Gas Chromatography Method for the Characterization of Ethanol Steam Reforming Products

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Abstract

Ethanol steam reforming is a promising reaction for producing fuel cell hydrogen. Depending on catalyst and reaction conditions, mixtures of condensable hydrocarbons and organic and inorganic gases are produced. This paper proposes an economic and effective solution for separating and detecting these compounds employing a gas chromatograph equipped with two columns, two 6-way valves, and two detectors.

Introduction

The production of hydrogen from bio-ethanol has received much research attention in the last few years. Ethanol derived from cellulosic materials is considered an eco-friendly hydrogen source because it is renewable, non-toxic, and could significantly reduce greenhouse gas emissions, making it a good candidate for hydrogen production. Ethanol steam reforming is the most commonly studied ethanol conversion process because of its high hydrogen and potentially low carbon monoxide yields. For hydrogen production, the overall ethanol steam reforming reaction is given in equation 1.

$$CH_3CH_2OH_{(g)} + 3H_2O_{(g)} \xleftrightarrow{\text{Catalyst}} 6H_{2(g)} + 2CO_{2(g)} \qquad \text{Eq. 1}$$

The ethanol steam reforming reaction, given in equation 1, is an endothermic equilibrium limited reaction that is not favored in the forward direction for reaction temperatures below 330°C.

The overall ethanol steam reforming reaction previously described is an idealized reaction. In real applications, depending on the catalyst and the operating conditions, a wide variety of reaction products could be expected, such as H_2, H_2O, CO, CO_2, methane, ethylene, ethane, propylene, acetaldehyde, ethanol, acetone, acetic acid, diethyl ether, ethyl acetate, crotonaldehyde, butanol, and deposited amorphous carbon. In general, ethanol steam reforming is conducted in continuous fixed-bed reactors at temperatures ranging from 300°C to 850°C on a variety of catalysts. The analysis of such a wide range of species by conventional gas chromatography (GC) is not trivial, especially on-line.

Throughout the ethanol steam reforming literature, the product gas streams have been analyzed by several techniques. A commonly used approach requires the partitioning of the sample by condensation, in which the incondensable species are detected and quantitated in an on-line manner, and the liquid sample is periodically collected and analyzed (1–4). This analytical approach generally requires multiple GCs, which can be prohibitively expensive; however, method development and column selection are relatively easy tasks. A major drawback of this analytical approach is the determination of the species and overall material balances due to the inaccurate measurement of the liquid flow rate, which is generally quite low. In addition, unlike the discrete gas sampling, the collected liquid sample represents a time-averaged sample, which leads to the inaccurate determination of species distribution and does not allow for an accurate determination of kinetics, especially when the studied system is inherently dynamic. Finally, the volatility of species in the collected liquid sample can be a problem and must be considered.

Another common analytical approach employs a single or multiple GC(s) with multiple columns, detectors, and sample injections (5–14). This approach requires the entire product sample to remain in the gas phase and the sample is separated into multiple injections. Each injection is analyzed for a specific species. This requires more thorough method development and column selection. The columns are usually selected so that the sample is divided into separable and inseparable fractions on each column or detector arrangement and all separable species are quantitated. This technique has been successful in accurately determining the composition of the detectable species in the product stream, but the quantitation of the amount of the undetectable species, especially water, is difficult because there are numerous undetectable species for each column or detector arrangement. The result is a lack of confidence for the quantity of water in the product stream, which is a major concern because water typically accounts for up to 50% volume of the total injected sample, and consequently, a lack of confidence in the species and overall material balances.

The single GC, multi-column, multi-detector, single injection approach described was developed to overcome the limi-

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tations previously mentioned. On the one hand, the product stream is analyzed in its entirety without necessitating any phase separation. On the other hand, all species are detected in one injection (no undetectable species) in this method, and the concentration of water can be determined with confidence by subtraction. This approach exploits differences in column selectivity and species affinity, in addition to temperature programming and column order switching to separate and detect the entire injected sample.

