Lawrence Livermore Laboratory

A PRELIMINARY STUDY OF THE RECYCLING OF SPENT
GASES FROM THE IODINE LASER

R. K. Pearson, editor

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A PRELIMINARY STUDY OF THE RECYCLING OF SPENT GASES FROM THE IODINE LASER

SUMMARY

We have proposed a process for recycling the spent gases from the iodine laser. Using a simplified form of this process, we have made a preliminary estimate of the energy cost to recycle the perfluoroisopropyl iodide-argon gas mixture used as the laser medium in the iodine laser. If we define r as the ratio of the recycling energy to the output energy of the laser, we arrive at a figure of 70 for the most optimistic conditions and 160 for the most probable conditions.

A major portion of the energy necessary for recycling is consumed in the synthesis of the perfluoroiodide compound.

An estimate of the cost to replace the lost perfluoroiodide, if purchased, is from \$2.4 to 10 million per year, based on a continuous operation at the 100-kJ laser power level.

INTRODUCTION

This study was made in response to a request from J. A. Maniscalco of Y Division and in fulfillment of a proposal of November 19, 1975, by R. K. Pearson, and amended on January 6, 1976, by H. F. Rizzo and Pearson. Four investigators contributed to the study. E. R. Bissell and R. E. Elson, chemists of the Organic Materials Division of the LLL Chemistry Department, proposed an open chemical recycling process in which C and O₂ are consumed, CO₂ discarded, and all fluorine and iodine are recycled. H. H. Otsuki and K. E. Cox, chemical engineers from the Inorganic Materials Division of the LLL Chemistry Department, made energy cost estimates for a simplified version of the proposed recycling process. Pearson coordinated this study, which consists of three parts: the first, by Bissell, reports the chemistry of recycling steps for fluorocarbon processes; the second, by Elson, discusses aspects of iodine recycling and fluorine recovery; the third, by Otsuki and Cox, deals with energy cost estimates for an abbreviated recycling process based on the proposal of Bissell and Elson.

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I. RECYCLING OF SPENT GASES FROM THE IODINE LASER

by E. R. Bissell

General Purification Scheme

Figure I-1 shows the general purification scheme. In laying out the flowchart, we have considered all the known volatile products from the C_3F_7I laser¹ despite the request that we limit our consideration to recovered C_3F_7I , C_6F_{14} , and I_2 . We have done this, first, because the assumption that these are the only products is based on computer calculations that were force-fit to the assumption. The absence in this calculation of the other products found by the Russian workers¹ is not an indication that the products fail to form, but rather a result of their not having been allowed. Second, all the processing steps required to handle the other products are also required to handle degradation products from C_6F_{14} or to convert the I_2 to the required form. For our calculations, we have followed the simplifying assumption. The calculations are so complicated and the assumptions and estimates so numerous that including more products at this stage is not warranted in such an abbreviated study. It should be pointed out, however, that this approach may introduce large errors. For example, if only 1% of the C_3F_7I is converted to CF_4 , the total amount of gases that have to be handled in the first five processing steps after distillation increases by 35%.

The processing steps of Fig. 1 are shown only schematically. Each would have to include some means of separating the products, probably a distillation column. We have not attempted to specify details of any of the processes or to show needed pumps, storage tanks, scrubbers, etc. The system is not a fully closed cycle. It requires input of carbon and oxygen and discharges carbon dioxide. About 2% of the input carbon exits as CO_2 . The cycle is closed, however, with respect to iodine and fluorine. Table I-1 shows the physical properties of the products from the laser.^{2,3}

The heart of the separation scheme is a distillation column. Such columns are common in both the fluorocarbon and petroleum industries. They have been operated on enormous scale and with great precision. However, the very large flow rates and massive amounts of helium may present problems requiring careful design consideration. It may not be possible to remove all the CF_4 from the helium stream; this problem has been ignored for the present because our

Table I-1. Yields and physical properties of the products from the iodine laser process.

