

INDIVIDUAL HYDROCARBON PATHS THROUGH AIR SEPARATION PLANT

L. W. Coleman
Rohm & Haas Co.
Houston, Texas

A hydrocarbon analyzer (1) using hydrogen flame ionization as the detector was installed about two weeks prior to reporting only a limited amount of actual data in the cited literature. Now certain data have been collected:

During the past nine months the analyzer has operated very satisfactorily. The original unit was found, on continued operation, to have a moderate amount of drift with occasions when the drift was somewhat excessive. This was traced to primarily temperature and battery instability of the amplifier system. A new simplified amplifier has been installed with good results. Practically the only maintenance has been replacement of batteries every 4 to 6 weeks and switching of hydrogen cylinders every 4 to 5 weeks. This is considered exceptional for a chromatographic unit.

Laboratory check

The data which have been obtained appear to be reliable and have been checked against numerous laboratory determinations in which the total hydrocarbons were run and compared to the sum of the individual components as determined by the analyzer. Laboratory samples have been cut to a very minimum sufficient

only to keep laboratory men trained and skilled in operation of the laboratory equipment, and as a periodic check on the analyzer.

The Hopcalite filter

It was particularly desirable to follow the efficiency of the Hopcalite filter installed on the air inlet and the silica gel filter used to remove contaminants from the liquid stream going to the low pressure column. Figure 1 shows a simplified schematic of the Air Separation Plant. The curves underneath give the percent of hydrocarbons showing up in the various streams based on the amount entering. Each component from methane through butane starts at 100%. No hydrocarbons could be found in the product nitrogen or waste streams other than those caught in the Trane exchangers.

Because simultaneous samples could not be readily taken throughout the entire separation unit, the analyzer was set up to repeatedly sample two or three points in place of the normal six streams. These were analyzed over a period of time and then summarized.

The Hopcalite, as is shown on the curve, removes no detectable amount of methane and only a relatively small proportion of the ethane and propane. Ap-

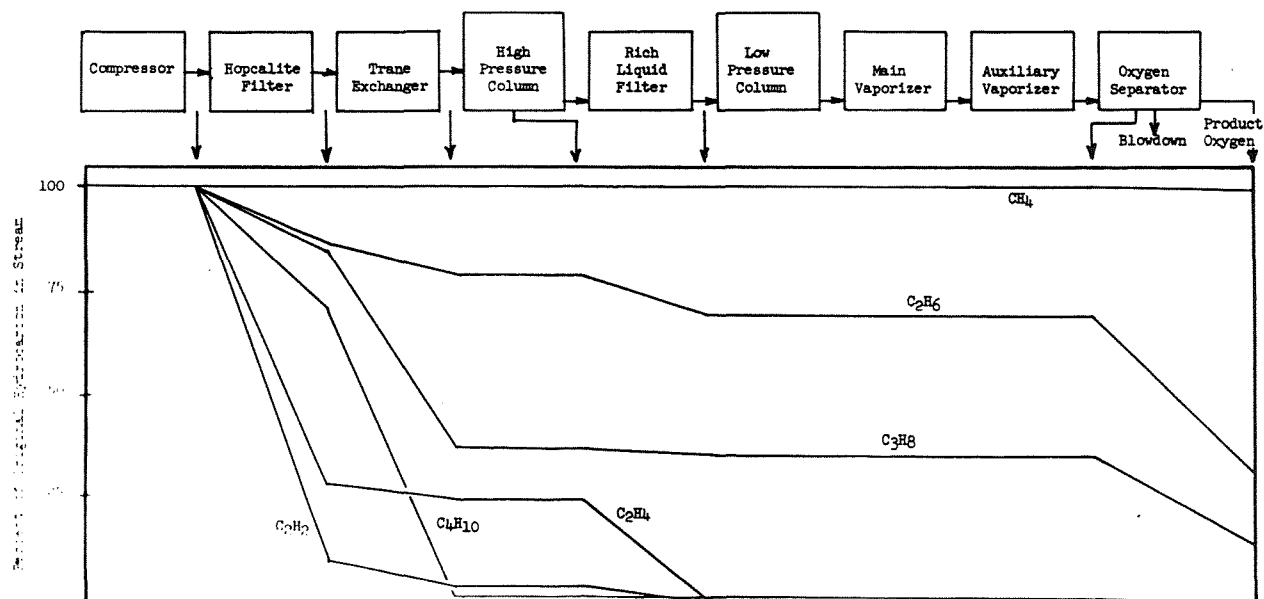


Figure 1. Hydrocarbon path through air separation plant.

proximately 65 to 70% of the ethylene is converted to carbon dioxide, whereas 90 to 95% of the acetylene is removed. Butane shows a 30% decrease in passing through the bed. The catalyst in the bed has shown signs of decreased activity. Half of the catalyst has been in service for approximately two years, whereas the other half has been in for only a year. During the past year the temperature of the air coming out has had to be increased from 160–165°C to 170–175°C in order to maintain the same approximate conversions of ethylene. The maximum temperature has been reached at which the compressors can operate without seriously impairing their efficiency. It will be only a matter of time until the catalyst will have to be replaced. Just when the catalyst is changed will depend upon the activity and contamination levels as indicated by day to day sampling.

