

N87-20540

STUDIES OF LONG-LIFE PULSED CO₂ LASER WITH Pt/SnO₂ CATALYST

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SUMMARY

Closed-cycle CO₂ laser testing with and without a catalyst and with and without CO addition indicate that a catalyst is necessary for long-term operation. Initial results indicate that CO addition with a catalyst may prove optimal, but a precise gas mix has not been determined as yet. A long-term run of 10⁶ pulses using 1.3% added CO and a 2% Pt on SnO₂ catalyst yields an efficiency of about 95% of open-cycle steady-state power. A simple mathematical analysis yields results which may be sufficient for determining optimum running conditions. Future plans call for testing various catalysts in the laser and longer tests, 10⁷ pulses. A Gas Chromatograph will be installed to measure gas species concentration and the analysis will be slightly modified to include neglected but possibly important parameters.

INTRODUCTION

Langley Research Center is actively engaged in the study of catalytic recombination of CO₂ dissociation products in pulsed, high-energy CO₂ lasers. This paper will present some results of that study, but will primarily concentrate on those aspects of laser operation which precede introduction of the catalyst. We will examine the effect which gas flow rates, laser pulse rates, and variable gas composition (e.g., adding CO to the gas mix) have on the laser output. We will then examine the implications which these variables have on the dissociation and recombination in the laser with attendant implications for use of catalysts.

PROCEDURE

Fig. 1 was presented in the survey paper of Schryer et al. (ref. 1) and, for convenience, is presented again here. It is a plot of laser output power versus time for 10⁶ pulses. The laser used is a Lumonics model 820 TEA laser. For this experiment we ran at 30KV discharge voltage, 10 p.p.s., with a gas mix 16% CO₂, 8% N₂, 1.3% CO, and the balance He. As the figure shows, the laser performed at an efficiency of ≈ 95% of initial power when operated closed cycle with a 2% platinum on tin oxide catalyst. However, the term "initial power" in the preceding sentence needs explanation to fully understand what happens before the catalyst is introduced into the flow cycle.

Figure 2 shows the exact sequence of events - the laser is operated initially open-cycle with an initial pulse energy of 0.8 joules/pulse. After approximately 30 minutes the gas mixture in the laser has achieved a steady-state with the pulse energy now about 0.7 J/pulse. At this time, the flow is switched to closed-cycle

through the catalyst and after a few minutes of operation the steady-state condition of figure 1 is achieved at approximately 95% of the value of steady-state open-cycle energy.

Since the drop in pulse energy from initial power-on to open-cycle steady-state value is larger than that from open-cycle steady-state to the catalyst-flow, closed-cycle value, we feel it important to analyze this time period and examine the specific events occurring in an attempt to understand and possibly to lessen this initial energy loss. To accomplish this goal, I have performed a mathematical analysis which, although extremely simple, seems to give reasonable results. The unknowns in the equations are determined from actual operating conditions and the equations are then applied to more complicated operating situations to determine their accuracy and usefulness.

We consider a carbon conservation analysis involving the two reactions illustrated in the first line of Fig. 3. A given flow of CO_2 is introduced into the laser where there is some dissociation of CO_2 governed by the rate constant K_D , some recombination of CO and O_2 governed by the rate constant K_R , and an output flow of CO_2 and CO . Referring to Fig. 3, carbon conservation is then written both for time-rate-of-change and steady-state with dissociation (CO production) and recombination (CO_2 production) described on lines 2, 3, and 4. Dissociation is assumed to occur primarily by impact of electrons with CO_2 molecules in the active discharge volume of the laser, V_A , only during the time the discharge is on, T_{on} . Recombination is assumed to occur by collision of a CO molecule, an oxygen atom and a third body, M , at any time in the total laser volume, V_L . (It is assumed that $[\text{O}]$ can be related to $[\text{CO}]$ by some proportionality constant.) The resultant equation

$$[\dot{\text{CO}}_2] = [\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}} - K_D'[\text{CO}_2] + K_R'([\text{N}] - [\text{CO}_2])^2$$

represents a closed-form solution which has considerable appeal since one can see what is going on in the laser gas more readily than with a more complicated solution involving more variables. Determination of

$$K_D' = K_D [e] (V_A/V_L)(T_{\text{on}}/T_{\text{off}}) \text{ and} \\ K_R' = K_R ([\text{O}]/[\text{CO}])[M]$$

can now be accomplished by experimental procedures.