	Yield (moles/mole of C_3F_7I)	mol wt	bp ^a (K)	mp ^a (K)
CF_4	0.-0.23	88.011	145	89*
C_2F_4	0.-0.25	100.022	197	
C_2F_6	0.-0.36	138.022	195 to 194	170 [†]
C_3F_6	0.-0.18	150.033	243.6	116.8
CF_3I	0.-0.31	195.921	250.5	
C_6F_{14}	0.0025-0.035	338.066	329 to 333	269
C_2F_5I	0.-0.07	245.932	285.5 to 286	
C_3F_7I	0.02-0.93	295.943	312 to 314	
I_2	0.07-0.60	253.820	457.35	

$$* \Delta H_v = 2947 \text{ cal/mole} + 1.75 \log T - 0.0076715 T^b$$

$$\log_{10} p = 5.0443 - 701.73/T$$

$$† \Delta H_v = 3859.7 \text{ cal/mol}$$

$$\log_{10} p = 14.225677 - \frac{1125.3291}{T} - 2.339171 \log T - 0.00109858 T$$

^aRef. 2

^bRef. 3

original assumption says CF_4 is not present. CF_4 , C_2F_4 , and C_2F_6 are sent to a carbon arc for conversion of the CF_4 and C_2F_6 to C_2F_4 . It might be advantageous to use a separate arc for the CF_4 or to send the stream through the polymerizer before sending it to the arc, but these are details that do not materially affect the calculations, hence are not considered. Any C_3F_6 would be reacted with IF or IF_5 to produce C_3F_7I for recycling. CF_3I and C_2F_5I are fluorinated to recover the iodine and then sent to the carbon arc. C_3F_7I is scrubbed to remove any traces of iodine and then recycled to the laser. C_6F_{14} and I_2 are sent to a fluorinator to convert the I_2 to IF or IF_5 ; after separation, the C_6F_{14} is pyrolyzed to produce C_3F_6 . The fluorinator for producing IF_5 may be the same as that for handling CF_3I and C_2F_5I , or it may be different. Schematically we have shown them as the same.

We have written a program (Table I-2) for the HP 9830 calculator to model the flows through the various processing steps.⁴ The model does not include

Table I-2. Program to model flows through the processing steps (for the HP 9830 calculator).

```

10 DIM AS[6,20],BS[5,20],CS[6,20],DS[5,20],ES[5,20],FS[5,20],GS[5,20],HS[5,20]
11 DIM KS[5,20],PS[5,20],QS[10],XS[2],YS[5],ZS[5]
12 R=20
20 Q[1]=0
21 Q[2]=0
22 Q[3]=0
23 Q[4]=0
24 Q[5]=0
25 Q[6]=0
26 Q[7]=0.92
27 Q[8]=0.04
28 Q[9]=0
30 X[1]=0.5
31 X[2]=0.5
31 X[2]=0.5
32 W=0.8
40 Y[1]=0.4
41 Y[2]=0.7
42 Y[3]=0.6
43 Y[4]=0.9
44 Y[5]=7-2*(Y[1]+Y[2])-3*(Y[3]+Y[4])
45 IF Y[5]>0 THEN 50
46 DISP "Y(5) IS NEGATIVE"Y[5]
47 STOP
50 Z[1]=0.05
51 Z[2]=0.1
52 Z[3]=0.05
53 Z[4]=0.1
54 Z[5]=1-2*(Z[1]+Z[2])-3*(Z[3]+Z[4])
55 IF Z[5]>0 THEN 140
56 DISP "Z(5) IS NEGATIVE"Z[5]
57 STOP
140 A[2,1]=A[4,1]=A[5,1]=A[6,1]=C[2,1]=C[4,1]=C[5,1]=C[6,1]=0
141 B[5,1]=D[3,1]=D[5,1]=H[5,1]=K[5,1]=0

