



# what was said at A. I. Ch. E. OXYGEN PLANT SAFETY CONFERENCE

**Earl C. Clark** (Moderator): My job is Director of Operations of Air Reduction Sales Company. We operate 72 air separation plants throughout the United States and Cuba. We have a total of 126 producing units, many plants having multiple units. About 70 of these units were designed and built by Air Reduction and the others were bought from commercial suppliers such as Air Liquide, Messer, Air Products, and others. These 126 air separation units range in capacity from one ton per day up to 75 tons per day so we have a wide experience in operating all types of plants in a lot of different sizes. The main reason I am here today is that we have no plant equipment to sell. We sell only the products from air plants. Incidentally, we have never had an explosion in an oxygen reboiler in any of the units we have purchased. Now this brings us to the topic of this forum: the discussion of factors which contribute to the safety of air separation plants. Most of us have read Frank Kerry's paper (*CEP*, 52 No. 11, Nov. 1956, 441-7) which has provided the basis for this discussion session.

**Latimer** (Linde Air Products): I'm quite interested in the graph accompanying the Kerry paper, that shows the higher total hydrocarbon content of the air when the wind is blowing from the acetylene plant toward the oxygen plant in Montreal. Could Mr. Kerry tell us how much of that six to eight parts per million of total hydrocarbons is acetylene?

**Kerry** (Air Liquide): I'd say the amount of acetylene was slightly under five at maximum peak of the graph.

**Latimer**: In other words, the total hydrocarbons in that case are mostly acetylene.

**Kerry**: Mostly acetylene, that's right.

**Latimer**: I have one more question.

We are quite interested in knowing what plant analytical methods you use for nitrogen oxides and ozone.

**Kerry**: We do have information on it—"Methods of Analysis of Impurities in Gases," available to Air Liquide clients.

**Latimer**: Are these primarily plant methods?

**Kerry**: That's right, they are not research methods.

In connection with the recent A.I.Ch.E. Annual Meeting in Boston, an informal discussion of oxygen plant safety was held as part of the regular program. Here is the transcript of the recording made of proceedings, in response to many requests. Readers may be interested in forthcoming symposia on oxygen and ammonia plant safety, to take place in connection with the Baltimore National Meeting in September, 1957.

**A Consultant**: On the general topic of explosions in air plants, where do they occur? Mr. Kerry has in his paper pointed to the area between the rich oxygen accumulation at the bottom of the high pressure column and the vaporizer after the low pressure column. That was probably true in the early plants which were located out by themselves, and acetylene was the main problem. But now, as he pointed out, there are other hydrocarbons, nitrogen oxides, and so forth causing explosions. I wonder if there is any comment on locations of the explosions physically in other parts of the low pressure plant besides the vaporizer?

**Kerry**: From our own company experience, we have never had any other significant explosions outside the main vaporizer. We have had reports of fires occurring in other areas, particu-

larly in the filters. However, these were not due to any apparent fault in the filter itself. As we have read from the report (after the explosion) there was a sudden accumulation of oil vapor due to an upset in the mechanical end of the plant.

**Consultant**: Would it be possible to have some comments on the safety of operation of external horizontal type reboilers compared to internal or external vertical reboilers?

**Moderator**: I don't think we want to get into detail designs. Does Frank Kerry care to comment on this in a general way?

**Kerry**: I don't like to start describing the merits or demerits of various types of reboiler designs. Inherently, they're all good if they're properly operated, and that is the most important thing that users and future users should keep in mind. Oxygen plants are not simply a sideline utility in an over-all project, but are very important units in their own right which require good operating control. And one of the main operating controls is to make sure that the reboiler is functioning properly and the liquid is always at top level. In talking this matter over with our own Operating Department, its experience shows that whenever there has been a mishap, it was very often after a sudden plant shutdown followed by a restart and in the interim the vaporizer was allowed to go down in level. As a matter of fact, even during normal operation, if the liquid in the vaporizer were to go down beyond its level, trouble could occur.