Separation and quantitation strategy

Figure 1 presents a schematic diagram of the GC's column, valve, and detector arrangement. The product stream exiting the reactor is continuously fed to the sample injection valve, which is maintained at the same temperature as the product stream. A block diagram of the initial column or detector arrangement is given in Figure 2A. The entire sample is injected, and the sample enters the first column, which is capable of separating condensable (heavy fraction) species.

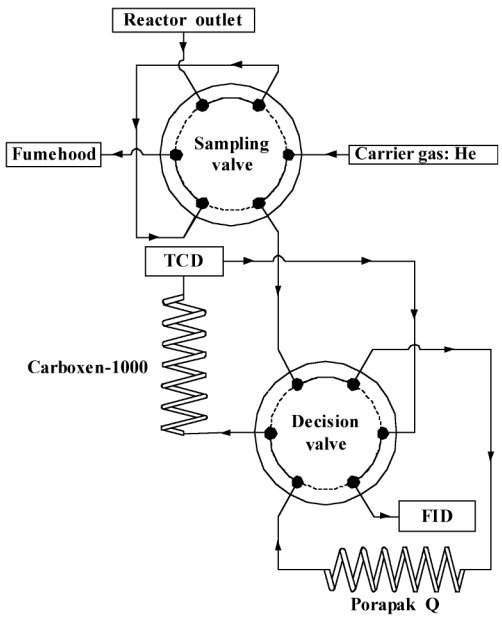

Figure 1. Block diagram of the multi-column, multi-detector, single injection GC.

The initial GC oven temperature is selected so that the condensable species adsorb in the heavy fraction column, and the non-condensable (light fraction) species continue to a second light fraction column. Once the light fraction species elute from the heavy fraction column, the decision valve, shown in Figure 1, switches to position 2. As shown in Figure 2B, the column or detector arrangement changes so that the carrier gas is fed directly to the light fraction column. The carrier gas enters the light fraction column, passes through a flow-through, preferably non-destructive, detector [e.g., thermal conductivity detector (TCD)], and continues to the heavy fraction column. A temperature program is applied, and species elute from their respective columns. The first detector (e.g., TCD), whose effluent becomes the carrier gas for the column separating the heavy fraction, detects the light fraction species initially. The heavy fraction column effluent, which contains the heavy and light fraction species, is sent to a second detector [e.g., flame-ionization detector (FID)] for analysis. This arrangement allows for double detection of the combustible light fraction components, such as methane. The temperature program must be developed so that the light fraction species do not adsorb on the heavy fraction column, but they are retained by the light fraction column, and the species eluting from the light fraction column do not interfere, or coelute, with the species from the heavy fraction column.

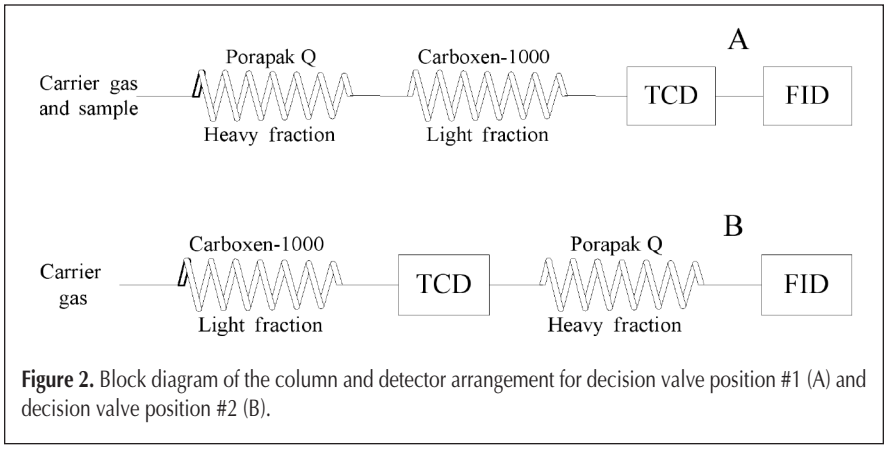

Figure 2. Block diagram of the column and detector arrangement for decision valve position #1 (A) and decision valve position #2 (B).