The experimental results used for determination of K_D' and K_R' are shown in Figs. 4 and 5. Fig. 4 is a plot of pulse energy as a function of time for open-cycle operation for two different flow rates ($F = [\text{CO}_2]_{\text{in}}$). For each flow rate, the laser is operated until a steady state is reached or $[\text{CO}_2] = 0$. Everything in the above equation (1) is known except K_D' and K_R' . N is the Loschmidt number and $[\text{CO}_2]_{\text{out}} = [\text{CO}_2]_{\text{in}} ([\text{CO}_2]/N)$. Therefore, for the two flow rates, K_D' and K_R' can be determined. A second experiment using closed-cycle operation while varying the pulse rate is shown in Fig. 5. For this condition, $[\text{CO}_2]_{\text{in}} = [\text{CO}_2]_{\text{out}} = 0$, and, from the data of Fig. 5, the assumption is made that $[\text{CO}_2] = \text{constant}$. The assumption is also made that $[\text{CO}_2]/[\text{CO}_2]_{\text{initial}} = \text{Power}/\text{Power}_{\text{initial}}$. Other values used were

$$[e] = 10^{13}, \quad V_A/V_L = 1/100,$$

$T_{\text{on}}/T_{\text{off}}$ is pulse width times pulse rate (where the pulse width is estimated to be 200 nanoseconds which is not the laser pulse width but rather an estimate of the time width of the electric discharge pulse when the electrons are active), and $[O]/[CO]$ was estimated to be 10^{-3} since published values indicate that $[O] + [O] + [M]$ is about three orders of magnitude faster than $[O] + [CO] + [M]$.

The numerical results obtained from this analysis were $K_D' = 2.5 \times 10^{-3}/\text{sec}$ or $K_D = 10^{-8} \text{ cm}^3/\text{sec}$ and $K_R' = 8 \times 10^{-20} \text{ cm}^3/\text{sec}$ or $K_R = 3 \times 10^{-36} \text{ cm}^6/\text{sec}$.

The quality of the foregoing analysis can be judged by comparison of the obtained values of K_D and K_R to published values. The published value of K_D is one or two times 10^{-9} for a temperature of 300K. Since K_D for this experiment is for a significantly higher discharge temperature, one expects a larger value of K_D so that a value of 10^{-8} is probably not far out of line. (There are other ways to obtain K_D for higher temperatures which will be explored in the future.) The situation for K_R is more susceptible to comparison since the published value is for 300K, and the actual recombination in the laser also takes place at this temperature. Accordingly, the obtained value of 3×10^{-36} compares favorably with the published value of two or three times 10^{-36} .

The usefulness of the analysis can be judged by the ability to predict the operating characteristics of the laser for those conditions when various percentages of CO are added to the gas mix (CO is added at the expense of He; CO_2 and N_2 are held constant). Fig. 6 shows power (t)/power (t=0) as a function of time for CO addition of 0, 1.3, 5.2, 10, and 15 percent. Initial power tends to decrease as CO is added - the initial power for the case of 15% added CO is anomalous probably due to the increased voltage (32KV) required to operate the laser for this condition (the other cases were operated at 30KV).

For increasing CO percentage, the operating lifetime is extended, but only for the 15% case is a steady-state achieved (the 10% case was terminated at 130 minutes due to some arcing in the discharge). The data of Fig. 6 are not presented here as representing a new result since gas addition measurements such as these have been carried out for several years. They are presented only as a device for comparing the data to the analysis presented earlier, which comparison is shown in Fig. 7. A slight modification to the equation allows for input flow of CO and the results for the 1.3, 10, and 15% cases are shown as solid lines in Fig. 7. The comparison of analysis with experiment is acceptable, the predicted slope for high percentage CO addition is somewhat faster than the measured slope, but predicted steady state values are close to the measured values. The results are surprisingly good considering the simplicity of the analysis.

