THE EFFECT OF A SIEMENS OZONIZER DISCHARGE ON THE REACTION OF ETHYLENE AND STEAM

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Abstract

In the presence of a Siemens ozonizer discharge, ethylene and steam react exothermally to produce a large number of gaseous and liquid products. At 8.5:1 steam-ethylene molar ratio, 160 hourly space velocity, one atmosphere pressure, 240°C, 460 volt-amperes power drawn by the reactor, and 10,000 Hertz A.C. frequency, a single pass ethylene conversion of 70 percent was obtained. The gaseous products consist of hydrogen, carbon dioxide, carbon monoxide, ethane, methane, propane, propylene, and isomeric butanes, butenes, pentanes, pentenes, hexanes, and hexenes. The liquid fraction is more complex. Characterization of this liquid by analytical liquid chromatography, gas chromatography, and mass spectrometry indicated the presence of at least 75 components consisting mostly of paraffins, olefins, and oxygenates. The oxygenates are largely alcohols. The experimental data indicate that ethylene conversion increases with steam-ethylene molar ratio, input electrical power, and temperature, and decreases with increasing flow rate. There is no reaction at the stated conditions in the absence of an electric field.

Introduction

Novel techniques are being investigated by the Bureau of Mines to find new uses for coal or coal products. One technique under study uses an ozonizer discharge to induce chemical reactions with industrial potential. Initially, the gas phase reaction of carbon monoxide and steam to produce carbon dioxide and hydrogen in the absence of a catalyst was investigated (12). The effect of 60 Hz input power, pressure, space velocity, and temperature on carbon monoxide conversion was determined. In the present paper, we report on the reaction of ethylene and steam in the electric discharge.

From a chemical viewpoint, the ethylene-steam and carbon monoxide-steam reactions are entirely different. Whereas the carbon monoxide-steam reaction yields carbon dioxide, hydrogen, and a trace of methane (less than 1%), the products from the ethylene-steam reaction number at least 88. This can be inferred from Reaction 1 and Figure 1. There were 13 gaseous and 75 liquid products detected in the particular experiment described, all of which cannot be seen in the reproduced gas chromatogram.

Equipment and Procedure

The electrical discharge unit and operating procedure employed in this investigation have been described previously (12). Briefly, metered ethylene from a compressed gas cylinder is passed through a steam generator. The water in the steam generator is maintained at a precalibrated temperature so that the resulting ethylene-steam flow rate and molar ratio meet the requirements of the experiment. The mixture enters a Siemens-type reactor, undergoes reaction, and exits through a cold trap. The noncondensible gaseous product continues through a sample collection train of six gas collection bottles in series, and finally through a wet test meter for exit flow measurement. The cold trap is maintained at -21°C by means of an ice-salt mixture.

The Siemens-type ozonizer reactor, and the methods used for electrical, flow rate, and temperature measurements are described in Reference 12.

After the desired ethylene and steam flow rates were obtained and stabilized, the discharge was initiated.

The gaseous product was analyzed by means of gas chromatography and mass spectrometry. The liquid portion was characterized by analytical liquid chromatography, gas chromatography, and mass spectrometry.

Results and Discussion

The primary characteristic of the ethylene-steam reaction in an ozonizer discharge is the complexity of the product mixture. A complete material balance for one set of conditions (Experiment No. 368) is given in Reaction 1. The organic liquid portion, immiscible with water, is characterized in Figure 1 and Table 1. Further characterization is in progress. Experimental results are given in Table 2.

Experiment No. 368		gas		-21°C cold trap
		69.9 mole % ethylene		
		10.2 hydrogen		
		4.9 butanes		
		2.6 ethane		
		2.1 carbon monoxide		
		2.1 pentanes		
		1.8 hexanes		
50 mole % ethylene	ozonizer discharge →	1.6 butenes	+	5.1 mole % organics
50 water		1.2 propane		
		1.1 hexenes		94.9 water (1)
		0.9 pentenes		
		0.7 methane		
		0.7 propylene		
		0.1 carbon dioxide		
		99.9		
0.0202 lb/hr		0.00844 lb/hr		0.00970 lb/hr
0.000882 lb mole/hr		0.000277 lb mole/hr		0.000392 lb mole/hr
0.30 SCFH		0.099 SCFH		