Experimental

Instrument

The GC used in this study was a Varian CP-3800 (Varian, Palo Alto, CA) equipped with a 1041 splitless on-column injector, TCD, FID, two 6-way valves (VICI, Houston, TX) enclosed in a dual valve heating oven, and electronic flow controllers controlling all gas flow rates. The GC was controlled and automated by the Star GC Workstation (Version 5.50) software package (Varian).

Ultra-high purity helium, 99.999%, (Praxair, Danbury, CT), which was further purified by passing through a helium purifier (Supelco, Bellefonte, PA) was used as the carrier and TCD reference gas. Hydrogen, 99.995% (Praxair), and in-house produced zero-gas air were used to generate the FID flame. A 15' × ⅛'' stainless steel column containing 60:80 mesh Carboxen-1000 (Supelco) was used for separation of the light fraction species. For separation of the heavy fraction species, a 6' × ⅛'' stainless steel column containing 50:80 mesh Porapak Q was used. The carrier gas flow rate was set at 55 mL/min. The valve heating oven, injector, and detectors were set at 250°C. The sample loop volume was 500 µL.

Chemicals

For species identification and calibration, two custom certified calibration gas

mixtures (Praxair), whose compositions are given in Table I, were used in addition to pure H_2, N_2, CH_4, C_2H_4, propylene, acetaldehyde, acetone, diethyl ether, ethyl acetate, crotonaldehyde, 1-butanol, and anhydrous ethanol (Commercial Alcohols, Toronto, ON). All gases were minimum 99.995% grade and supplied by Praxair and all liquids were American Chemical Society grade and supplied by Sigma-Aldrich (Oakville, Ontario, Canada), unless otherwise stated.

Results and Discussion

The first step of method development was the characterization of the light and heavy fractions and identification of suitable light and heavy fraction columns. The Carboxen-1000 column was identified from the literature (15) as a good candidate for separating the light fraction, permanent gases, and light (C1–C2) hydrocarbons. The heavy fraction column was identified on a trial-and-error basis because the constraints for selection of this column were more stringent. The heavy fraction column must adequately separate the heavy fraction species, have no activity for the separation of the light fraction species, and its integrity cannot be hindered by any of the species in the injected sample. Porapak Q, a high surface area, cross-linked polymer packing without a stationary phase coating, typically used for separating small chain, slightly polar species, was selected as the heavy fraction column.

The next step was the identification of the light fraction and determination of its retention time in the heavy fraction column. This was achieved by connecting the Porapak Q (heavy fraction) column directly to the TCD and injecting a prepared mixture of the two certified calibration gases with the column oven at 35°C. The permanent gases (H_2, N_2, CO, CH_4, and CO_2) coeluted in less than 4 min, and the C2-species from calibration gas #2 were adequately separated and eluted after 4 min. The 4-min mark was selected as the time to actuate the decision valve to position 2.

The column, detector, and valve arrangement given in Figure 1 was then implemented. The temperature program suggested by Supelco Application Note 112 (15) for the separation of permanent gases and C2 hydrocarbons using the Carboxen-1000 column was selected as the starting point for temperature program development. The proposed temperature program consisted of a temperature hold at 35°C for 4 min and an aggressive temperature ramp rate of 20°C/min to 225°C. Mixtures containing the two custom calibration gases and condensable species (e.g., water, ethanol, acetaldehyde, etc.) were used to "tailor" the temperature program. Analysis of the simulated product stream resulted in good separation and quantitation of the permanent gas species, C2 hydrocarbons (acetylene, ethylene, and ethane), but resulted in coelution or peak shouldering of acetaldehyde and methane from the heavy fraction column and poor separation of the remaining hydrocarbons. The temperature ramp rate was reduced to 5°C/min from 155°C to 225°C to allow for better separation of these species. The resulting temperature program is given in Table II.