```

Table I-2 (Continued)

```

150 FOR J=2 TO R
151 A[1,J]=(1-X[1])*(Q[1]+A[2,J-1]+A[4,J-1]-A[6,J-1])
152 C[1,J]=(1-X[2])*(Q[3]+C[2,J-1]+C[4,J-1])
153 P[1,J]=X[1]*(Q[1]+A[2,J-1]+A[5,J-1]-A[6,J-1])+Q[2]
154 B[1,J]=P[1,J]+X[2]*(Q[3]+C[2,J-1]+C[4,J-1])
160 A[2,J]=A[1,J]+A[5,J-1]
161 C[2,J]=C[1,J]+C[5,J-1]
162 K[2,J]=2*(B[1,J]+B[5,J-1])
170 D[3,J]=0.5*(1-W)*(Q[4]+D[3,J-1]+D[5,J-1])
171 G[3,J]=W*(Q[4]+D[3,J-1]+D[5,J-1])
172 K[3,J]=1.5*(1-W)*(Q[4]+D[3,J-1]+D[5,J-1])
180 A[4,J]=Q[5]
181 C[4,J]=Q[6]
190 A[5,J]=Y[1]*(Q[8])+Z[1]*(K[2,J]+K[3,J]+K[5,J-1])
191 B[5,J]=Y[2]*(Q[8])+(Z[2]*(K[2,J]+K[3,J]+K[5,J-1]))
192 C[5,J]=Y[3]*(Q[8])+(Z[3]*(K[2,J]+K[3,J]+K[5,J-1]))
193 D[5,J]=Y[4]*(Q[8])+(Z[4]*(K[2,J]+K[3,J]+K[5,J-1]))
195 K[5,J]=Y[5]*(Q[8])+Z[5]*(K[2,J]+K[3,J]+K[5,J-1])
196 A[6,J]=0.25*(G[3,J]+Q[5]+Q[6])
199 NEXT J
200 FORMAT F4.0,8F8.3
201 PRINT " J A1 A2 A4 A5 A6 B1 B5 "
202 FOR J=R-5 TO R
203 WRITE (15,200)J,A[1,J],A[2,J],A[4,J],A[5,J],A[6,J],B[1,J],B[5,J]
204 NEXT J
205 PRINT
210 PRINT " J C1 C2 C4 C5 D3 D5"
211 FOR J=R-5 TO R
212 WRITE (15,200)J,C[1,J],C[2,J],C[4,J],C[5,J],D[3,J],D[5,J]
213 NEXT J
219 PRINT
220 PRINT " J G3 K2 K3 K5"
221 FOR J=R-5 TO R
222 WRITES (15,200)J,G[3,J],K[2,J],K[3,J],K[5,J]
223 NEXT J
228 PRINT

```

Table I-2 (Continued)

```

229 J=R
230 PRINT " TOTAL FLOW FROM CARBON ARC ="A[1,J]+B[1,J]+C[1,J]
231 PRINT " TOTAL FLOW FROM POLYMERIZER ="A[2,J]+C[2,J]+K[2,J]
232 PRINT " TOTAL FLOW FROM IF5 REACTOR ="A[3,J]+G[3,J]+K[3,J]
233 PRINT " TOTAL FLOW FROM FLUORINATOR ="A[4,J]+C[4,J]+Q[8]
234 PRINT " TOTAL FLOW FROM PYROLIZER ="A[5,J]+B[5,J]+C[5,J]+D[5,J]+K[5,J]
250 END

```

the distillation column since input and output are equal for this process. Calculations are made on the basis of an input of 1 mole of C_3F_7I to the laser. The quantities of the various products are taken as independent variables. Additional assumptions are discussed under the various processing steps.

Carbon Arc

CF_4 , C_2F_4 , and C_2F_6 from the primary distillation column, and CF_4 and C_2F_6 recycled from the polymerizer and the fluorinator, are passed through a carbon arc operating at about 1973 K. Here CF_4 and C_2F_6 are converted into C_2F_4 . This is a process that has been patented by DuPont⁵ but, so far as we know, not yet developed into a commercial process. Making it work successfully would require considerable developmental effort. The patent abstract gives no clue as to the yield per pass of C_2F_4 from either CF_4 or C_2F_6 but states that good yields are obtained if unused starting materials are recycled. A second patent⁶ indicates that using C_3F_8 as feed gives a product containing 50 mole % C_2F_4 , so we have assumed a 50% yield per pass from both CF_4 and C_2F_6 for the flow model. With an adequate developmental effort, that yield could be raised considerably. The model indicates that a 60% yield per pass would result in about 9% decrease in flow through the arc. The model presumes no products other than C_2F_4 and assumes that the C_2F_4 , fed to the arc, passes through unchanged.

Polymerizer

The output from the carbon arc would be cooled and sent to a chamber for polymerization of the C_2F_4 to oils of suitable molecular weight, volatility,

and viscosity. This is an industrial process for manufacturing both teflon and fluorocarbon oils, but the optimum conditions to produce oils with the desired properties are yet to be worked out. The flow model assumes 100% conversion of C_2F_4 to CF_2 liquids. This is a fairly accurate assumption, any lower yield only meaning a slightly larger amount of material to recycle to the carbon arc. A source of free radicals and a means of chain termination would have to be provided. These could be uv light, small amounts of peroxides, or some of the CF_3I , C_2F_5I , or I_2 from the laser.

