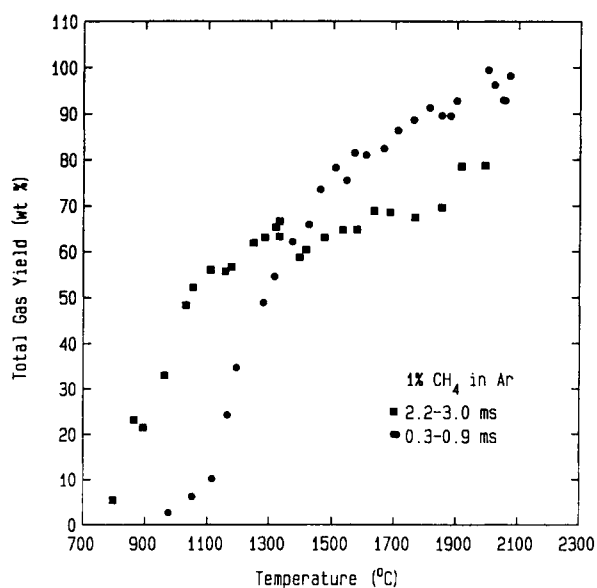

Figure 6   Effect of reaction time on the total gas yield.
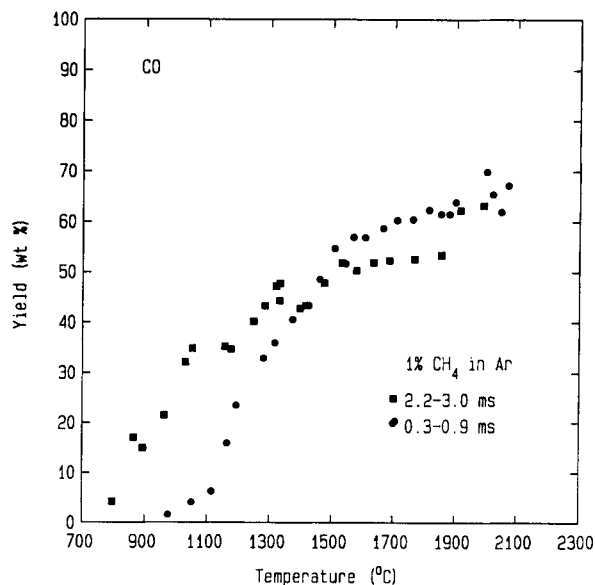

Figure 7   Effect of reaction time on the yield of carbon monoxide.

The decrease in the total gas yield in methane is due to the decrease in the yields of carbon monoxide, carbon dioxide, and acetylene. Although the amplitudes are different, the two curves exhibit a similar pattern in both atmospheres. It can be noticed that some data points in Figure 1 are higher than 100%. This is, as mentioned in the first study, due to the sampling technique utilized in this work.

Comparisons of the yields of CO and CO_2 from the pyrolysis of cellulose with methane and pure argon are shown in Figures 2 and 3. Methane atmosphere resulted in a significant decrease in the yields of CO and CO_2 as compared to the yields in Ar. This decrease is about 10–20% in CO and 10–30% in CO_2. A drastic decrease in the yield of C_2H_2 by nearly a factor of 2 can be seen from Figure 4 in methane atmosphere. This decrease might be explained due to the fact that C_2H_2 may be reacting with CH_4 or with the decomposition products of methane to form other hydrocarbons.

Ethylene is the only major pyrolysis product that was promoted with the pyrolysis of cellulose in methane. A noticeable increase of about 25% in the yield of C_2H_4 at 1100°C is observable in Figure 5. This finding agrees with the results of Steinberg et al.,[6] where an increased ethylene yield with methane over hydrogen, nitrogen, and helium atmosphere was observed from the pyrolysis of various biomass materials. A free-radical mechanism was proposed as one explanation for the enhanced ethylene yield with methane.
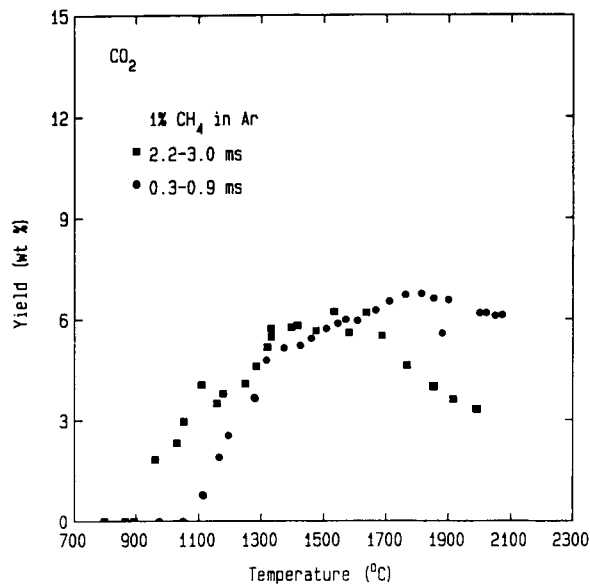