CONCLUDING REMARKS

Obviously, several simple refinements could be accomplished to increase the quality of the analysis and its comparison to measurements and these will be done in the near future. First and foremost will be the introduction of a Gas Chromatograph to measure species concentration as a function of time. Measurement of gas temperature and the introduction of a gain term in the equations should also improve the analysis. Closed-cycle CO_2 laser testing with and without a catalyst, and with and without CO addition, indicates that a catalyst is necessary for

long-term operation. Initial results indicate that CO addition with a catalyst may prove optimal, but a precise gas mix has not been determined as yet. A long-term run of 10^6 pulses using 1.3% added CO and a 2% Pt on SnO₂ catalyst yields an efficiency of about 95% of open-cycle steady-state power. A simple mathematical analysis yields results which may be sufficient for determining optimum running conditions. Future plans call for testing various catalysts in the laser, and longer tests, 10^7 pulses. A GC will be installed to measure gas species concentration and the analysis will be slightly modified to include neglected but possibly important parameters.

REFERENCE

1. Schryer, David R., Sidney, Barry D., Miller, Irvin M., Hess, Robert V., Wood, George M., Batten, Carmen E., Burney, Lewis G., Hoyt, Ronald F., Paulin, Patricia A., Brown, Kenneth G., Schryer, Jacqueline, and Upchurch, Billy T.: NASA-LaRC Research on Catalysts for Long-Life Closed-Cycle CO₂ Lasers, NASA CP-2456, 1987.