IF₅ Reactor

The C_3F_6 from the distillation column, together with that from the pyrolizer, can be reacted with IF_5 to regenerate C_3F_7I for recycling to the laser. It should be possible to effect the same result using IF , but this has not been reported. The reaction with IF_5 is reported in the patent literature to give "satisfactory" yields in a flow system at 448 K.⁷ For the flow model, we have assumed that the yield was 80% C_3F_7I , the remainder being 10% recycled and 10% high-boilers that were sent to the pyrolizer. The model indicates that a 70% yield would increase the loads on the carbon arc, polymerizer, and pyrolizer each by about 7%; the load on the IF_5 reactor would increase by 18%.

Pyrolizer

The C_6F_{14} from the distillation column would pass through the fluorinator unchanged, being separated in a subsequent distillation. It would then go to a pyrolizer operated at a platinum-filament temperature of 1373 K to 1473 K (the walls are cold). This is a process that has been used to degrade a number of volatile fluorocarbons; it produces substantial amounts of C_3F_6 . There are no data available under these or any other conditions on the pyrolysis of C_6F_{14} . Based on what data are available for C_5F_{12} and lower fluorocarbons^{8,9} and some firsthand experience with thermal decomposition of fluorocarbon polymers such as teflon, we estimate the yields to be roughly as follows:

	From C_6F_{14} (moles/mole)	From CF_2 (moles/mole)
CF_4	0.4	0.05
C_2F_4	0.7	0.1
C_2F_6	0.6	0.05
C_3F_6	0.9	0.1

Everything else is assumed to be CF_2 , and the flow model calculates its yield on the basis of a fluorine balance. If the program calculates a negative yield of CF_2 from either C_6F_{14} or from CF_2 recycling, the program stops and indicates the problem. This means that one or more of the yields listed above is unrealistic and needs to be changed. The above yields are best guesses based on sparse data. They are strongly influenced by reaction conditions and need to be determined experimentally. The model indicates that an increase in yield from 0.9 to 1.0 of C_3F_6 , which would require a decrease of CF_4 from 0.7 to 0.6 to maintain the fluorine balance, would decrease the flow through the carbon arc and pyrolizer by 10 to 11% each and through the pyrolizer by about 15%.

Alternate Approaches

Aside from details in the scheme presented in Fig. 1 — such as one or two arcs, putting the polymerizer before the arc, etc. — there are a few other possible approaches:

- Try other chemical reactions — CF_3I can be added to C_2F_4 to make $\text{C}_3\text{F}_7\text{I}$. $\text{C}_3\text{F}_7\text{I}$ is the normal isomer, however, not the iso one. This normal isomer, n- $\text{C}_3\text{F}_7\text{I}$, could be carbonated by means of a Grignard reagent and pyrolyzed to give C_3F_6 , which could then be reacted with IF_5 .

It would be possible to convert all of the fluorocarbons to HF by means of combustion. The HF could then be used in an electrolysis cell to convert iso-butyric acid to perfluoro-iso-butyric acid, yielding i- $\text{C}_3\text{F}_7\text{I}$ in the Hunsdiecker reaction.

It might be possible, using high temperatures or silent discharges, to effect reactions between I_2 and fluorocarbons to produce recyclable products. It might even be possible in a silent discharge to convert C_4F_{14} and I_2 back to $\text{C}_3\text{F}_7\text{I}$, but this has never been done.

All the alternate chemical processes thus far conceived seem much less desirable than the one we are proposing. The alternates are more complex, less energy-efficient, and, in most cases, less "closed."

- Market the byproducts — It might be economically advantageous to separate products from the laser by distillation and simply sell them as raw materials for the fluorochemical industry. A marketing study is needed to assess the feasibility of this approach.

- Look at other feedstocks — Other feedstocks, such as CF_3I , $\text{ICF}_2\text{CF}_2\text{I}$, BI_3 , etc., might be a lot easier to recycle. A search of the literature might uncover more suitable candidates with very little additional effort.

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II. IODINE LASER PROCESSING

by R. E. Elson

Iodine Removal

Assume that all extraneous iodine to be removed from the exit stream of the laser is present as molecular iodine and carried in a large excess of He. The iodine can best be collected in a blowing-out tower,¹ the capacity of which will depend upon the He volume. This type of tower is claimed to be greater than 90% efficient per stage. If we desire to separate the bulk of the iodine from everything else, the temperature of the tower should be above 337 K. If we desire to separate all material other than He (and possibly CF_4), a cold-trap type of column is necessary with all the volatiles later separated by boiling off at a temperature above 337 K. This latter operation will probably carry considerable I_2 to the distillation column and will require cold baffles to minimize carryover.

