
IN COOPERATION WITH COLORADO STATE UNIVERSITY
Richard Kingman, Executive Director
2785 N. Spear Blvd., Suite 230, Denver, Colorado 80211

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# USE OF NATURAL GAS FOR $CO_2$ PRODUCTION IN GREENHOUSES

JOE J. HANAN

Ethylene is produced in the complete combustion of natural gas. Concentrations as high as 650 ppm in the visible flame region have been measured, with three ppm to be expected in undiluted flue gases. Significant concentrations have been measured in flue gases from various types of $CO_2$ burners in Denver, depending upon the method for distributing the $CO_2$ in the greenhouse. Wind socks for distributing $CO_2$ throughout the entire greenhouse are a necessity. There appears to be considerable recirculation of flue gases through burners unless provision is made to distribute the gases equally throughout the house by means of plastic distribution tubes. Testing for carbon monoxide is not a reliable measurement for ethylene. There is no direct correlation between CO and $C_2H_4$. Flue gases must be diluted with excess air, and code requirements should be doubled to two square inches of free-air inlet per 5000 BTU per hour input. The relationships between primary and secondary air, and impingement of flames on cold surfaces are critical in determining ethylene formation. Failure to take all precautions in the use of any combustion process for $CO_2$ production results in serious risk.

## INITIAL DATA

Recurring injury attributed to flue gases in Colorado led to a project supported in part by the Public Service Company of Colorado and CFGA. A small, modified burner, enclosed in a glass box, was employed to study ethylene production. The total air to the burner could be controlled by regulating the free-air aperture size in the bottom of the box, and a copper sample tube in the chimney allowed flue gas sampling. Figure 1 shows that ethylene concentration in the flue gas was a logarithmic function of aperture size. At an average gas flow rate of 0.15CFM, $C_2H_4$ in the flue gas exceeded 5 ppm when the aperture was less than one square inch, with the flame extinguishing at 10 ppm. On a per

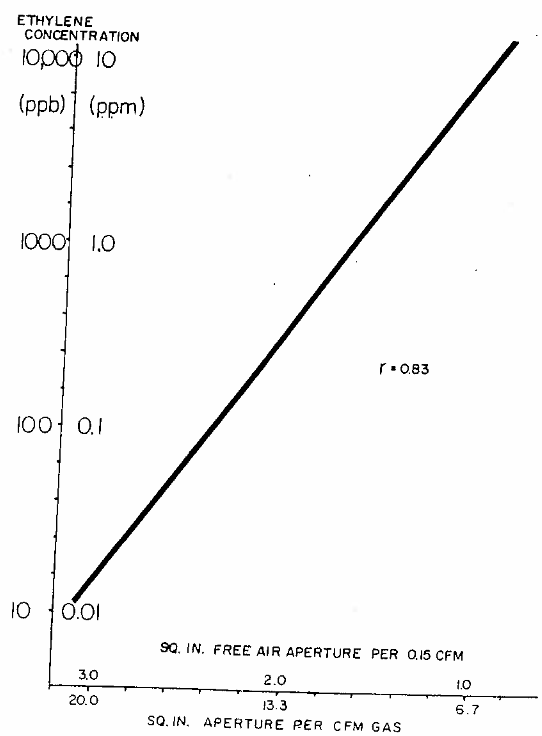


*Figure 1. Ethylene concentrations in the flue gas from a natural gas burner where total air was controlled by free-air, aperture size. Mean rate of gas flow 0.15 CFM.*

cubic foot basis, minimum ethylene concentration was obtained when the total aperture area was about 20 square inches. The low concentration probably resulted from dilution of flue gas with excess air. This aperture area is approximately double the minimum required by the NFPA code which calls for one square inch per 5000 BTU/hour input. At one CFM (880 BTU/$ft^3$), NFPA's code calculates to 10.6 square inches as required. Our results suggest 21 square inches as better.

## COMBUSTION OF NATURAL GAS

High school chemistry courses usually oversimplify methane combustion. That is:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O.$$

In fact, there are numerous intermediate steps, and the exact sequence, which varies with conditions, has not been completely settled. Depending upon ratios of primary and secondary air, physical characteristics of the burner, amount of oxygen, etc., numerous exotic materials may form, including ethylene. The presence of other gases with methane (Table 1) assures that reactions will not be simple.