Unbalanced exchange system

The Trane exchangers remove a considerable proportion of the hydrocarbons, particularly the heavier ones such as propane and butane. On several occasions the exchange system has become unbalanced to the point where liquid was found in the reversing valves on the cold end. This liquid had up to 6 ppm of acetylene, as well as other hydrocarbons. This would more or less be expected. However, it does point out that with all the safety measures that are taken in the other parts of the system, particularly the low pressure section, this part might be overlooked. One could visualize the liquid forming, condensing out acetylene, and later evaporating the liquid air with a resultant large accumulation of acetylene. Since this was found, more emphasis has been placed on keeping the Tranes balanced and the low spots have been set up on a routine blowdown schedule.

Silica gel bed

The rich liquid filters remove practically all of the remaining ethylene and as far as can be detected all of the remaining acetylene. Only a small proportion, however, of the saturated hydrocarbons, which appear in quantities large enough to be determined, are adsorbed in the silica gel bed. One reason for this may be that these beds have now been in service for slightly over three years without any change of gel. The low 70°C reactivation temperature (the maximum attainable with

existing equipment) may be insufficient to effectively remove water which would reduce the capacity of the bed.

Oxygen separator

It is rather surprising to note that the oxygen separator, while it contains quite high concentrations of hydrocarbons, actually removes, in our particular case, a relatively small amount of the total contamination. The methane, for instance, is reduced only a fraction of a per cent and over 99% of this material appears in the product oxygen. Similarly ethane and propane are not very effectively removed when considered on a total pounds basis. One reason for this may be the low percentage of blowdown which is used. Normally this will be maintained between 1/3% to 1% of the oxygen production. The amount of blowdown is controlled by the contamination concentration.

Table 1 shows the degree of contamination which is experienced. Liquid samples were taken in all cases except the air entering and the product oxygen. The contamination level is low in comparison to that experienced by most other oxygen producers. Much of our contamination except for methane enters mainly in slugs which depend upon atmospheric conditions, wind direction, and of course, degree of venting of surrounding plants. It has been surprising to find that methane is a normal contaminant and never appears to drop below 1 ppm. Other streams are rather free of hydrocarbons except the oxygen blowdown. Here the concentration of methane and ethane becomes rather high, but because of their high solubility, they are not felt to be particularly dangerous. The total hydrocarbons in the product oxygen are due almost entirely to the methane. If the rate of blowdown were regulated by the total hydrocarbons (i.e. carbon atoms), an excessive amount of production could be thrown away. Little attention is given to the actual methane content of any of the streams and blowdown rates are based on ethylene and the higher saturated hydrocarbons.

When to derime

From data so far obtained, no fixed derime schedule has been established. Table 2 lists the quantities of hydrocarbons removed after various periods of time on stream. It appears that even after 30 days on the line, the amount of build-up may be dangerous.

Table 1
HYDROCARBON CONTAMINATION LEVELS
All Values in ppm (by volume)

	Compressor	Hopcalite Filter	Trane Exchanger	High Pressure Column	Rich Liquid Filter	Low Pressure Column	Main Vaporizer	Auxiliary Vaporizer	Oxygen Separator
Methane	1-3	1-3	1-3	3-8	3-8		6-18	20-45	6-18
Ethane	0.01-0.1	0-0.09	0-0.08	0-0.2	0-0.16		0-0.3	0.5-16	0-0.05
Ethylene	0-2	0-0.7	0-0.7	0-1.2	< 0.02		0-0.02	0-0.9	0-0.02
Acetylene	0-1	0-0.1	0-0.03	0-0.1	< 0.02		< 0.02	< 0.02	< 0.02
Propane	0-0.1	0-0.09	0-0.03	0-0.06	0-0.06		0-0.1	0.2-6	0-0.1
Butanes	0-0.2	0-0.07	< 0.02	< 0.02	< 0.02		0-Trace	0.2-7	0-0.02
Pentanes	0-0.08	< 0.02	< 0.02	< 0.02	< 0.02		0-Trace	0-0.6	< 0.02

There are several factors influencing the build-up: the general contamination level during the period; the rate of blowdown; and uniformity in maintaining blowdown. In other words, if operations are such that all the oxygen is evaporated for several hours, the accumulation may be rather rapid.

Conclusions

Under existing conditions the Hopcalite filter is quite effective in decomposing unsaturated hydrocarbons but progressively less effective in removal of butanes and lighter components. The Trane exchangers remove substantial quantities of propane and butanes but have little effect on other components. The rich liquid filters appear to be almost specific in the removal of unsaturates. Some contamination is taken out in the auxiliary vaporizer but, due to prior removal, low blowdown rates and generally low contamination levels, a relatively small proportion is removed in this manner. It would be wrong to infer, however, that the auxiliary vaporizer is not a valuable and necessary piece of safety equipment, for it affords a means of

DISCUSSION

WELLS: On your analyzer, has it ever given you any false or erroneous high readings as a result of some difficulty with the analyzer and, if so, has this ever exceeded your shutdown limits for any of the materials?

