Predicting gas decomposition in an industrialised pulsed CO_2 laser

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ABSTRACT

A model is developed for the breakdown and regeneration of component gases in an industrialised TEA CO_2 laser, both with and without internal catalysts, and is found to be in excellent agreement with experimental data. The laser was found to be stable at O_2 levels in excess of 2%, whereas previously reported values suggest stable operation at values of less than 1%. This is thought to be related to the unusually high starting CO_2 concentration of the gas mix, and the short time pulse of the laser ouput. Long term catalytic behaviour however shows a decay in the catalyst activity, corresponding to higher energy variation and lower average power.

Keywords: TEA lasers, catalysts

1. INTRODUCTION

The CO_2 gas fraction in a TEA CO_2 gas laser decomposes over time to CO, O_2, and other by-products, as a result of the electrical discharge between two electodes. This is a problem for a number of reasons: firstly, as the CO_2 decreases, so the power output from the laser decreases. Secondly, as the O_2 increases the discharge becomes very unstable, with rapid power losses. The CO increase appears not to have any deleterious effects on the laser power output. This decomposition process can be reduced, or its effects negated, by the use of self catalytic mixes to regenerate the CO_2, or by employing a blow through system (continuously replenishing the depleted gas). In some applications neither of these options are solutions and yet long-life operation is a necessity. One such application is the industrial use of a high repetition rate TEA CO_2 laser for the non-destructive testing of composite materials in aircraft, through ultrasound generation. In this application the requirements are: (a) short time pulses with no characteristic tail (< 65ns FWHM pulse), (b) higher energy and higher repetition rate operation (min 400mJ at 400Hz), and (c) closed loop system with extended component lifetime (> 2 billion pulses). These requirements prohibit the use of self catalytic mixes, since to achieve such characteristics one requires very rich mixes, with at least a 40% CO_2 and low nitrogen content. As a solution, the laser was operated with internal room temperature catalysts, mounted downstream of the gas flow through the discharge, but just upstream of the heat exchanger. Thus the hot depleted gas first passes through the catalysts for regeneration, and then through the heat exchanger for cooling. In an ideal system, one round trip would regenerate the initial gas conditions so that the process repeats endlessly.

The role of the catalysts is to reverse the breakdown reaction, by oxidation of CO to CO_2. In the case of room temperature catalysts (usually Pt/Sn based), the mechanism by which this happens seems not to be well understood. Some studies[1] indicate that an excess presence of CO improves catalyst performance, as well as reduces O_2 formation in the discharge, while others[2,3] contradict this by arguing that a lower CO concentration results in better catalyst activity. It seems generally agreed[1,2,3] that excess O_2 is poor for both laser action and catalyst activity. In the particular case of a Sn-Pt/SiO_2 catalyst, just the presence of pure O_2 for a period of 15 minutes resulted in complete loss of catalyst activity.[2]

Discharge O_2 generation rate (*from ref 1*)	4.2×10^{-5}mols/kJ
Discharge O_2 generation rate (*this study*)	14.3×10^{-5}mols/kJ
Catalyst activity @0.6% O_2 (*from ref 1*)	6.9×10^{-7}mols/s per g Pt
Catalyst activity @0.6% O_2, 400Hz (*start of tests*)	5.5×10^{-7}mols/s per g Pt
Catalyst activity @0.6% O_2, 400Hz (*after 1.3 billion pulses*)	1.6×10^{-7}mols/s per g Pt

Table 1. Comparison of data from this study to that found by others. Results show catalyst behaviour at the start of the tests and after extended operation.

2. DISCHARGE ONLY

We wish to derive an expression that describes the change in O_2 levels in a laser over time, both when catalysts are present and when they are not. The starting point is to assume a rate law for the forward and reverse reactions, and then test this against experimental data. This is because rate laws must be determined from measurements of reaction rates, and cannot be deduced from reaction stoichiometry. The reader is refered to standard physical chemistry texts[5] for further information on this subject.

Experimental data suggests that the rate at which O_2 is generated within the discharge is independent of both gas mixture used, and gas temperature, and in fact depends only on input energy into the discharge. However, some recombination takes places as the hot gas mixes, as is evident from the fact that the oxygen levels within the laser do stabilise at some point, albeit at an unexceptably high level. After some trial and error attempts, the following rate law is proposed:

$$\dot{x}(t) = k_d - k_g x(t),\tag{1}$$

with solution

$$x(t) = \left(x_0 - \frac{k_d}{k_g}\right)\exp(-k_d(t - t_0)) + \frac{k_d}{k_g}.\tag{2}$$

Here $x(t)$ is the O_2 concentration as a function of time, measured in ppm, k_d is the oxygen generation rate within the discharge, with units ppm/s and k_g is the self catalytic rate converting the oxygen back to carbon dioxide, with units s^{-1}. The equation is written in terms of the starting conditions of the gas mix: x_0 amount of oxygen at time t_0. The value of k_g is very small, and consequently the second term on the RHS of Equation (1) only becomes significant at large oxygen concentrations. Experimentally one finds that $k_d = 19.3P_{in}$, where P_{in} is the power deposited into the discharge (see Figure 1(a)). The data collected with catalysts present fits the trendline, as expected if k_d is not gas species dependent.