Table 1. Colorado natural gas analysis, 1969.

| Constituent | Percent by volume |
|---|---|
| Methane ($CH_4$) | 85.6 |
| Ethane ($C_2H_6$) | 5.51 |
| Propane ($C_3H_8$) | 1.4 |
| n-Butane ($C_4H_{10}$) | 0.09 |
| $CO_2$ | 1.0 |
| Nitrogen ($N_2$) | 6.17 |
| Isobutane | 0.08 |
| Isopentane | 0.01 |
| n-Pentane | trace |

According to Rosenberg, et al. (7), who studied flame chemistry under rigorously controlled conditions, the concentration of ethylene is strongly dependent upon the fuel-air ratio in the primary mixture. With an air deficiency of 84%, peak $C_2H_4$ in the visible flame region (about 0.04 inches above the burner) was 800 ppm, with 650 ppm at the burner centerline. With a primary mixture for complete combustion, the concentration was 400 ppm; and with an air excess of 120%, the maximum concentration was 300 ppm. At one inch from the centerline, $C_2H_4$ dropped to 50 ppm. Air in the primary mixture tended to decrease $C_2H_4$, whereas oxygen in the secondary air increased ethylene. Quenching the flame by impinging it upon a cold surface could increase $C_2H_4$ by preventing downstream reactions (7). One might expect a burst of ethylene from cold unit heaters, and this appears to have been the situtation on February 28 when warm, outside temperatures required the burners to be started manually in order to sample for $C_2H_4$ (Table 2). Temperature and air supply interact in the secondary air, with oxygen enhancing the reaction. But, lower temperature slows down reactions, and the latter is probably the stronger of the two in influencing complete combustion. Rosenberg, et al. (7), stated that flue gases may contain about 3 ppm $C_2H_4$ under conditions of complete combustion.

Analysis for $C_2H_4$ required sophisticated equipment which cannot be brought into the greenhouse. Public Service Company wanted to know if a correlation could be found between $C_2H_4$ and CO, the latter requiring much simpler equipment. However, none of our tests showed any relationship between ethylene and carbon monoxide. Rosenberg (8) stated that the presence of CO is no guarantee that $C_2H_4$ is present. The reaction sequence for the two gases is different, with CO being the most stable and last to disappear in combustion. Neither does $CO_2$ analysis of the flue gases appear to be reliable. As shown in Figure 2, $CO_2$ concentration may be low because of excess or deficient air. We should keep in mind, that even with so-called "complete" combustion, significant quantities of ethylene may be produced. Excess air is required to dilute $C_2H_4$ to permissible levels.

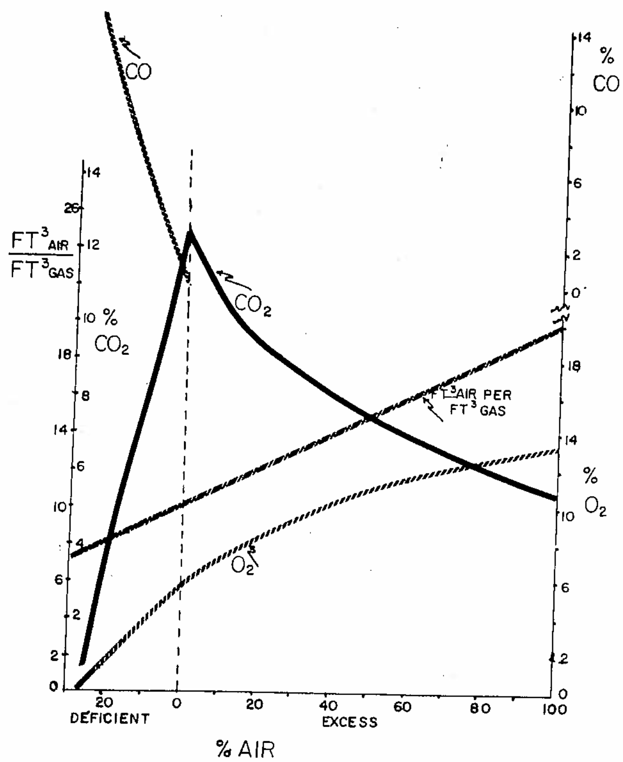


*Figure 2. Relationships between cubic feet of air per cubic foot of gas, $CO_2$, CO, and $O_2$ concentrations in flue gas as a function of the percent excess or deficiency of air.*

