

AN EXPERIMENTAL STUDY ON THE CONDITIONS OF SAFE OXIDATION OF TOLUENE WITH OXYGEN—CARBON DIOXIDE MIXTURES

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Summary

The flammability limits of saturated vapours of toluene in oxygen—carbon dioxide mixtures have been measured up to 180°C and 10 atm using a direct experimental technique that avoids the time-consuming extrapolation procedure necessary when using the standard technique.

The flammability data have been presented in a pressure versus temperature diagram. The convenience of this form of diagram to determine the conditions of safe operation of the liquid-phase oxidation processes of hydrocarbons, at both steady and transient states, is discussed.

Introduction

The relevance of the upper flammability limits of saturated hydrocarbons to the evaluation of the conditions of safe operation of the liquid-phase oxidation processes has been discussed in a previous paper [1], where a set of experimental data for toluene—oxygen—carbon dioxide mixtures has been reported for the ranges 40–120°C and 1–15 atm.

The extension of this work to a wider temperature range appeared to be useful for a more complete and satisfactory safety evaluation of the toluene oxidation process. Therefore new experiments have been carried out for mixtures of oxygen, carbon dioxide and saturated vapours of toluene up to 180°C with the previously developed experimental technique [1], except for the inductive—capacitive spark igniter being replaced by an adjustable duration hot-wire igniter. This modification served also to test the sensitivity of the flammability limits to different ignition sources.

Experimental apparatus and technique

The experimental apparatus and technique have been described in detail elsewhere [1,2]. The test vessel, a stainless steel cylinder 45 mm inside diameter

and 145 mm long, located in a temperature-controlled oven, is fed with liquid toluene by the pressurized oxygen—carbon dioxide mixture. The amount of toluene is chosen to give a saturated gaseous phase and a residual liquid phase in the vessel. With this technique, the actual conditions present in the industrial equipment are simulated in the experimental apparatus so that the experimental data may be used directly, without the time-consuming extrapolation procedure which is necessary when using the more common technique with an unsaturated gaseous phase [3].

The hot-wire igniter consists of a thin, spiral shaped, nickel—chrome wire (150 mm long, 0.5 mm diameter), that is rapidly heated by means of a large current (about 20 A) from a low-voltage (about 20 V) generator. The heating current is switched off by a timer after about 0.4 s; this duration was chosen to obtain a rather high temperature (about 1200°C as determined by an optical pyrometer) and to avoid the melting of the wire.

This igniter avoids the time-consuming replacement of the “fusing-wire” igniter after each test and is preferable to the standard “hot-wire” apparatus, in which generally lower temperatures are attained and maintained for much longer times. In fact, when enough energy is released in a short time, a very hot but relatively small flame kernel is formed and its ability to propagate in the remaining undisturbed mixture may be tested effectively. On the contrary, any slow heating procedure induces in the gases a convective flow field where a significant part of the released energy is wasted, so that the temperature and pressure of the unreacted mixture are changed before flame development; moreover the long residence times at a relatively high temperature in the proximity of the ignition wire may enhance, in some cases, catalytic effects.

The energy released to the hot wire was computed to be 150 ± 10 J by recording the voltage drop across the hot wire and the relative current as a function of time using a Nicolet Explorer III digital transient recorder.

Experimental results and discussion

The upper flammability limits for toluene—oxygen—carbon dioxide mixtures, measured with the technique described in the previous section, are presented in Fig. 1 as Y_{Ox} , the oxygen percentage on a toluene-free basis, versus the initial pressure P , for four different temperatures up to 180°C. At constant temperature and Y_{Ox} the flammable region is reached by increasing the initial pressure, that is the oxygen—toluene ratio. The standard flammability limits, expressed as fuel percentage Y_F , may be easily computed from these limit pressures as

$$Y_F = \frac{P^\circ(T) \cdot 100}{P} \quad (1)$$

where P° is the vapour pressure of toluene. The limit pressure P increases slightly on decreasing Y_{Ox} : this behaviour can be explained in terms of equivalence ratio i.e., the ratio (fuel/oxygen)/(fuel/oxygen)_{stoich} [1,2]. As the