Table 1.- Characterization of Organic Liquid Product

Experiment No. 368

Average molecular weight (ALC[a])	150
Maximum carbon number detected	
Gas chromatography	C_{13}
Mass spectrometry	C_{14}
Molecular types present	
Paraffinic (FIA and MS[b]), approx.	30% by vol.
Olefinic + Oxygenates (FIA and MS)	
Heavy ends, approx.	20% by vol.
Light ends, approx.	50% by vol.
Bulk density	0.76 g/cc

a. Analytical liquid chromatography.
b. Fluorescent indicator analysis (ASTM D-1319-56T) and mass spectrometry.

Table 2.- Experimental Results

10,000 Hz A.C. frequency
1 atmosphere pressure

Exp't. No.	Percent Ethylene Conversion[a]	Steam-Ethylene Molar Ratio	Space Velocity, hr^{-1}	Temperature, °C	Secondary Power,[b] volt-amperes	Secondary Voltage, r.m.s. volts
368	54.9	1.0	56	125	231	7000
377	66.1	8.5	160	240	380	6390
377A	68.0	8.5	160	240	420	6530
377B	70.0	8.5	160	240	460	6670
378	11.2	2.8	270	230	380	6620
378A	16.3	2.8	270	230	420	6920
378B	21.3	2.8	270	230	460	7220
379	10.2	1.0	100	245	380	6790
379A	14.0	1.0	100	245	420	7000
379B	17.7	1.0	100	245	460	7210
380	0	0.61	320	140	380	7060
380A	1.5	0.61	320	140	420	7380
380B	2.4	0.61	320	140	460	7700
381	11.2	7.0	140	140	380	7100
381A	36.7	7.0	140	140	420	7020
381B	53.5	7.0	140	140	460	6940
382	3.2	0.70	325	220	380	6690
382A	3.8	0.70	325	220	420	7160
382B	4.5	0.70	325	220	460	7620
383	2.0	3.0	270	140	380	7260
383A	7.5	3.0	270	140	420	7250
383B	13.1	3.0	270	140	460	7240
384	5.0	1.0	105	120	380	7290
384A	8.8	1.0	105	120	420	7500
384B	12.7	1.0	105	120	460	7720
385	0	8.5	160	240	0	0

a. Percent conversion = $[(SCFH_{in} - SCFH_{out})/(SCFH_{in})]$ (100).
b. Volt-amperes drawn by the reactor.

As part of a larger program to delineate the effect of process variables on product characteristics, the effect of steam-ethylene feed molar ratio, space velocity, and temperature on ethylene conversion was determined.

The data were analyzed by means of a linear hypothesis statistical empirical model (9). With this model it is assumed that the conversion of ethylene is dependent on all variables studied to the first power only. The dependent variable could be chosen from any measured product characteristic: amount of organic product or single compound produced, ethylene or steam conversions, product density, average molecular weight, etc. We chose the percentage conversion of ethylene.

The following regression equation resulted from this model:

$$\text{Percent Ethylene Converted} = 17.35 - 2.31\,(MR) - 0.0529\,(SV) - 0.0191\,(T) + 0.04079\,(MR)(T), \quad (1)$$

where: MR = steam-ethylene feed molar ratio
SV = space velocity, hr^{-1}, flow rate/reactor volume
T = temperature, °C.

Equation 1 represents the experimental data of Table 2 at 420 volt-amperes secondary power. Secondary power does not appear as a variable in the regression equation because ethylene conversions obtained at 380, 420, and 460 volt-amperes secondary power were not obtained from experiments carried out in a randomized sequence. This could, and did in a test equation including secondary power, lead to spurious regression coefficients for terms containing secondary power. As seen in Table 2, molar ratio, space velocity, and temperature were randomized with respect to sequence. Randomization eliminates any apparent correlation of independent variables. However, Table 2 does indicate that ethylene conversion increases with power drawn by the reactor.

The effect of steam-ethylene molar ratio, space velocity, and temperature on ethylene conversion can be easily seen from Table 3, which was calculated from Equation 1.