Calculations on the amount of air required for complete combustion of natural gas given in Table 1 result in about 9.5 $ft^3$ air per $ft^3$ of gas, which will produce 2.4 $ft^3$ water and 2 $ft^3$ $CO_2$. Public Service Company considers 9 $ft^3$ air per $ft^3$ of gas as the lower limit for human safety. For plant safety, the amount of air should be in excess of 10 $ft^3/ft^3$ gas. A distinct problem in greenhouses is recirculation of combusted gas through the burner. Although there may be sufficient air entry at some point in the structure, the air may be "contaminated" by flue gas before reaching the burner. Table 2 indicates a significant problem of ethylene build-up due to recirculation. The safest method is to evenly distribute the $CO_2$ throughout the greenhouse by means of polyethylene tubes, and to duct fresh, outside air directly to the burner.

## NFPA CODE REQUIREMENTS

The National Fire Protection Code for 1969, Section 54(5), states that, in unconfined spaces, a permanent opening of not less than one square inch per 5000 BTU/hour input of total input rating shall be provided. We feel this should be doubled where unvented heaters are used for $CO_2$ production. It is not sufficient to assume that air infiltration, normally present in greenhouses, will be adequate since air infiltration can be zero, depending upon outside air temperature and wind velocity. Even where some burners, used solely for heat, are vented to the outside, oxygen deficiency within the house may cause an ethylene surge into the house. Fresh air supply directly to heaters, whether vented or unvented, is a safe — although expensive — precaution.

Section 5.1.1 of the code states that such appliances as unit heaters, etc., shall be vented. Section 5.1.2 states that only listed appliances with inputs not over 5000 BTU/hour may be unvented. When the total input exceeds 30 BTU/$ft^3$ of room space, one or more appliances in the room must be vented to reduce the aggregate below 30/$ft^3$/hour. Calculations of total input for growers 1, 4, and 5 (Table 2) showed a total unvented input of less than 2.0 BTU/$ft^3$. This code restriction is meaningless to most greenhouse operators using natural gas for $CO_2$ production.

## ANALYSES OF FLUE GASES IN DENVER

During 1972, several locations in Denver were selected for direct sampling of flue gases from burners intended primarily for $CO_2$ production. Table 2 presents the results. Of particular concern was the marked variation in ethylene concentration

Table 2. Ethylene analyses of flue gases from various $CO_2$ production units in the Denver region.[a]

| Grower | Burner type | Conditions | Date | | | |
|---|---|---|---|---|---|---|
| | | | Jan. 19 | Jan. 26 | Feb. 21 | Feb. 28 |
| 1.[g] | Modified Unit heater | Distribution tube (hot)[b] | 0.5 | 1.6 | ---- | 4.0 |
| | Modified Unit heater | Distribution tube (hot) | ---- | ---- | ---- | 7.1 |
| | Modified Unit heater | Distribution tube (hot) | ---- | ---- | 11.0[i] | 7.8 |
| | Modified Unit heater | Distribution tube (hot) | ---- | ---- | 1.1 | 9.2 |
| | Modified Unit heater | Distribution tube (hot) | ---- | ---- | 2.4 | 7.7 |
| | Modified Unit heater | Same as above, tube removed | ---- | ---- | ---- | 18.4 |
| 2.[cg] | Modified Unit heater | Distribution tube (hot) | ---- | ---- | 2.9 | 205[d] |
| | Modified Unit heater | Distribution tube (hot) | ---- | ---- | 3.3 | 212[d] |
| | Modified Unit heater | Distribution tube (hot) | ---- | ---- | 3.8 | 62[d] |
| | Modified Unit heater | No distribution tube (hot) | ---- | ---- | 22.6 | 136[d] |
| 3.[g] | Modified Unit heater | No distribution tube, cross-house (cold)[e] | ---- | ---- | ---- | 389[d] |
| | Modified Unit heater | No distribution tube, cross-house (cold) | ---- | ---- | ---- | 677[d] |
| | Modified Unit heater | No distribution tube, cross-house (cold) | ---- | ---- | ---- | 695[d] |
| | Modified Unit heater | No distribution tube, cross-house (cold) | ---- | ---- | ---- | 751[d] |
| 4. | Modified Unit heater | No distribution tube, cross-house (cold) | 502[fe] | ---- | ---- | ---- |
| 5. | Modified Unit heater | No distribution tube, lengthwise (hot) | 70.1[f] | 222[h] | ---- | ---- |
| 6. | Hi-Lo Burner | No distribution tube (hot) | 26.0 | 21.2 | ---- | ---- |
| 7. | Kerosene burner | No distribution tube (hot) | 94.0 | 254 | ---- | ---- |