The separation strategy can be described with the aid of the schematic diagram (Figure 1), the column or detector arrangements (Figures 2A and 2B), and the resulting TCD and FID chromatograms given in Figures 3 and 4, respectively. The product gas stream exiting the reactor was injected into the GC. The sample passed through the decision valve and entered the Porapak Q column that was held at 35°C. The heavy condensable species adsorbed onto the column, while the light gaseous species continued, unresolved, to the Carboxen-1000 column. Hydrogen, being the least retained species, was detected by the TCD (Figure 3) at minute 2 and was subsequently burned by the FID (no detection). After 4 min, the decision valve was switched to position 2, and at minute 5, the column oven temperature was ramped at a rate of 20°C/min to 155°C. During this temperature ramp, ethylene, acetylene, ethane, and propylene eluted from the Porapak Q column and were detected by the FID (Figure 4). In addition, nitrogen and carbon monoxide, eluted from the light fraction column, were detected by the TCD, and then fed to the heavy fraction Porapak Q column as a pseudo-carrier gas. These species were not detected by the FID and did not interfere with the quantitation of species eluting from the Porapak Q column. The oven temperature was then increased to 225°C at a reduced ramp rate of 5°C/min to give better separation of the more strongly adsorbed species. At minute 10.5, the FID sensitivity was reduced from attenuation level 12 to 11, because the concentrations of acetaldehyde, methane, and ethanol were expected to be high, and would, therefore, create very large saturated peaks. Acetaldehyde was the next species to desorb from the heavy fraction column, though shortly afterwards, methane eluted from the light fraction column. Methane was detected by the TCD and then eluted from the heavy fraction column and was detected by the FID. Ethanol desorbed from the heavy fraction column at minute 12.75, fol-

Table I. Composition of Custom Certified Calibration Gases

Calibration gas 1		Calibration gas 2	
Species	Concentration (vol%)	Species	Concentration (vol%)
H_2	30.03	C_2H_2	0.499
O_2	3.0	C_2H_4	3.09
Ar	9.0	C_2H_6	3.00
CO	30.0	N_2	93.0
CH_4	7.97	Trace hydrocarbon	Balance
CO_2	20.0	Mixture	

Table II. GC Oven Temperature Program

Temperature (°C)	Rate (°C/min)	Hold (min)	Total time (min)
35	0.0	5.0	5.0
155	20.0	0.0	11.0
225	5.0	0.0	25.0

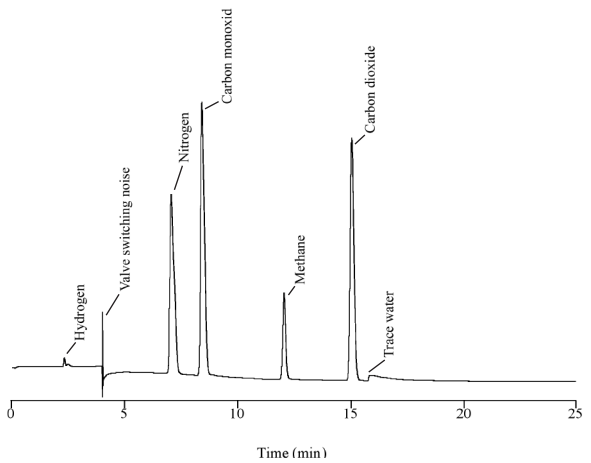

Figure 3. TCD plot of light fraction (Carboxen-1000) column separation.