Figure 9   Effect of reaction time on the acetylene yield.

Effect of Reaction Time

A series of experiments in methane was conducted at temperatures of 700–2200°C for long (2.2–3.0 ms) and short (0.3–0.9 ms) reaction times to determine the effect of reaction time on the major pyrolysis products. The shock tube used in this study is limited with respect to reaction times, which can only be varied approximately from 0.3 to 3.0 ms, however, a variation from 0.3 to 3.0 ms causes significant changes in the yields of the total gas and

Figure 8   Effect of reaction time on the yield of carbon dioxide.

Figure 10   Effect of reaction time on the ethylene yield.
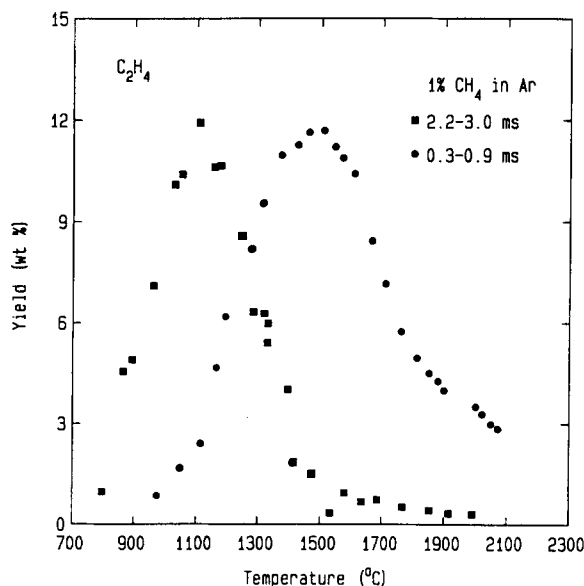
Table I   Elemental Mass Balances for Cellulose and Gas Products in Methane

T (°C)	Cellulose (mg)	Gas Yields (mg)				Mass of Elements (mg)		
		CO	CO_2	C_2H_4	C_2H_2	C	O	H
	20					8.889	9.877	1.235
1150		6.970	0.76	2.12	1.26	6.18	4.54	0.40
1400		8.680	1.15	0.72	1.50	6.04	5.80	0.22
1600		10.18	1.18	0.61	1.90	6.58	6.68	0.17
1900		12.46	0.72	0.07	2.40	7.81	7.64	0.20

principal pyrolysis products, as can be seen from Figures 6–10.

The total gas and carbon monoxide yield are lower by about 10–20 and 5–10%, respectively, for temperatures above 1500°C at the short reaction time than as compared with the long reaction time, as shown in Figures 6 and 7. On the other hand, the onset of evolution of total gas and CO occurs at lower temperature (about 200°C) at the long reaction time. The yield of carbon dioxide as a function of temperature is illustrated for both reaction times in Figure 8. A higher yield of CO_2 at short reaction time begins above 1650°C, and it is about twice as high at 2000°C.

One of the most striking effects of reaction time on the product yield is seen in the yield of acetylene, as presented in Figure 9. A higher yield of C_2H_2 at the shorter reaction time starts at temperature above 1700°C and gets increasingly higher with increasing temperature. Above 1900°C the yield of C_2H_2 is about 1.5 to 2.0 times higher at the shorter reaction time. As mentioned earlier, during the pyrolysis at long reaction time, acetylene may directly react with methane or with the decomposition products of methane to form other gases. Given sufficient time, cracking of C_2H_2 may also take place resulting in carbon and hydrogen.