[a] *Gas sampled directly above heat exchangers, in the flue.*
[b] *Burner operating for period prior to sampling, distribution wind sock the length of the house.*
[c] *Indication of internode shortening prior to tube installation.*
[d] *Burners tested immediately after start-up.*
[e] *Burners located in center to fan across the house, rather than lengthwise.*
[f] *Previous history of internode shortening.*
[g] *Outside ethylene concentrations: Feb. 28, grower 1, 0.8ppb; grower 2, 12.1; grower 3, 6.2.*
[h] *Outside ethylene concentration: Jan. 26, grower 5, 6.4ppb.*
[i] *Distribution tube broken loose from unit.*

between various burners. The tests on February 21 and 28 proved that the main difference between burners resulted from the means by which the $CO_2$ was distributed in the greenhouses. This was confirmed by a significant $C_2H_4$ increase when the distribution tubes were removed from some unit heaters. Isolated units, injecting flue gases directly into the immediate area, apparently set up their own independent circulation patterns in which a significant portion of the flue gases was recirculated through the burners, preventing dilution with infiltrated air, and causing an ethylene build-up in the flue gases. Cases of internode shortening have been associated with burners without distribution tubes, particularly where heaters blow across the house rather than lengthwise. It is apparent that ducting the heater output the length of the greenhouse ensures that there will be a sufficient air circulation pattern to bring fresh, infiltrated air to the burner. Even in the case of an ethylene burst from cold heaters, a distribution tube caused a marked reduction in the amount of ethylene produced (Table 2).

## SOME PENCIL PUSHING

Information that would put natural gas combustion for $CO_2$ injection on a firm basis is nonexistent. There are approximate values to be found, but all lack: 1) the actual amount of $CO_2$ that will be used by the crop, 2) the air infiltration of the greenhouse, and 3) the volume of space into which the $CO_2$ is to be injected. First, no one has ever calculated $CO_2$ used by a bench of carnations or roses — even if the basic data were available. Second, the best information shows infiltration rates range from about one or more complete air exchanges per hour, downward to 0.6 changes per hour, depending upon greenhouse type. Most cases of flue gas damage are associated with tight greenhouses and low temperatures. Infiltration rates must be known. And third, the $CO_2$ level that results from a given quantity of gas depends upon total volume of the space into which injected — not the square feet of area covered. However, most manufacturers' recommendations are based upon square feet.

As a first approximation, Figure 3 shows the quantity of natural gas required per hour for different levels of $CO_2$ and infiltration rates for a total greenhouse volume of 100,000 $ft^3$. This volume would be roughly equivalent to 8,300 $ft^3$. On the basis of data obtained by Holley and Goldsberry (1-4), it is assumed that roses will utilize four CFH $CO_2$ per 1000 $ft^3$. It is further assumed that conditions are steady, and that the different $CO_2$ levels have been reached. The results are striking. At an infiltration rate below 1000 CFH, any $CO_2$ concentration may be maintained with little difficulty (16 to 18 CFH gas), with a minimum air infiltration rate of 160 to

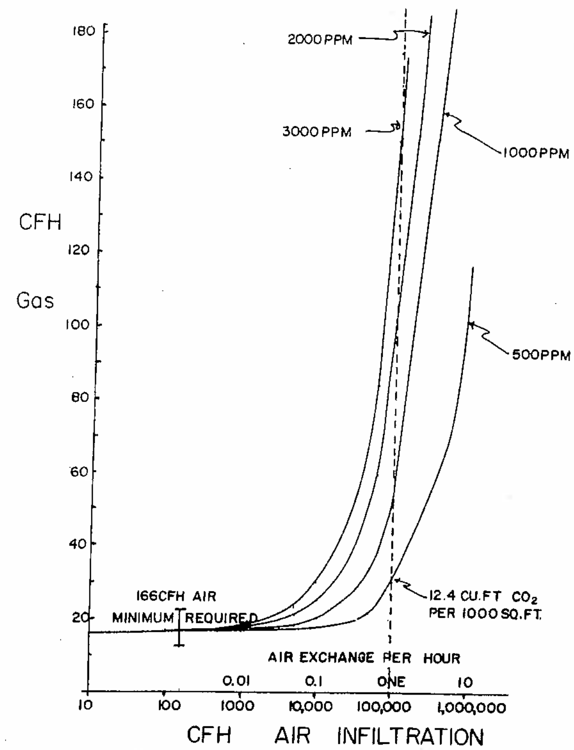


*Figure 3. Cubic feet per hour (CFH) natural gas required to maintain various $CO_2$ concentrations in 100,000 cubic feet at different rates of air infiltration. The basic assumption is that 4 CFH $CO_2$ per 1000 square feet are actually utilized by the plants.*