As the He stream needs to be free of I_2 (below 1 ppm) before recycling, the last traces can be removed by a number of methods: (1) reaction with I^- in aqueous solution, (2) absorption on charcoal at room temperature or below, (3) reaction with fairly strong alkaline solution, or (4) solution in a variety of organic solvents. For (1), the KI is commonly used, the solubility of I_2 being of the order of 0.5 the concentration of KI at low concentrations and about 0.3 at high. As the association constant for I_2 at 298 K is of the order of 10^3 (about 10^4 at 273 K), solutions of about 1-2 M in KI should have less than 10^{-5} M of $[\text{I}_2]$. The vapor pressure of I_2 at 273 K is about 0.03 Torr, so the maximum concentration in the exit gas at 1 atm should be approximately 40 ppm. Two scrubbers operating at 273 K should bring the $[\text{I}_2]$ well below 1 ppm. Solutions would be changed as they approach saturation.

For (2), only the capacity is given in the literature — 60 gm of I_2 per 100 gm of charcoal. If we assume that the vapor pressure of I_2 over unsaturated charcoal is well below its normal equilibrium value, one charcoal trap operated at 223 K should be effective. The capacity at that temperature is not known, but it should not be drastically different (although greater) than that at room temperature.

Option (3) is less desirable because it requires subsequent chemistry to regenerate I_2 (reduction with SO_2 followed by oxidation with Cl_2), while option (4) introduces solvent vapors that have to be removed.

If recovery is necessary, heat is needed for both options (1) and (2) — probably temperatures of the order of 423 K to 473 K. If recovery is not required, either one or a combination is effective. Option (1) probably requires the subsequent removal of H_2O .

These methods can also be used to scrub I_2 from other process streams.

Fluorine Recovery

Since CF_4 is the most difficult constituent to decompose completely, the literature was checked only for methods applicable to it. A number of techniques have been developed for quantitative decomposition for analytical purposes, but few of these lend themselves to large-scale plant operations. The possible large-scale processes that have some pertinent data available are: (1) decomposition in an $\text{H}_2\text{-O}_2$ flame to yield CO_2 and HF , and (2) reaction with H_2 to yield CH_4 and HF .

The $\text{H}_2\text{-O}_2$ flame has been well developed for analytical purposes.² It is relatively rapid, easy, and quantitative. Temperatures of the order of 2273 K are generated. The mechanism is unclear, i.e., simultaneous oxidation-reduction, fluorine extraction or pyrohydrolysis with the H_2O formed in the flame. No work was found regarding the optimum $\text{H}_2\text{:O}_2$ ratio or the maximum amount of fluorocarbon capable of sustaining combustion or fluorocarbon's effect on flame temperature. However, some data is available on the effect of added CF_4 (and other fluorocarbons) on the flammability limits of $\text{H}_2\text{-O}_2$ mixtures.³ At ambient conditions, the explosion limit is narrowed but flames can still be made to propagate with up to 90.5% CF_4 (less for higher fluorocarbons). Flame temperatures are unknown, but the reactions are more exothermic than $\text{H}_2\text{-O}_2$. Calculations and experimental results indicate the $\text{H}_2\text{:O}_2$ ratio should be ~0.6 rather than stoichiometric.

The $\text{CF}_4\text{-H}_2$ reaction has been studied to some extent.⁴ Rates were of the order of 1.5%/sec for 2:1 $\text{H}_2\text{-CF}_4$ (theory = 4:1) at 1473 K with N_2 diluent. The rate had a $[\text{H}_2]^{1/2}$ dependency and the form $-\text{d}[\text{CF}_4]/\text{dt} = 1.4 \times 10^{15} \exp(-95,800/\text{RT}) [\text{CF}_4][\text{H}_2]^{1/2}$ over the range 1323-2423 K. Reaction products were 4HF:1CH_4 with traces of C_2H_4 , C_2H_2 , and C. Contact times must be greater than 0.2 sec (5 sec was used). Addition of O_2 increased the rate (about 8% doubled the rate) and might be helpful in removing traces of C that could complicate things.

Pyrohydrolysis is thermodynamically a very attractive process, but insufficient information is available in the literature to define operating conditions.