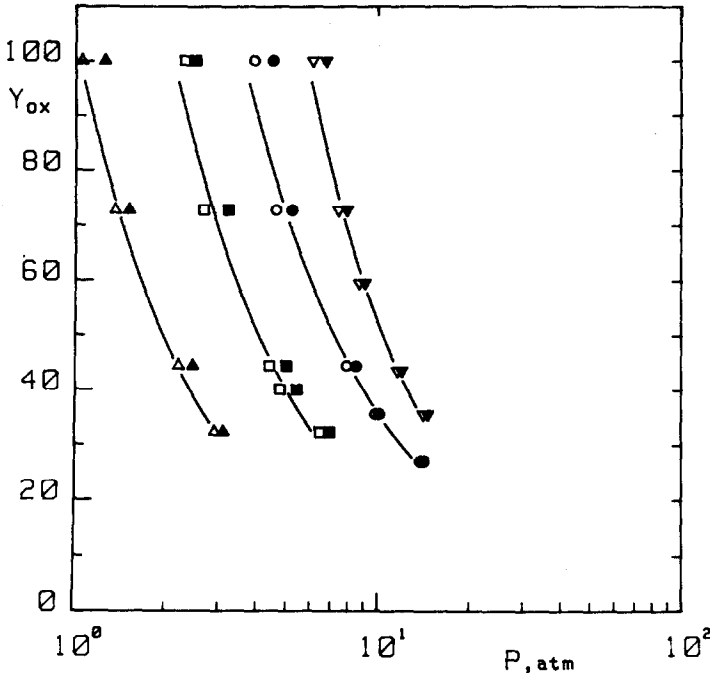


Fig. 1. Flammability limits of saturated toluene-oxygen-carbon dioxide mixtures, presented as oxygen percentage on a toluene-free basis Y_{Ox} , versus the initial pressure P . Hollow symbols = non-flammable mixtures, full symbols = flammable mixtures. Δ , $T = 80^\circ\text{C}$; \square , $T = 120^\circ\text{C}$; \circ , $T = 150^\circ\text{C}$; ∇ , $T = 180^\circ\text{C}$.

diluent percentage increases the limit equivalence ratio of flammability decreases, moving towards the stoichiometric value, and therefore a higher pressure is measured.

In Fig. 2 the flammability limits in pure oxygen are reported as the limit pressure P versus the temperature T . In this figure these data are also compared to the results obtained when using the spark igniter which releases about 0.1 J at atmospheric pressure. The hot wire appears to be more effective at the higher temperatures (which correspond to higher pressures), while no significant difference is observed at the lower temperatures. The similar data reported in Fig. 3 for $T = 80^\circ\text{C}$ and different Y_{Ox} confirm this observation.

The dispersion of energy in the electrical insulation, because of the higher breakdown voltages, must be taken into account to explain the lower effectiveness observed for the spark igniter at the higher temperatures and pressures.

No direct comparison with literature data is possible because no data on the toluene-oxygen-carbon dioxide system are available. Yantovski et al. [3] report, for the upper flammability limits of unsaturated toluene-air mixtures, a slight dependence on pressure (ranging from $P^{0.3}$ to $P^{0.6}$) while