180 CFH. Beyond infiltration rates of 1000 CFH, it becomes difficult to maintain $CO_2$ levels much in excess of 500 ppm. The 500 ppm level can be achieved easily at one complete air exchange per hour. But, if 1500 ppm $CO_2$ are required, the CFH gas required increases from about 260 to over 700 CFH. If the greenhouse is equipped to maintain a 1500 ppm $CO_2$ concentration at one air exchange per hour, there is a correspondingly greater chance of flue gas damage if the greenhouse is tight and the outside temperature is low.

Let us assume that sufficient air is provided for complete combustion (10 CFH air per CFH gas). According to Rosenberg, et al. (7), 3 ppm ethylene may be found in the undiluted flue gas under those conditions. What will be the ethylene concentration at the end of one hour for different rates of gas combustion? The rate of air infiltration will increase to maintain the air:gas ratio at 10 to 1. No allowance is made for ethylene loss during infiltration, which would lower the curve in Figure 4. At 100 CFH gas, air infiltration of 1000 CFH, the $C_2H_4$ level will be 30 ppb after one hour. At gas consumption rates in excess of 300 CFH, the concentration will reach 100 ppb, even though air infiltration is 3000 CFH.

These calculations are intended to show problems in maintaining $CO_2$ levels in greenhouses with natural gas. The values I have calculated in Figure 3 appear high. We lack sufficient information to make the values a basis upon which management decisions can be made.

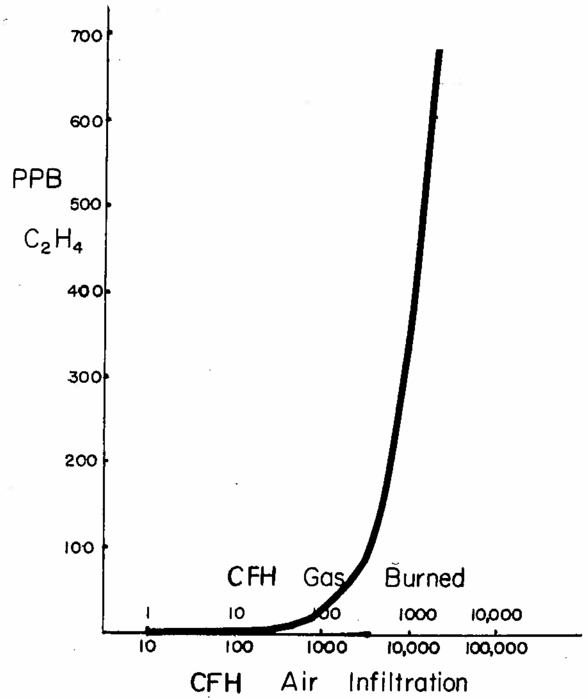


*Figure 4. Calculated ethylene concentration at the end of one hour in 100,000 cubic feet for different gas combustion rates, assuming: 1) Ten CFH air per one CFH natural gas; 2) ethylene concentration in the flue gas is 3 ppm; and 3) no ethylene is lost to the outside.*

## RECOMMENDATIONS AND CONCLUSIONS

1. Definite provision should be made in the greenhouse structure for a minimum of two square inches of free air per 5000 BTU per hour input. It should not be left to chance that cracks in the structure are sufficient under all conditions.

2. A definite distribution system should be attached to the heater, forcing $CO_2$ to be distributed throughout the length of the greenhouse. There will be an ethylene build-up due to recirculation of flue gases around heaters injecting gases in the immediate vicinity of the burner.

3. For absolute safety, each appliance should have its own fresh air supply ducted directly to the burner. This does not appear necessary when the burner is fitted with a wind sock distribution tube.

4. In calculating air infiltration requirements, all vented and nonvented appliances should be included.

5. Satisfaction of requirements for plant safety will automatically fulfill requirements for human safety.

6. Apparently, most combustion processes produce ethylene, and the recommendations given here should be followed regardless of burner type.

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