

A LIQUID PHASE OXIDATION INCIDENT

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The investigation of a fire arising in a butane oxidation process is described. The influence of pipe flow divisions is examined.

This contribution describes a liquid phase oxidation incident which it appears was caused by an ignition mechanism analogous to that given in Mr. Alexander's paper.

The L.P.O. plant involved in the incident was the manufacture of acetic acid from butane of commercial purity. In common with all L.P.O. processes this was conducted at high pressure and temperature, about 50 atmospheres and 180°C respectively.

Figure 1 illustrates the air distribution piping serving the spargers within the reactor. Figure 2 shows an experimental rig which was constructed to examine the pneumatic behaviour of the pipework. It will be noted that a bifurcation of the air piping existed outside the reactor. Again in common with best L.P.O. practice there were no 'sumps' within the air pipework - any reactor liquor could not remain - other than as a film and then only for a short period - whilst air (or purge gas) was flowing.

As often seems to be the case in major chemical plant disasters this incident occurred whilst plant operating conditions were being changed. In fact on this occasion the plant was on start-up several hours after an air compressor fault had necessitated an emergency shut down.

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Normal start-up, which in every respect this was initially, involved a period of purge with natural gas during which time the reactor and the downstream product processing vessels were brought to the right conditions of temperature and pressure. Again normally, a short period of further purging with nitrogen would have ensued before air was introduced. The air flow to the reactor was then gradually increased as permitted by reactor and process vessel conditions.

Inadvertently the nitrogen purge was omitted whilst the methane purge continued into the first stages of air injection. The only observation of note at this stage was made by a plant operator who observed, as he was about to set foot on to the plant from the control room, that the T-piece, at the point of bifurcation of the air line, was glowing red. He was able only to shout a warning and retreat into the control room before the T ruptured. Unavoidably a major plant fire resulted.

This incident posed a number of problems, two of which are thought to be of particular relevance here :

1. What was the source of ignition; and
2. What was the source of fuel?

Under the circumstances ignition could not have been otherwise than spontaneous. Acetaldehyde seemed to be the likely culprit. Analysis had revealed that it was present as a minor constituent of the normal reactor contents. Such would indeed be anticipated, if not analytically determined, as acetaldehyde is clearly on the routes to acetic acid from butane. At one atmosphere the spontaneous ignition temperature of acetaldehyde is 175°C (1). So far as is known no value has been reported for 50 atmospheres.

The second question proved more difficult although manifestly there was no lack of combustible material. Immediately attention was directed toward the possibility of a flame stabilised in the air pipework at the division of flow. Clearly this was in principle possible as at the time a mixture of methane and air was being conveyed into the reactor. The real difficulties were that the gas mixture contained 32% by volume of methane and was flowing in a 150 mm. pipe (before flow division) and 100 mm. pipes at a minimum velocity of 80 cm/sec. The flammable range of methane/air at 50 atm. is 4% to 48% (1) so whilst the mixture was very rich it was combustible, but the maximum laminar burning velocity at that pressure (for the stoichiometric mixture) is only 6.5 cm/sec (2). Examination of the effects of pipe turbulence on flame burning velocities (3) indicated that on this basis, as well as flash back criteria (4), flame could not possibly have traversed the distance from the likely point of ignition (close to the sparger holes) - some 4 m.

The experimental rig already illustrated in figure 2 was built and scaled to give operational similarity based on both Reynolds No., and combustion and heat transfer characteristics. The operating pressure was atmospheric. Ignition was

positively achieved by a single shot spark discharge at a sparking plug in a sparger tube. Ignition occurred on all ignition attempts - the course of which was followed by pressure transducer. Though not every ignition was associated with stabilised combustion, those that were led in every case to flame stabilisation at the upstream T-piece. There was no apparent correlation between methane/air flow velocities and failure to stabilise. The highest mean gas flow velocity employed in the tests - found in the tube before the first T-piece - was 630 cm/sec. or about eight times the maximum value of turbulent burning velocity reported in the literature. Figure 3 illustrates the consequence. The combustion behaviour provided no reason to believe this was a limiting flow condition.

Reference 3, despite criticisms of its form (5), is the only equation in the scientific literature which relates turbulent burning velocity u_T to the fundamental laminar burning velocity u_L and pipe-flow parameters :

$$u_T = 0.1761 \cdot u_L \cdot d^{0.2564} \cdot Re^{0.238}$$

The appropriate (maximum) values of the variables in this equation are :

	u_L	d	Re	u_T
LPO reactor	6.5 cm/sec.	15 cm	~70,000	33 cm/sec.
Test pipework	35 cm/sec.	5.7 cm	~40,000	120 cm/sec.

Plainly theory predicts that flash-back should not be possible. The reason for this behaviour is that, when ignition occurs within a 'closed' pipework system, pressure transients are created which can be vastly greater than the pressure gradients which exist to maintain stable flow. Thus at the very least flow disturbances are caused, but more likely flow reversal occurs which assists flame movement or 'flash-back'. Where only one air supply pipe is involved, such a flame is likely to be swept into the reactor, and thus quenched, when the impetus provided by the ignition phase has been dissipated. This may not be the case however if the sparger pipes exist in branched form since flame stabilisation, especially at the upstream T, is likely. If that T is within the reactor then poor operation and product result : if the T is outside the reactor, and thus experiences the full 50 atm. pressure difference, a disaster could be the more likely outcome.

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