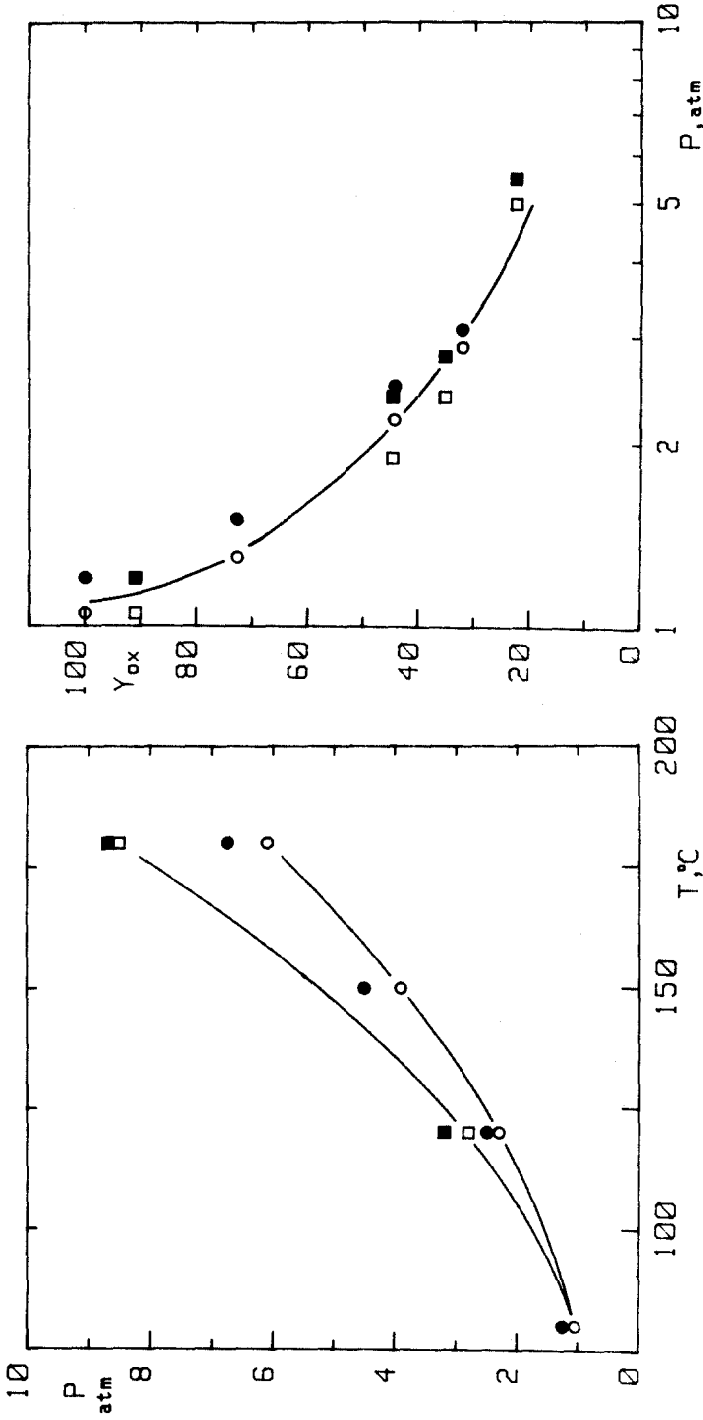


Fig. 2. Limit flammability pressure P as a function of temperature T , for toluene-oxygen mixtures and different ignition systems. Hollow symbols = non-flammable mixtures, full symbols = flammable mixtures. \circ , hot-wire igniter; \square , spark igniter.

Fig. 3. Oxygen percentage on a toluene-free basis Y_{ox} at the flammability limit as a function of the initial pressure P , for $T = 80^{\circ}\text{C}$ and different ignition systems. Hollow symbols = non-flammable mixtures, full symbols = flammable mixtures. \circ , hot-wire igniter; \square , spark igniter.

only very scattered data are presented for the temperature dependence which appears to be negligible compared with the experimental uncertainty.

This result is partially confirmed by the semi-empirical rule available [4] for the temperature dependence

$$\Delta Y_F = \frac{0.75 \cdot \Delta T}{-\Delta H} \quad (2)$$

based on the constancy of the flame temperature at the flammability limits; this gives a very slight increase in Y_F when appropriate values for the heat of combustion ΔH at the rich limit are inserted.

Of course it is not possible to determine independently the pressure and temperature dependence of the flammability limits of saturated vapours. However, if the experimental data are corrected for the temperature using eqn. (2), the pressure dependence of the upper flammability limit Y_T appears to be fairly well described by a power law, as shown in Fig. 4 for mixtures of toluene in oxygen. The exponent of this correlation ($n = 0.45$), is in good agreement with the values proposed by Yantovski et al. [3], whose data are also given in the figure for the purpose of comparison.