Although the maximum points for the yields of ethylene at both reaction times occur at different temperature, neither the value of the maximum

point nor the pattern of ethylene yields are affected with methane. However, as seen from Figure 10, the yield is just shifted to about 200°C higher temperature at the short reaction time.

Material Balance

Elemental mass balances for the principal products at different temperatures were made and are given in Tables I–III for methane, hydrogen, and argon atmospheres, respectively. Relatively low carbon balance in methane as compared to hydrogen and argon is obtained. The oxygen balance in methane is comparable to the value in hydrogen, but it is lower than the balance obtained in pure argon. The results suggest that some of the missing hydrogen in material balance combined with the missing oxygen to form water and some of them are in the form of molecular hydrogen.

Kinetic Analysis

The same kinetic model utilized in the previous two studies is used to determine the global kinetic parameters.[1,2] The values of the energy of activation (E) and the Arrhenius preexponential factor (k_0) for the major pyrolysis products and the global decomposition of cellulose in methane are given in Table IV. The calculated global activation energy for the disappearance of cellulose in methane is 123.3

Table II   Elemental Mass Balances for Cellulose and Gas Products in 1% H_2 (Diluted in Argon)

T (°C)	Cellulose (mg)	Gas Yields (mg)					Mass of Elements (mg)		
		CO	CO_2	CH_4	C_2H_4	C_2H_2	C	O	H
	20						8.889	9.877	1.235
1150		8.360	0.93	1.35	1.70	1.40	7.60	5.45	0.69
1350		8.653	1.24	1.40	0.60	2.60	8.02	5.85	0.64
1550		9.818	1.35	1.00	0.10	3.40	8.55	6.59	0.53
1700		10.31	1.40	0.39	0.07	3.55	8.43	6.91	0.38

Table III Elemental Mass Balances for Cellulose and Gas Products in Pure Argon

T (°C)	Cellulose (mg)	Gas Yields (mg)					Mass of Elements (mg)		
		CO	CO_2	CH_4	C_2H_4	C_2H_2	C	O	H
	20						8.889	9.877	1.235
1300		13.47	1.223	1.192	1.107	2.770	10.50	8.587	0.669
1550		14.08	1.586	0.867	0.239	3.464	10.52	9.199	0.419
1750		14.47	1.986	0.276	0.065	3.458	10.20	9.715	0.342
1950		14.75	1.336	0.273	0.050	3.350	10.02	9.398	0.333

kJ/mol, which is very comparable to the values obtained in hydrogen (127.4 kJ/mol) and pure argon (130.5 kJ/mol), and is in very good agreement with the values reported in the literature for the fast pyrolysis of cellulose, which is approximately 120 kJ/mol.[3]

CONCLUSIONS

The results of a single-pulse shock tube study of the thermal decomposition of cellulose strongly support the conclusions of the previous fast pyrolysis studies that biomass can be completely converted to valuable gas products under conditions of high temperature, high heating rate, short reaction time, and rapid quenching.

Methane atmosphere significantly influenced the major product yields. The yields of carbon monoxide, carbon dioxide, and acetylene were greatly decreased in methane. The only improvement in product yield was observed with ethylene, which increased about 25%.

Table IV Global Kinetic Parameters for Cellulose and Gas Products in Methane

Material	k_0 (s^{-1})	E (kJ/mol)[a]
Cellulose	2.0×10^7	123.3 ± 29.9
CO	1.1×10^7	117.1 ± 27.3
CO_2	2.1×10^6	90.60 ± 1.90
C_2H_4	4.8×10^8	150.7 ± 2.90
C_2H_2	4.1×10^6	115.9 ± 3.70

[a] The error limits are defined by $[\sum_{i=1}^{n} (V_{i,model} - V_{i,exptl})^2 / (n - 3)]^{1/2}$, where n is the number of data points.

The onset of the evolution of the principal gas products and the magnitude of the yields were changed with a variation in reaction times, which also affected, in some degree, the pattern of the product yields as a function of temperature.

The overall yields of major pyrolysis products in methane are comparable to the yields in hydrogen, however, they are significantly lower as compared to the yields obtained in pure argon.

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