PERFORMANCE OF LUMONICS TEA -820 LASER WITH AND WITHOUT
CO-O₂ RECOMBINATION CATALYST

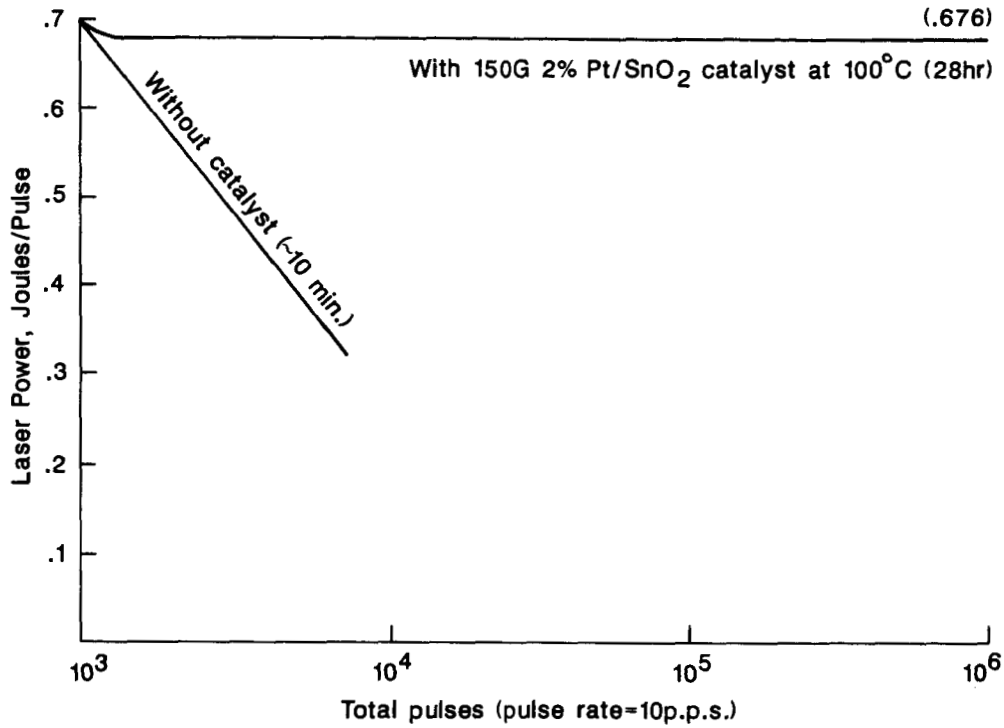


Figure 1

PERFORMANCE OF LUMONICS TEA -820 LASER
OPEN CYCLE FOLLOWED BY CLOSED CYCLE WITH CATALYST

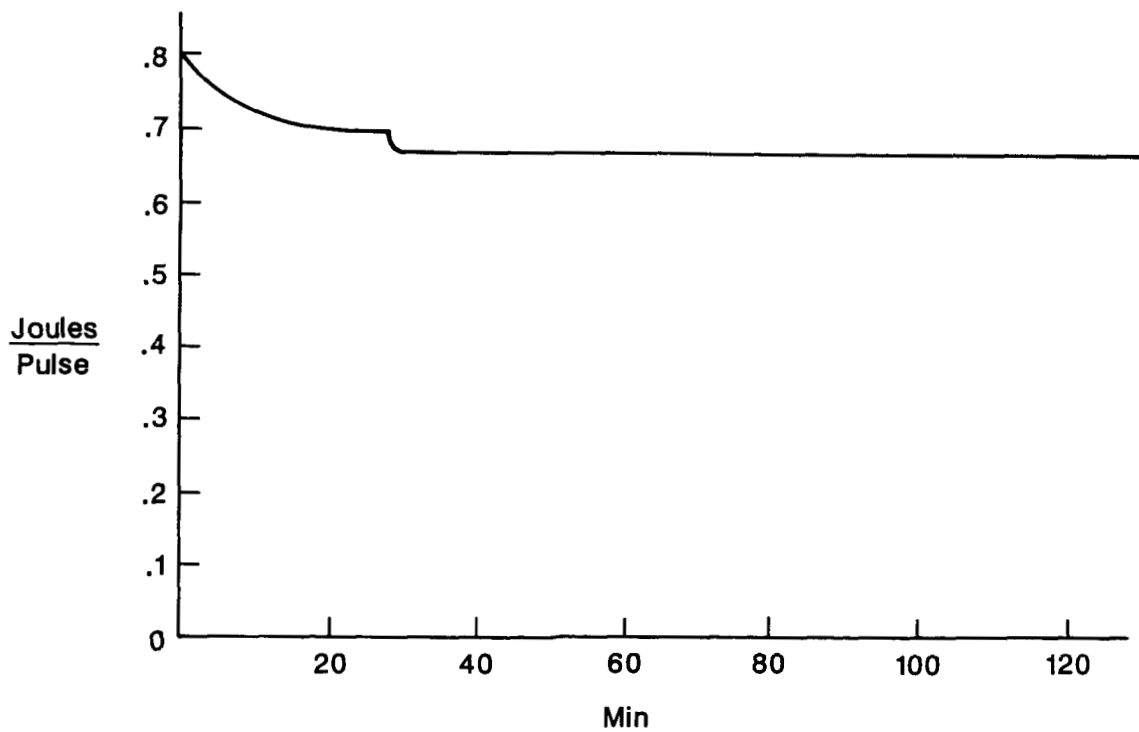
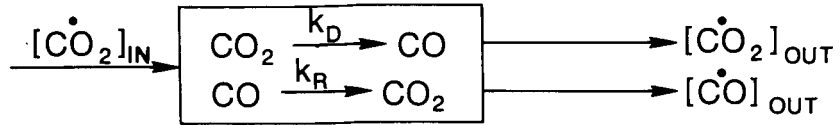


Figure 2

ANALYSIS



Carbon conservation: $[\dot{C}O_2] = [\dot{C}O_2]_{IN} - [\dot{C}O_2]_{OUT} - [\dot{C}O]_p + [\dot{C}O_2]_p$
 $[CO_2] + [CO] = [N]$