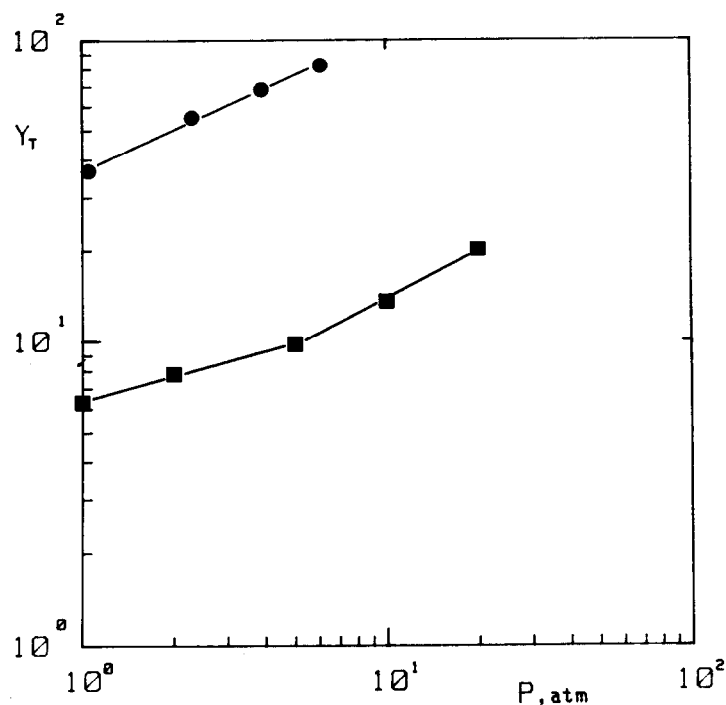


Fig. 4. Toluene percentage Y_T at the upper flammability limit as a function of the initial pressure P . ●: this work, toluene—oxygen mixtures; ■: Yantovski et al. [3], toluene—air mixtures.

The practical use of the flammability data for liquid-phase oxidation equipment

The flammability limits measured with a spark igniter for temperatures up to 80°C [1] and those measured with the adjustable-duration hot wire at higher temperatures may be used together for the complete evaluation of the flammable region as a function of pressure, temperature, and oxygen/carbon dioxide ratio.

Usually, the flammability data for three-component systems are reported in triangular diagrams as curves at constant pressure and temperature. This method is not valid for saturated vapours, as it is not possible to have isobaric and isothermal conditions at the same time since eqn. (1) consumes one degree of freedom. When an isothermal (isobaric) diagram is plotted, the isobaric (isothermal) lines correspond to unequally spaced lines at constant fuel percentage Y_F . Therefore, any change in pressure and/or temperature is not easily plotted on such diagrams. On the other hand, such changes dramatically affect the composition of a saturated system and therefore their effect must be carefully evaluated from a safety point of view.

The data are more conveniently presented in a different way in the temperature vs. pressure diagram [5] shown in Fig. 5. Curves at constant Y_{Ox}