3. CATALYSTS PRESENT

With catalysts present in the laser, the oxygen concentration stabilise quickly and at lower levels than in the case of no catalysts. Using the model already found for the discharge chemistry, it is tempting to write the rate law in the following form:

$$\dot{x}(t) = k_d - k_g x(t) - k_c M_c x^n(t),\tag{3}$$

where we have kept the form of Equation (1), but added an additional term $-k_c M_c x^n(t)$ to allow faster convergence to lower oxygen levels, where M_c is the mass of the catalysts (Pt content only) in grams. By trial and error the rate law that worked the best for the catalysts under consideration was the simple case with $n = 1$, with the solution as before:

$$x(t) = \left(x_0 - \frac{k_d}{k_g + k_c M_c}\right)\exp(-(k_g + k_c M_c)(t - t_0)) + \frac{k_d}{k_g + k_c M_c}.\tag{4}$$

However, since $k_c M_c \gg k_g$, the sum $k_g + k_c M_c \approx k_c M_c$; this simplification will be used in this paper when comparing recombination to published values. The catalysts discussed in this paper were supplied by STC Catalysts Inc; Pt/SnO_2 based, with 2% Pt ($\pm$140g per catalyst) and of honeycomb structure (dimensions 4.9 in x 5.1 in x 1.97 in). They have the quoted advantages of low pressure drop (400 cpsi), and room temperature operation, making them suitable for use inside the laser head. Eight such catalysts were used in a grid 1 layer deep (1120g Pt in a total honeycomb weight of 4kg). The findings of this study are compared to literature values in Table (1). The success of the model is shown in Figure 1(b), where the prediction for a cooldown period followed by an on period is shown.

The catalyst activity at the start of the tests was comparable to that of good catalysts quoted elsewhere, but had degraded to only 30% of that activity by the end of the first 1 billion pulses. This, coupled to the high discharge generation rate of O_2 resulted in very high equilibrium levels of oxygen: 2.4% after 1.3 billion pulses compared to 0.7% at the start of the tests. This means that one would have to increase the number of catalysts by a factor of about 3.5 to get the same benefit as at the start of the tests – a very expensive solution.

3.1. Stoichiometry

It was assumed implicitly in the development of the model that CO, O_2 and CO_2 all react in stoichiometric ratios. This was tested by coupling a GC to the laser, as well as a Teledyne O_2 detector. The results indicated that the $CO:O_2$ ratio at equilibrium was 2.1 ± 0.07 (stoichiometry predicts a value of 2). Furthermore, observations of water vapour, ozone and NO_x gases indicated minimal concentrations throughout the tests, with only the NO_x levels measurable at 75ppm, although without catalysts ozone was measured at 50ppm. A possible means of increasing the catalyst activity might be to increase OH^- concentrations by the addition of water vapour or hydrogen.

4. MODEL PREDICTIONS

One can used the model to make certain predictions as to the behaviour of the gas in the presence of catalysts. Although it is useful to know the time evolution of the oxygen concentration (Equation (4)), one is usually interested in predicting the final equilibrium concentrations of oxygen in the system, since this is the level at which the laser will be expected to operate at for extended time periods. If the equilibrium value is too high, the laser will be unstable in operation (e.g., high arc rate or low energy etc.).

4.1. Equilibrium Condition

Allowing $t \to \infty$ in Equation (4), one finds the predicted oxygen levels at equilibrium as

$$[O_2]_{eq} = \frac{k_g + k_c M_c}{k_d}. \tag{5}$$

It is generally assumed that rate constants follow the Arrhenius law[5]:

$$k_c = \exp\left(-\frac{E_a}{RT}\right), \tag{6}$$

where E_a is the activation energy of the reaction. The temperature of the gas after passing through the discharge can easily be calculated from basic thermodynamics, and can be shown to be given by:

$$T_g = T_0\left(\frac{P_{in}R}{P_0 l dv C_v} + 1\right), \tag{7}$$

where l and d are the electrode length and gap respectively, v is the gas speed through the electrodes, and C_v, T_0 and P_0 are the gas heat capacity, temperature and pressure respectively of the gas entering the discharge. Now both k_d and k_c are functions of the power input to the discharge: k_d directly, and k_c through the fact that an increase in power causes an increase in gas temperature. One can ask the question: do oxygen levels ever *decrease* with *increasing* input power? Combining Equations (5) – (7), one finds that they do, with the turning point in power given by:

$$\tilde{P}_{in} = \frac{P_0 l dv C_v}{RT_0} \cdot \frac{E_a - 2RT_0 - \sqrt{E_a(E_a - 4RT_0)}}{2R}. \tag{8}$$