IF₅ Preparation

Fluorine is allowed to flow through I₂ in IF₅ at 293-333 K.⁵ In one case, a 0.5 wt% solution of I₂ is used countercurrent to the F₂ in a Raschig ring reactor. Flow rates of 30.5 gal/hr and 3 lb/hr, respectively, with an 18-sec contact time yielded 7 lb/hr of IF₅. In the other case, 4.57 kg of I₂ suspended in 4.5 kg IF₅ had F₂ passed through at the rate of 0.475 kg/hr for 10 min to give 8 kg of IF₅. Construction of material was not stated. Laboratory scale preparations are carried out in glass or iron. If glass is used, precautions must be taken to keep it dry and free of air.

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III. ENERGY COST ESTIMATE FOR RECYCLING IODINE GAS LASER MEDIUM

by H. H. Otsuki and K. E. Cox

The proposed 100-200-J atomic iodine laser system consists of 32 equivalent amplifier chains (UCRL-77523). The final power amplifier in the chain is 40 cm in diameter and 300 cm in length. The laser medium is

Fig. III-1. A simplified flow diagram for processing iodine laser medium (the process-step numbers correspond to those in Table III-1).

Table III-1. Summary of flow to and from process steps (the numbers correspond to those in Fig. III-1).^a

	Temperature (K)	Pressure (atm)	(g-moles/sec)					Ratio of CF ₄ to C ₂ F ₄	(g-moles/sec)		
			Ar	C ₃ F ₇ I	C ₆ F ₁₄	I ₂	C ₃ F ₆		HF	F ₂	IF ₅
1.	300	5	2429	12.88	7.19						
2.	500	5	2429	11.97	7.6	0.45					
3.	300		2429	11.97	7.1	<1 ppm					
4.	240	0.015			0.45						
5.						0.45					
6.(a)							0.75	4.50			
(b)							0.41	2.46			
7.(a)								1.80			
(b)								3.84			
8.(a)				0.75							
(b)				0.41							
9.(a)											0.75
(b)											0.41
10.(a)										1.5	
(b)										0.82	
11.(a)										0.30	
(b)										0.98	
12.(a)											0.15
(b)											0.49
13.										0.56	
14.(a)											
(b)											
15.										0.90	
16.(a)										1.2	
(b)										3.92	
17.(a)										2.1	
(b)										4.82	
									C ₃ H ₇ COOH	C ₃ F ₇ COOH	
18.(a)									0.15		
(b)									0.495		
19.(a)											0.15
(b)											0.495
20.(a)				0.15							
(b)				0.49							

^aSteps 6-20 are divided into (a) and (b) parts. Values listed as (a) are based on maximum C₃F₆ yield; those listed as (b) are based on the most probable C₃F₆ yield.

iso-perfluoropropyl iodide (i-C₃F₇I) in argon* at a total pressure of 5 atm. The ratio of i-C₃F₇I to argon is 1 to 190 in the mixture. Each chain in the system is to be pulsed between one and ten times every second. Following

* Helium was assumed to be the diluent gas for parts I and II of this paper. However, prior to energy costs studies (part III), Y Division directed us to use argon as the diluent.

each pulse, the spent gases (i.e., the laser medium) must be replaced to ensure high average output power of acceptable beam quality. It is estimated that more than 2×10^8 lbs of $i\text{-C}_3\text{F}_7\text{I}$ will need to be cycled through the laser in one year's time, assuming an 80% duty time. The quantity of argon circulated with $i\text{-C}_3\text{F}_7\text{I}$ is about 5×10^9 lbs. This enormous quantity of spent gases, too valuable to be discarded, must be purified of its degradation products and recycled back to the mix tank. The degradation products, assumed to be C_6F_{14} and I_2 , must be synthesized to $i\text{-C}_3\text{F}_7\text{I}$ to maintain the inventory. Whether the $i\text{-C}_3\text{F}_7\text{I}$ iodine laser is indeed a viable energy source for fusion application then depends on the overall efficiency of the gas-handling system. The gas-handling system (i.e., purification, circulation, and synthesis of $i\text{-C}_3\text{F}_7\text{I}$) is the energy-intensive element in the iodine laser.