Table 3.- Ethylene Conversions Calculated from Equation 1

10,000 Hz A.C. frequency
1 atmosphere pressure
420 volt-amperes drawn by reactor

Percent Ethylene Conversion	Steam-Ethylene Molar Ratio	Space Velocity, hr^{-1}	Temperature, °C
12.0	1	100	100
14.1	1	100	200
1.5	1	300	100
3.5	1	300	200
15.5	3	100	100
25.8	3	100	200
5.5	3	300	100
15.2	3	300	200

An inspection of Table 3 shows that steam-ethylene molar ratio and temperature have a positive effect on conversion, whereas space velocity exerts a negative effect.

According to Table 2, maximum conversion of ethylene within the range of Equation 1 was found in Experiment No. 377A. The experimental value of 68.0 percent compares with a value of 67.7 obtained by calculation. Regions of interest suggested by the equation and Table 3 would be high steam-ethylene molar ratio, low space velocity, and high temperature.

It was found that no ethylene was converted to gaseous or liquid products in the absence of an electrical field in Experiment No. 385. These conditions matched those yielding the highest ethylene conversion, Experiment No. 377. Thus there is no thermal reaction at these conditions and it is the discharge which supplies the energy necessary for reaction. The authors' previous investigation (12), using the water-gas shift reaction ($H_2O + CO = H_2 + CO_2$), has indicated that the discharge is necessary in that case also, and further that the quartz walls of the ozonizer are probably not involved. By analogy, it appears that the ethylene-steam reaction in an ozonizer discharge is also a homogeneous gas phase reaction.

We have obtained some preliminary experimental results at 60 Hertz A.C. frequency. With identical conditions, except frequency, the gaseous and liquid product characteristics appear to be identical. However the product yield is less. This variable will be studied further in future experiments.

The overall ethylene-steam reaction is exothermic. The heat of reaction is sufficient to keep the reaction temperature above the condensation point of steam. In practice, sectional heating and cooling were employed. The discharge by its nature has a tendency to localize, producing hot spots. These areas could become the sites for arc formation, with subsequent quartz reactor perforation and failure. A relatively even and stable discharge was obtained with the judicious intermittent use of small cooling fans and sectional heaters.

Comparison with Other Ethylene Reactions

There appears to have been no previous investigations of the ethylene-steam reaction in an electrical discharge. This includes any form of electrical discharge: arc, glow, microwave, ozonizer, or radiofrequency. However similar systems have been studied by others. The decomposition and polymerization of ethylene in nondisruptive discharges was studied by Andreev (1), Dem'yanov and Pryanisnikov (2), Eidus (3), Eidus and Nechaeva (4), Fujio (5), Jovitschitsch (7,8), Mignonac and De St. Aunay (10), Stratta and Vernazza (14,15,19), and Szukiewicz (16). The ethylene-air system has been investigated by Sugino, Inoue, Koseki, and Gomi (17), Vernazzi and Stratta (18), and the authors (13). Vernazzi and Stratta and the authors also investigated the ethylene-carbon dioxide system. Ethylene plus nitrogen was studied by Miyamoto (11). The ethylene-nitrogen-propane system in a glow discharge was investigated by Hinde and Lichtin (6) for the purpose of elucidating the mechanism of olefin reactions with active nitrogen. Most of the above citations were concerned with ozonizer discharges at or around atmospheric pressure; however the A.C. frequencies employed varied greatly.

The above investigations can be qualitatively summarized by the following reactions:

References 1,2,3,4,5,7,8,10,14,15,16 and 19

$$\text{Ethylene} \xrightarrow[\text{near atmospheric pressure}]{\text{nondisruptive discharges}} \begin{array}{l}\text{acetylene}\\\text{butadiene}\\\text{butene-1}\\\text{ethane}\\\text{hexene-1}\\\text{hydrogen}\\\text{methane}\\\text{liquid + solid products}\end{array} \qquad (2)$$