A plot of this prediction is shown in Figure 1(c), together with experimental data. In this case the power input to the laser was achieved through increasing the laser repetition rate. Unfortunately the laser under consideration could not reach high enough repetition rates to test the prediction thoroughly. The results are however encouraging.

5. IMPACT ON LASER PERFORMANCE

Figure 1(d) shows the energy drop as measured over a period of time; the energy and oxygen concentrations are plotted with time as the parameter. Coupled to this is a marked increase in energy variance at high oxygen levels. Long term data over more than a billion pulses shows a more complicated relationship between energy and oxygen concentrations, and it is suspected that water content also plays a significant role in this relationship.
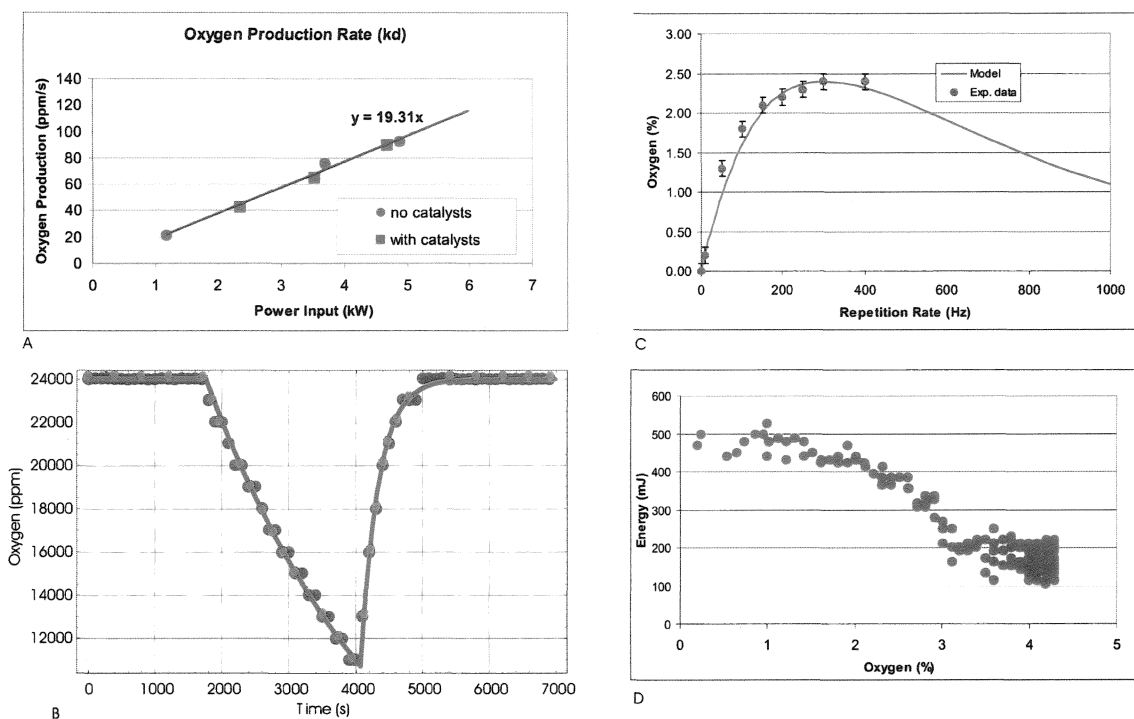
Figure 1. (a) Empherical data for the generation rate of oxygen in the discharge, (b) model prediction of oxygen levels as a function of time, with experimental data points, showing excellent agreement, (c) model prediction of the oxygen equilibrium values as a function of repetition rate, and (d) energy values as a function of oxygen levels in the laser.

6. CONCLUSION

We have found a simple rate law that describes the O_2 generation as a function of time, and also the CO_2 and CO concentrations by stoichiometric arguments. Predictions of the model indicate least favourable operating coniditions, and indicate that for this particular laser to operate at lower oxygen levels, either the catalysts must be heated, or significantly more catalysts are needed. Monitoring of the catalyst behaviour over extended periods showed a marked decrease in catalyst activity, and corresponded to a decrease in energy output from the laser. It would appear then that using STC catalysts is not an ideal choice for extended operation under these conditions.

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