Dissociation: $[\dot{C}O]_p = k_D [CO_2] [e] \frac{V_A T_{ON}}{V_L T_{OFF}} = k'_D [CO_2]$

Recombination: $[\dot{C}O_2]_p = k_R [CO] [O] [M] = k'_R [CO]^2$

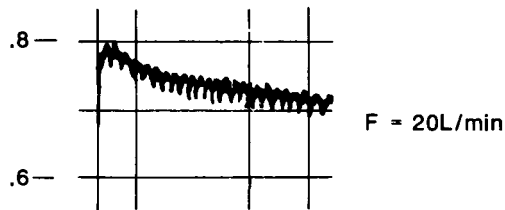
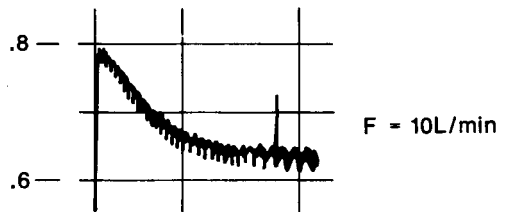
$$[\dot{C}O_2] = [\dot{C}O_2]_{IN} - [\dot{C}O_2]_{OUT} - k'_D [CO_2] + k'_R ([N] - [CO_2])^2$$

Figure 3

OPEN-CYCLE

LASER ENERGY/PULSE VS TIME

Joules
Pulse



→ | 10 min | ←