Reference 17

$$\begin{array}{l}\text{1.68 ethylene}\\\text{5.00 air}\end{array} \xrightarrow[\text{atmospheric pressure}]{\text{ozonizer}} \begin{array}{l}\text{acetaldehyde}\\\text{carbon dioxide}\\\text{diformyl peroxide}\\\text{ethyl alcohol}\\\text{ethylene oxide}\\\text{formaldehyde}\\\text{hydrogen}\\\text{methane}\\\text{methyl alcohol}\\\text{propargyl alcohol}\\\text{water}\end{array} \qquad (3)$$

Reference 18

$$\begin{array}{l}\text{1 ethylene}\\\text{5 air}\end{array} \xrightarrow[\text{near atmospheric pressure}]{\text{ozonizer}} \begin{array}{l}\text{carbon dioxide}\\\text{water}\end{array} \qquad (4)$$

Reference 13

1 ethylene 1 air	ozonizer 10,000 Hz A.C. freq. → atmospheric pressure	carbon monoxide formaldehyde hydrogen methyl alcohol paraformaldehyde water other liquid products	(5)

Reference 11

2 ethylene 1 nitrogen	"silent discharge" → near atmospheric pressure	acetylene hydrogen cyanide liquid + solid products	(6)

Reference 18

ethylene carbon dioxide	ozonizer → 1:4 to 4:1 ratios	carbon monoxide hydrogen methane liquid sat'd. hydrocarbons	(7)

Reference 13

1 ethylene 1 carbon dioxide	ozonizer 10,000 Hz A.C. freq. → atmospheric pressure	butanes butenes carbon monoxide ethane hexanes hydrogen pentanes pentenes liquid products	(8)

In practically all cases the above reactions did not proceed to completion. The residence time was too short for the complete reaction of feed material.

Factorially designed experiments are in progress to simultaneously determine the effect of A.C. frequency, molar ratio, power drawn by reactor, pressure, space velocity, and temperature on the various dependent variables previously mentioned. Following these experiments it should be possible within the limitations of the chemistry involved, to produce product with specified characteristics.

Conclusions

The ethylene-steam reaction holds potential engineering applications. It is novel, exhibits good reactivity from a technical viewpoint, can be carried out under mild conditions, and produces a myriad of alcohols, olefins, and paraffins. As a mixture analogous to crude petroleum, Fischer-Tropsch synthesis product, or the product from destructive distillation of coal, the ethylene-steam reaction product may prove to be a rich source of synthetic organic chemicals.

Within the limits of this investigation, the following conclusions can be drawn:

(1) Ethylene conversion is higher at higher steam-ethylene molar ratios, power inputs, and temperatures, and at lower space velocities.

(2) No ethylene or steam was converted to products in the absence of an electric field.

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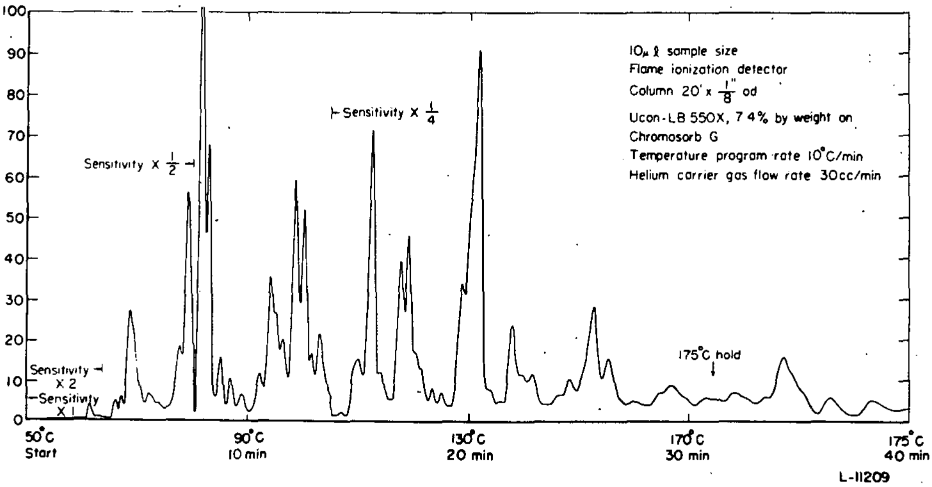

Figure 1.- Typical Gas Chromatogram of the Organic Liquid Products from the Ethylene-Steam Reaction in an Ozonizer Discharge.