COLEMAN: No. I can't think of any time when it has given us high readings. I would say that there is one thing that we have run into that you have to watch and that is the quantity of sample. I have had discussions with various people and they say "maybe the sampling method isn't too good." But the way we do it is to remove a rather large sample continuously, and while one of the samples is being analyzed, the others are purged to the atmosphere. In that way, our residence time in the sample line is very short. As a matter of fact, it figures out to be somewhere in the range of fifteen to twenty seconds and we can reproduce our results within three to five percent without any difficulty. On occasion, you will find that you get a somewhat lower value on methane than what you might really have and this is due to the concentration of oxygen. In other words, the oxygen, in going through the chromatographic column, will tend to mask methane if the oxygen concentration is very high. The remainder of the results have been very good.

JENKINS: How do you obtain your liquid samples?

COLEMAN: We have stainless steel lines coming from various points to the outside of the box. From there, it is run through aluminum lines to the analyzer. At a point just ahead of the analyzer we have rotameters on each line. The flow in each is maintained in the range of 8,000 cu. cm. of gas a minute. We allow the liquid to vaporize in the line. Periodically these lines are opened wide to flush out anything that might have accumulated. We have never had any indication of a serious accumulation.

JENKINS: The thing that we have wondered about is the reproducibility with just simple vaporization in the line. We have been very hesitant to get a liquid sample in this method.

COLEMAN: We have checked this analyzer against taking the usual liquid oxygen sample and running it for

Table 2

HYDROCARBON ACCUMULATION IN AUX. VAPORIZER AND O₂ SEP.

Time on line	Time On Line—Days		
	41 days	60 days	175 days
Ethane (gms)	4.6	41.7	13.3
Propane (gms)	14.4	87.0	30.1
Butanes (gms)	39.0	89.0	188
Pentanes (gms)	2.1	12.7	12.5

periodically removing materials which would otherwise accumulate in larger and less accessible equipment.

The hydrocarbon analyzer itself has proven to be reliable and very helpful in following the operation of the plant and in removing much of the guesswork associated with day to day operations. It provides a more sound basis for blowdown control, changing of Hopcalite catalyst and renewal of silica gel beds, in addition to substantial savings in analytical laboratory costs.

total hydrocarbons in the lab. They have agreed very well. I don't know what other clues I can give that the sampling method is satisfactory.

HEPP: I just wanted to describe the sampling method we use. We have infrared analyzers which have to accept a gas sample. We have a small pot about six inches in diameter and about a foot high. We heat it to about 150° and let the liquid sample vaporize in that pot right next to the box and then transport the sample as a gas to the analyzer. We have inspected them and we don't find any accumulation in the pots.

GIBSON: We have a continuous blowdown from our low pressure reboiler and take liquid samples from this stream in a Dewar flask for hydrocarbon analysis. We have checked samples where the liquid has been allowed to evaporate in the line. We were unable to get reasonable checks in these two methods.

JENKINS: I think we are going to buy a hydrocarbon flame analyzer for air inlet, and I would like to hear someone who has possibly had some experience comment on the difference between an infra-red and hydrocarbon flame. From everything that we can obtain, it appears that the hydrocarbon flame is highly superior and much more reliable.

WEIGERS: I don't think it is a question of reliability. It is rather a question of getting sufficient information. We are in the process of buying a chromatographic analyzer because we find that the infra-red total hydrocarbon analyzer does not give us enough information. The total hydrocarbon analyzers are fine, but as has been said many, many times—unless you know which specific hydrocarbons are present, you don't really know whether you are in trouble.

WELLS: It may depend a little bit on the type of IR analyzer that you have. We have an IR analyzer with a ten-meter cell which gives us a complete profile of the hydrocarbons. We have had very good performance from it. It has been reliable and not given us false information. We can't get samples as quickly as some have with the flame analyzers. It also is a pretty expensive instrument, but can be reliable and does give the complete profile.

PINNEY: We don't have an infra-red. We have a couple of differently designed flame ionizers. I might point out this matter of economics becomes rather important. You can put a flame ionizer together, sensitive to 0.5 ppm acetylene or below for around \$1,200. Infra-red, for that sensitivity, is going to cost you \$14,000—\$15,000.

SEFTON: Has anybody done an ozone analysis? And, if so, what levels did they get?

HEPP: We have analyzed for ozone using the so-called "KI" method, but we have never found anything in the years that we have done it.

COLEMAN: That is just about what we have found. We haven't been able to find any ozones or oxidants in our liquid oxygen. We feel that probably the Hopcalite has done its work.

REFERENCE

1. L. W. Coleman, Chem. Eng. Prog., 57, No. 4, 55-58 (1961).