**Moderator**: It has been my experience that when an explosion does occur it occurs in the lower part of the oxygen compartment in the reboiler. Some reboilers are more susceptible than others. We had a number of them in our company that were very

susceptible. We licked the problem by very carefully checking the acetylene concentration in the liquid every shift and maintaining a purge to keep the concentration down. Our experience has since been very good (over the past five years). We use acetylene as the tracer because we can easily and fairly accurately check the concentration of acetylene in the liquid oxygen. We feel that if the acetylene is present, other hydrocarbons are there too. If we can get rid of the acetylene, which we've always thought was probably the detonator, we've gotten rid of the other combustibles as well. We feel that if these plants are operated the way they were designed and intended to be operated, there should be no trouble.

**Unidentified** (General Chemical Division): I'd like to ask what method you use for analyzing such a small concentration of acetylene, either in liquid or gas phase?

**Kerry:** I think most plants use the Ilosvay solution method, which is a colorimetric method. You compare the color of the sample with those of predetermined standards.

**Moderator:** We also use a colorimetric method employing Ilosvay solution which analyzes down below 5 p.p.m. I wonder if any of you have any better method?

**Kerry:** We use infrared analyzers in our laboratories and we use them in large plants when we're starting up to check their performance, but we don't use them on a routine basis after we get down to normal operation. We want to know about acetylene in the area below 5 p.p.m. In fact, we want to know when it gets between one to two.

**Karwat:** (At this point Dr. E. Karwat of Linde Company, Munich, Germany, read a comment which is the basis of a communication appearing separately in this issue of *C.E.P.*—see page 188.)

**Julian Rogers** (W. R. Grace): I'd like to comment on the use of synthetic lubricants. We are currently using a synthetic lubricant in the higher stages of the air compressors for our air plant. We do not have sufficient operating time to draw any definite conclusions. The experience to date, which has lasted for a few months, is excellent. We understand that the Ingersoll-Rand Company has surveyed synthetic lubricants and the results will probably be available to any one who is interested. We also understand that there are numerous operating companies using these synthetic lubricants in their compressors

and getting very good success. I'd like also to add a few comments to the references Mr. Kerry has made regarding the operation of oxygen plants, that "you cannot design into them features to prevent their misoperation." That is true, but we should continue to strive toward this goal. There is one point that I feel has been somewhat overlooked in the discussion so far and this has to do with proposals to correct dangerous conditions. Many of the comments seem to be based on the assumption of a moderate or gradual influx of impurities into the system. From our experience we have found that in industrial plants there can be upsets in conditions entirely outside the air plant which will contaminate the atmosphere; and that the atmosphere, so contaminated, can change the hydrocarbon content of the liquid oxygen in the air plant within a matter of an hour or less by as much as one hundred fold. Fortunately, our case dealt with methane from natural gas, and our own experience, plus the literature, indicates that methane is not nearly as dangerous as acetylene or some of the other contaminants of air separation plants. The point I want to raise here is, wouldn't it be wise to channel some of our thinking toward safety measures to handle the *unexpected* in the plant by anticipation and prevention? In that regard, there has been quite a bit of work done on analyzers, particularly infrared. But considerable time lag is involved in these instruments and so far, much of the work has been done in analyzing liquid oxygen which only tells you (after the dangerous condition has occurred) that you have a time bomb sitting out there in the middle of the plant and you had better do something about it before it goes off. I might add that our immediate action was to relocate the air intake; however, this may not provide a complete or final solution.

**McKinley** (Air Products): I would like to comment just a bit upon the hydrocarbon impurity influx which can occur. I think that a constructive way of viewing the hydrocarbons that are, let's say, chemically unreactive, ones that will not form ozonides and peroxides, is to bear in mind at all times that they are fuels and can be made to explode with the oxygen provided they're concentrated. There is essentially no information in the literature concerning the explosibility of liquid mixtures of hydrocarbons and oxygen. There is, however, published explosion data for hydrocarbon gas-phase mixtures with oxygen. Since we are concerned with the lower explosibility

limit, as a first approximation, either air or oxygen data may be considered as applying.