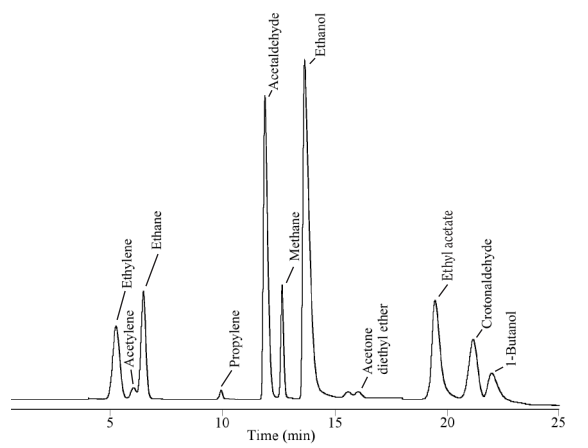

Figure 4. FID plot of heavy fraction (Porapak Q) column separation.

lowed by CO_2 from the light fraction column. Again, when CO_2 eluted from the light fraction column, it passed through the TCD, where it was detected, then passed through the heavy fraction column and the FID. However, being non-combustible, it was not detected by the FID. The elution of acetone and diethyl ether from the heavy fraction column occurred at minutes 15.6 and 16.0, respectively. At minute 18, the FID sensitivity was increased from attenuation 11 to 12 to allow for the detection of trace amounts of the remaining species. The remaining hydrocarbon species (ethyl acetate, crotonaldehyde, and butanol) eluted from the heavy fraction column and were detected by the FID. The method ended at minute 25, at which point the decision valve was returned to position 1 and the column oven cooled to its initial temperature.

Once the separation method was developed, a calibration of each species was obtained using combinations of the two custom calibration gases, pure gases (H_2, N_2, CH_4, and C_2H_4), water, and liquid organics. The results of the calibration are given in Table III. The calibrated range for hydrogen was quite broad (3.0–99.0%), but the flow rate of the carrier gas, helium, was very large, resulting in a hydrogen concentration seen by the detector below 5%. The polarity of the hydrogen peak was positive for the entire range (no peak inversion); however, the relationship between a hydrogen concentration and peak area was quadratic, not linear. The resulting concave-upward quadratic model accounts for the nonlinearity in the thermal conductivity of the hydrogen and helium mixture (16).

Table III. GC Calibration Results

Species	Range (%mol)	Detector	Model	R^2	No. of data points*
Hydrogen	3.0–99.0	TCD	Quadratic	0.9996	17
Nitrogen	1.0–99.3	TCD	Linear	0.9991	33
Carbon monoxide	3.0–30.0	TCD	Linear	0.9991	6
Methane	0.8–20.0	TCD	Linear	0.9991	10
		FID	Linear	0.9990	10
Carbon dioxide	2.0–20.0	TCD	Linear	0.9995	6
Acetylene	0.05–0.499	FID	Linear	0.9977	6
Ethylene	0.031–30.0	FID	Linear	0.9951	14
Ethane	0.30–3.0	FID	Linear	0.9973	6
Propylene	0.01–0.1	FID	Linear	0.9989	6
Acetaldehyde	0.44–18.0	FID	Linear	0.9987	7
Ethanol	0.30–84.0	FID	Linear	0.9991	12
Acetone	0.01–0.17	FID	Linear	0.9999	3
Diethyl ether	0.01–0.1	FID	Linear	0.9975	3
Ethyl acetate	0.01–0.16	FID	Linear	0.9996	3
Crotonaldehyde	0.01–0.1	FID	Linear	0.9829	3
1-Butanol	0.01–0.09	FID	Linear	0.897	3

* Each data point represents an average of a minimum of five replicate injections.

Conclusion

The composition of the stream resulting from ethanol steam reforming varies with the catalyst, employed reaction conditions [temperature, reactant feed concentration, feed gas flow rate, and time on-stream (catalyst deactivation)]. The analysis of such a complex and varying gas composition is no trivial task. The described analytical method provides a versatile and

inexpensive tool for separating and detecting samples containing both gaseous and condensable species. By adjusting the time of the decision valve actuation, temperature program, and detector sensitivity, the method can be fitted to obtain a desirable degree of separation and detection for different species produced in various reactions, all in one GC. The authors believe that by simply employing appropriate column selections, temperature programming, and detector type and sensitivity, a broader range of applications can be achieved.

Acknowledgments

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