Pulse rate 10 PPS

$[C\dot{O}_2] = 0$ at T Large

Figure 4

CLOSED-CYCLE ENERGY/PULSE VS TIME

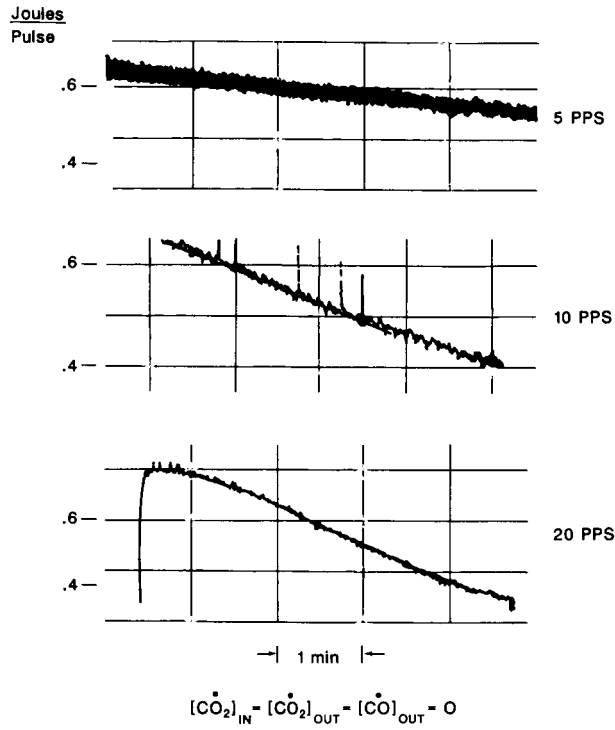


Figure 5

VARIATION OF AVERAGE POWER WITH TIME AS A FUNCTION OF INITIAL CO CONCENTRATION

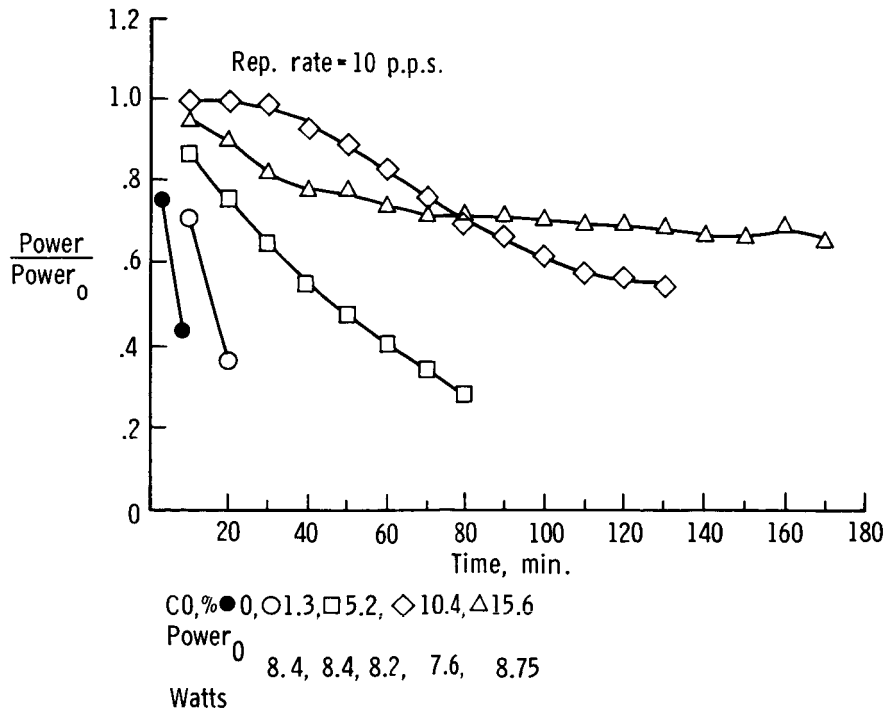


Figure 6

**VARIATION OF AVERAGE POWER WITH TIME AS A FUNCTION
OF INITIAL CO CONCENTRATION**

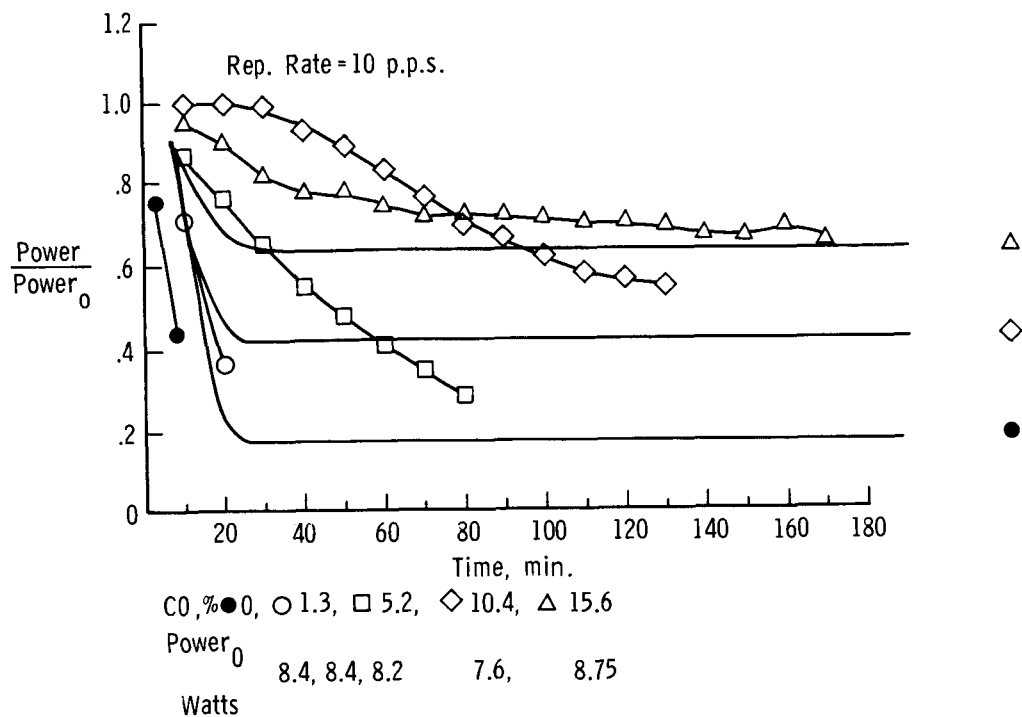


Figure 7