Experimentally, in dealing with the liquid oxygen system, the lower explosion limit may not appear just when we thought it should for the simple reason that it is a function of the method of initiation. If we put enough energy into that local volume or section associated with the hydrocarbon oxygen mixture, and if the molecules have in the liquid phase the same level of energy they would have if they were in the gas phase, then they should behave as if they were originally a gas mixture. In talking about methane, the lower limit is going to be something like five or more per cent. Now, dealing with the soluble hydrocarbons, these can exist up to their explosion limits in solution, and we can stand this situation as long as there aren't any side reactions. Many hydrocarbons, other than acetylene and methane, can come in with the air feed in some locations. Many of these will have solubility limits far lower than their explosion limits, so the explosion limit is not reached as a single phase mixture. But the explosion limit may be reached if conditions are such that there can be a local concentration. We have a two-phase mixture as a result of reaching the lower soluble limit and we have conditions set up for explosion. Mr. Clark pointed out that they keep the acetylene low. One of the reasons for this is simply to avoid reaching the solubility limit. We can view all the other hydrocarbons in the same light. Fortunately, most of the others have rather substantial solubility limits so they won't misbehave. We don't have to hold them to such low concentrations. On the other hand, there are several hydrocarbons that do have low solubilities. Methane is a rather universal atmospheric contaminant but has a high solubility limit—it is one that we can dispose of safely. In general, the solubilities of hydrocarbons in oxygen behave in this way: with the saturates or the higher the molecular weight, the higher the solubility; for a given number of carbon atoms in a molecule, the higher the unsaturation, the lower the solubility. As a first rule, if you have a higher molecular weight material, if it is highly unsaturated it is going to be quite insoluble, and since it is insoluble, it will reach the solubility limit. Since it's unsaturated, it has some of the properties of acetylene.

Now one last thing—we've spoken of solid acetylene. From our laboratory work, I would agree that it's a rather inert material if you have pure oxygen and pure acetylene. But if

we had a beaker here on the table with a few crystals of acetylene floating in the oxygen of the beaker and if we just passed over the surface of the beaker a very low concentration of ozone, the acetylene would immediately explode. This doesn't take very much ozone, obviously. Perhaps an ozonide is formed that sets off the rest of the acetylene. Acetylene is tough to trigger but its ozonide is easy. The unsaturated hydrocarbons may partake of some of this characteristic of acetylene.

**Maley** (Mine Safety Appliance Co.): In conjunction with the comment on infrared analyzers, I would like to state that there are about five plants now installing continuous nondispersive infrared analyzers with full-scale ranges of five parts per million or less and sensitivities of  $\pm 0.1$  p.p.m. on the air intake streams. The first of these is going in shortly, and therefore, within the next six months there should be accumulated considerable data regarding the acetylene in air intake streams over a period of days or fortnights, or sudden surges that may occur. A device is also being tested that will enable continuous measurement of acetylene in the liquid oxygen pool by means of infrared analysis.

**Farquhar** (Foster-Wheeler Co.): In connection with the question Rogers brought up concerning sudden large influxes of hydrocarbons, the thought occurs to me that one method of dealing with the air stream has not been mentioned. It is scrubbing the cold air feed just before it enters the column. Liquid holdup on the trays should provide capacity to prevent break-through of temporarily high hydrocarbon concentrations into the column and subsequently into the liquid oxygen. Such a system has been used in an industrial plant; however, I don't know of any being offered now. I wonder if any of the air plant people would care to comment on the possibility of this being a feasible (both technical and economic) method of protecting oxygen plants?