In this memo, we present an estimate of the energy cost for recycling the laser medium. The flow diagram for the gas (laser medium) handling system is shown in Fig. III-1. The flow rates are given in Table III-1. It is a simplified version of the flow diagram developed by Bissell and not a closed cycle, but it will serve our purpose. The flow diagram for the process consists of the following components, listed with their functions:

● supply tank	- mixture preparation.
● laser	
● separator	- heat extraction, separation of I_2 and C_6F_{14} decomposition products, compression.
● pyrolizer	- split of C_6F_{14} to C_3F_6 , CF_4 , C_2F_5 , etc.
● IF_5 reactor	- conversion of C_3F_6 to $i\text{-C}_3\text{F}_7\text{I}$.
● combustor	- combustion of CF_4 , C_2F_4 , C_2F_6 , etc. to HF.
● electrolytic cell	- conversion of HF to F_2 and H_2 .
● converter	- generation of IF_5 .
● electrolytic fluorinator	- conversion of butyric acid to its fluorinated analog.
● IF_5 reactor	- conversion of the fluorinated analog of butyric acid to $i\text{-C}_3\text{F}_7\text{I}$.

Separator

Three important functions are carried out in the separator unit (see Fig. III-2). First, since the pumping efficiency of the flashlamp used to excite the laser medium is of the order of 1%, almost all of 10 MJ of pumping energy is deposited as thermal energy for every 100 kJ of laser output. The average temperature of the gases leaving the laser is thus about 500 K, and substantial cooling must be provided. The gas mixture is cooled to 240 K in three heat exchangers, HX-1, HX-2, and HX-3. In HX-1, the gas stream is cooled to near ambient condition, i.e., about 325 K. This cooling can be done with water, in which case the thermal energy in the gas stream is wasted; or, alternatively, HX-1 can be designed as a steam generator coupled to a turbine to produce useful work, in which case about 1400 kW of useful work can be realized. HX-2 is a recuperative heat exchanger in which the warm (~325 K) incoming gas stream leaves the HX-2 heat exchanger at ~300 K. Next, the separation of the degradation products is performed in these heat exchangers. The partial pressure of iodine in the spent gas, assuming 7% net decomposition of C_3F_7I , is about 0.7 Torr. The equilibrium vapor pressure of iodine is about 0.02 Torr at 265 K exit temperature (see Fig. III-3). Thus more than 95% of the iodine will condense out of the argon stream before it leaves HX-2. The recovery of the separated iodine on a continuous basis will require having two HX-2 units arranged in parallel. The residual iodine is stripped in HX-3, where the argon stream is further cooled to 240 K by an auxiliary refrigeration system. The iodine content in the return stream is thus reduced to less than 1 ppm. The vapor pressures of $i-C_3F_7I$ and C_6F_{14} is estimated to be about 24 and 12 Torr respectively at 240 K (see Fig. III-4). Since the $i-C_3F_7I$ partial pressure in the spent gas stream is about 18.5 Torr, it will pass through the heat exchanger system without condensation. The partial pressure of the C_6F_{14} degradation product in the argon stream will build up to about 12 Torr, as a steady state value (i.e., the composition of the laser medium at steady state will be 99.17% argon, 0.526% $i-C_3F_7I$, and 0.3% C_6F_{14}). The auxiliary refrigeration load to effect the gas separation is 770 kJ per 100 kJ of laser energy output.

The third function of the separator is to rebuild the pressure head lost in forcing the gases through the various heat exchangers and piping. This pressure drop is 11 or 13 psia. The lower value of 11 psia is for the case where the initial cooling in the HX-1 is accomplished using water. A pressure drop of 13 psia will result if steam generator is used. The compressor power

Fig. III-2. Separator.

Fig. III-3. Iodine vapor pressure.

Fig. III-4. Estimated vapor-pressure curves (the i-C₅F₁₂ curve is from J. H. Simons, ed., *Fluorine Chemistry* [Academic Press, New York, 1954], vol. 2, p. 436).

requirement to rebuild the pressure back to 5 atm is then 2.4 or 2.8×10^3 kJ per 100 kJ of laser energy output (see Fig. III-5).

Pyrolizer

The C_6F_{14} gas in excess of 12 Torr at 240 K is condensed in HX-3. The liquid C_6F_{14} together with the residual iodine is directed toward the pyrolizer. C_6F_{14} is separated from iodine and pyrolized to yield C_3F_6 and lower fluorocarbons. Based on a carbon-fluorine balance, the maximum C_3F_6 yield (assuming the other product is CF_4) is 1.67 moles of C_3F_6 and 1.0 mole of CF_4 per mole of C_6F_{14} . The most probable yield of C_3F_6 , according to Bissell's calculation, is 0.9 mole of C_3F_6 and 0.4, 0.7, and 0.6 moles of CF_4 , C_2F_4 , and C_2F_6 , respectively, per mole of C_6F_{14} pyrolized. The average net bond cleavage is 1.3 per C_6F_{14} molecule. Assuming a C-C bond energy of 144 kcal per mole (602 kJ per mole), the minimum energy requirement for the 0.45 mole of C_6F_{14} is 350 kJ per 100 kJ of laser energy output.