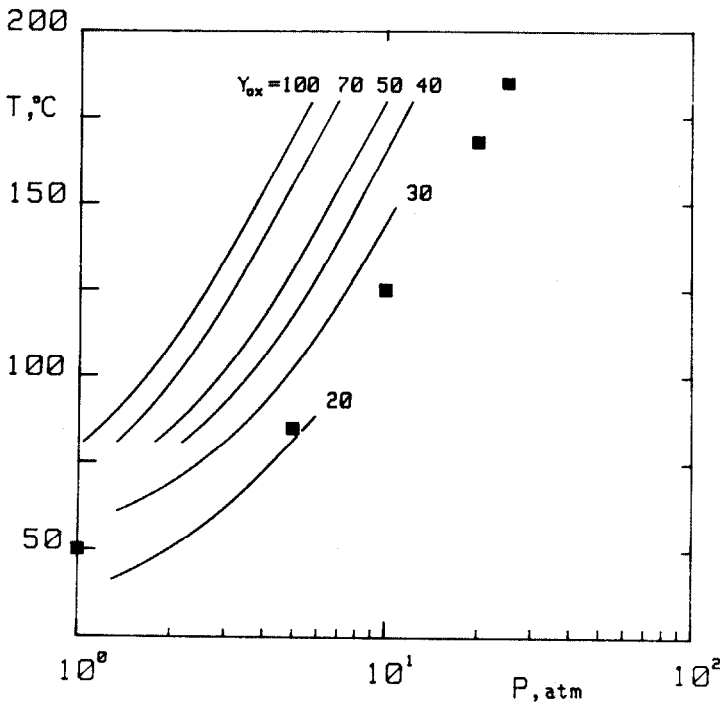


Fig. 5. Flammability limits of toluene—oxygen—carbon dioxide mixtures as a function of temperature and pressure. ■: Yantovski et al. [3], toluene—air mixtures.

are drawn that mark the upper side of the flammable region. The relative lower limit curves have not been plotted because it appeared that the presence of toluene fogs makes uncertain the measurements of the lean limit with the proposed technique. For different amounts of liquid fed to the test vessel remarkable widenings of the limit have been observed [2]. In Fig. 5 the squares refer to the data obtained by Yantovski et al. [3] for toluene-air mixtures, with the standard experimental technique and an extrapolation procedure. Good agreement is observed, when one considers that the experimental techniques are very different.

The conditions of safe operation for the liquid-phase oxidation process can be easily evaluated using the flammability limits reported as in Fig. 5. The operating pressure and temperature and the pressure-temperature paths to be followed during the start-up and the shut-down procedures may be easily drawn on the diagram as a function of the oxygen percentage.

For a safe start-up, it appears that the reactor must be first heated to the operating temperature. During this period a gaseous stream must be fed to the reactor to keep the liquid phase well-stirred: in this way dangerous local heating may be avoided. An inert gas must be used because at ambient pressure the toluene-air mixtures are flammable up to about 50°C. After the reaction temperature is reached, both the pressure and the oxygen content may be gradually increased. A reverse procedure must be used when the reactor is shut down.

The procedures to be followed during the emergency shut-down must be carefully considered. A temperature increase, possibly due to failure of the cooling system, must be accurately controlled because it may cause a run-away reaction in the liquid phase, but it is not dangerous if only the gaseous phase is considered. In fact, both the increase in temperature and the decrease in the oxygen content due to the vaporization of the fuel lead the system further away from the flammable region. In contrast, a temperature decrease, possibly caused by a decrease in the reaction rate, may lead to dangerous conditions; in fact the flammable region is reached because the temperature decreases and the residual oxygen content in the gas increases. In this case a suitable depressurization must be provided by means of safety valves. The use of an inert gas may be avoided if the temperature decrease is rather small and if the reaction conditions may be rapidly recovered, for instance by the addition of new catalyst.

The danger related to constant-pressure cooling may also be present in the off-gas line if a condenser is used to recover the unreacted hydrocarbon. In fact, a condenser designed for a constant pressure cooling may work safely only if the oxygen content in the off-gases is suitably low. Otherwise, both the addition of an inert gas and a lower design pressure must be considered. Finally, the safety problems related to an accidental increase of the oxygen content in the off-gases must be considered also for the condenser, as previously discussed for the reactor.

Conclusions

The flammability limits of saturated toluene—oxygen—carbon dioxide mixtures have been measured up to 180°C. The technique used allows reliable results to be obtained without any extrapolation and may therefore be used with confidence for different fuels.

The flammability data for mixtures containing saturated vapours are best represented in a pressure vs. temperature diagram. This representation is strongly recommended to determine safe operating conditions for the oxidation process of liquid hydrocarbons, both for standard operation and for start-up and shut-down transients.

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