**Moderator:** Anybody like to comment on that?

**Kerry:** I'm sure other design groups may want to answer that question—the only thing we do know is that we're well aware of the system of scrubbing air with rich liquid in order to remove hydrocarbons. With this, however, one has a purge loss and the objective of every design engineer is to produce oxygen at the lowest possible energy consumption. Oxygen itself is a utility in many

metallurgical processes or chemical processes and it must be available at low cost and sometimes from a design standpoint so that purge loss may be comparatively high. Now I'm sure some other designers may have some comments on that.

**Clyde McKinley** (Air Products): An aspect inside of it is, if we know what's happening, then we have 90% of the problem solved—we can do something about it. Now a way of knowing what's going on at any point that you want to monitor in the plant would be to ascertain what is the total hydrocarbon or total acetylene content or total of any specific material you want to look for at that point. Some of you may have seen a hydrocarbon analyzer (Continuous Total Hydrocarbon Analyzer) which we have had on display here at this meeting, which operates on the principle of infrared measurement of all hydrocarbons totalized as  $\text{CO}_2$ . This technique can be used to monitor the hydrocarbon content on the entering stream or at any other points in the plant. If the tolerable level of a certain hydrocarbon is fifty parts per million and if your total hydrocarbon content is five, then you have the situation well in hand. Now gas chromatography was mentioned (by Karwat); this might be a supplementary technique to know occasionally what the make-up of the total 5, 10, or 50 p.p.m. hydrocarbons was. Of 50, perhaps 48 will be methane, a few tenths of a part per million will be acetylene, and the other hydrocarbons will account for the other 1.9.

**Moderator:** Thank you, Clyde. One more question.

**Karwat** (Linde Co., Germany): This concerns the method of cleaning the adsorbers of the desorbent. There could be quite great losses of liquid which would be wasted. Our normal practice is to warm up an adsorber which needs to be desorbed. This is done in system via pressure, and the liquid in the adsorber is sent back to the high pressure column. There is no loss of fluid.

**Moderator:** Well, we've heard a lot at this session about designing these plants safely, the theories behind the designs, and the reasons we do things. I still think, as Frank Kerry said before, that plants are as safe as the operators who handle them. If they're operated the way they're intended to be operated, you shouldn't have any trouble. We had our troubles, we have had explosions, but steps were taken to stop them and we haven't had one in five years. The air compressors

are cleaned every 60 days. After a study of the water condition, intercoolers are washed every six months or a year. This is done on schedule regardless of production demands in the plant. When the time comes, we pull the switch and do our maintenance. We have thermometers on the discharge of air compressor cylinders so we know what the temperatures are. On machines that we are concerned about we have temperature alarms that shut them down if the water should fail and the operator doesn't notice it. I told you about our trial with synthetic oils. We've eliminated a lot of compressor fires, we know, and probably many fires we never knew we had. Several of the old high pressure four-stage air compressors had fires in the valve parts and in the connecting piping that one never knew about. In such cases, products of combustion go right over to the liquid oxygen, so by installing temperature alarms on some compressors we feel that we've caught many such occurrences. No mention has been made of filters after expanders—they should be there and they should be used. No mention has been made of washing of columns, at least the oxygen side of the reboiler. We feel these should be washed once a year and we do that. Trichlor, perchlor, carbon tet, or any good solvent can be used, but be sure you get rid of it afterwards. Nothing has been said about the defrosting time in a plant. One of the most critical times in the operation of the air separation plants is when you shut down to defrost. If you do it wrong you can cause an explosion in the reboiler. We feel the safest way to stop a plant is to drop the load on the air compressor and pull the switch and let the whole plant die. As the plant dies, the nitrogen on the upper trays comes down and dilutes the liquid oxygen in the reboiler and stops the boiling action and then we drain the liquid oxygen fast. I don't think I have anything more. I'm certainly pleased at the number (more than 200—Editor) who have shown such great interest in this subject. I hope a lot of good comes of it. It points out that the builders of this equipment are very aware of what has to be done to minimize trouble and I think they have done a very good job. Our experience has been excellent, but again, proper operation is awfully important.