The C_3F_6 product is separated from the lower fluorocarbon and sent to the IF_5 reactor. The lower fluorocarbon waste product is sent to the combustor for recovery of fluorine as HF.

Combustor

The fluorocarbon waste product is burned in the presence of hydrogen to yield HF. The combustion process is highly exothermic; some of the heat will be used for process heat, but otherwise it will be wasted. Part of the HF stream will be directed toward the electrolysis cell and the remainder to the electrolytic fluorinator.

Electrolysis Cell/Converter

Fluorine is generated in the electrolysis cell. The estimate of the power requirement for the electrolysis is 129 kcal per mole of F_2 , or 540 kJ electric/mole F_2 , based on bond energy considerations for the reaction $HF = 1/2H_2 + 1/2F_2$. Since the fluorine requirement is 0.45 mole per 100 kJ laser output, this corresponds to a power requirement of 730 kJ. The F_2 stream goes to the converter, where it reacts with iodine from the separator to form IF_5 . Part of the product goes to the IF_5 reactor-3, with the remainder going to IF_5 reactor-8.

Fig. III-5. Compressor load.

IF Reactors

In the IF_5 reactor, the IF_5 reacts with the fluorocarbon to form the starting material, $\text{i-C}_3\text{F}_7\text{I}$. The product is sent on to the mixing tank. The reaction is slightly exothermic with no net power consumption.

Electrolytic Fluorinator

Since there is a net loss in the $\text{i-C}_3\text{F}_7\text{I}$ material as the flow diagram is constructed, the $\text{i-C}_3\text{F}_7\text{I}$ is synthesized from butyric acid assumed to be available at no energy cost to our system. The butyric acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, is converted to perfluoro-isobutyric acid in the electrolytic fluorinator. The energy requirement for this fluorination process, again estimated by Bissell, is about 8240 kJ (electric) or 3.4×10^4 kJ per mole of fluorinated acid. Thus the energy consumed in the electrolytic fluorinator to produce the $\text{i-C}_3\text{F}_7\text{I}$ makeup amounts to between 3600 and 12 000 kJ for 0.15 and 0.5 moles of $\text{i-C}_3\text{F}_7\text{I}$ (the quantity required to maintain the necessary inventory).

Thermal Efficiency

The most energy-intensive component in the gas handling system is the electrolytic fluorinator. Even with the most optimistic operation of the pyrolizer, where the waste generation is at a minimum, the energy expected in the synthesis of fluorocarbon compound (with $\text{i-C}_3\text{F}_7\text{I}$ makeup), represents

Table III-2. Summary of energy requirement for the individual components of the gas handling system.

Separator	Minimum energy (kJ)	Maximum energy (kJ)
Compressor energy needed with power generator	1400	
without power generator		2400
Auxiliary refrigerator	770	770
Pyrolizer	350	350
Electrolysis cell	730	730
Electrolytic fluorinator	3600	12 000
Total energy required	6850	16 250

about 50% of the total energy requirement. For the case of most probable yield in the pyrolizer, the makeup requirement completely dominates the total energy consumption. These results are summarized in Table III-2.

The ratio r , defined as the energy consumed to the laser energy output, ranges from a most optimistic value of about 70 to a most probable value of about 160.

The recovery of $i\text{-C}_3\text{F}_7\text{I}$ can be improved by cycling the lower-molecular-weight fluorocarbon waste through a polymerizer and back through the pyrolizer, as suggested by Bissell. Great uncertainty as to the energy cost and yield factor in the operation of the necessary carbon arc do not seem to warrant its consideration at this time.

As an alternative, the makeup $i\text{-C}_3\text{F}_7\text{I}$ can be purchased. The price of $i\text{-C}_3\text{F}_7\text{I}$, excluding the cost of iodine, is about \$1.00 to \$1.50 per pound, i.e., about \$0.65 to \$1.00 per g-mole. The replacement cost will range between \$0.10 to \$0.50 per 100-kJ laser pulse or about \$2.4 to \$10 million per year.

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