

A COMPARISON OF ETHYLENE REMOVAL BY MEANS OF CATALYTIC COMBUSTION AND CHEMICAL ABSORPTION

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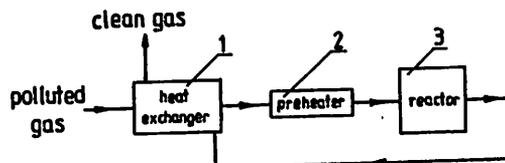
Several systems have been proposed for removal of ethylene gas from the atmosphere of commercial storage and transport facilities for horticultural crops. Two of these systems, catalytic oxidation and chemisorption, are presently used in commercial storage facilities. In this paper we will describe these two systems and conclude with an economic comparison based on data collected at commercial CA apple storage facilities in New York.

Catalytic Oxidation

Ethylene and other hydrocarbons may be oxidized catalytically according to following reaction: $C_2H_4 + 3 O_2 \rightarrow 2 CO_2 + 2 H_2O$. Heated platinum (10), copper (3) or copper-zinc (6) catalysts are often used to accelerate this reaction.

A typical scheme of catalytic purification adapted to ethylene removal is shown in Fig. 1. The gas stream from storage is pumped through the heat exchanger 1 and preheater 2 to the catalytic reactor 3 and then returned to the heat exchanger 1, to be finally turned back to the storage. The cost of this process is determined mainly by the amount of energy required to heat the catalyst bed and gas stream up to the temperature necessary for catalytic conversion of ethylene. The conversion reaction occurs at a minimal temperature of 160-190°C using a platinum catalyst.

Fig. 1. Scheme of conventional process of catalytic purification.



Energy consumption during catalytic oxidation may be reduced if (8):

- heat is supplied to the gas stream not ahead but at the middle of the catalyst
- the direction of the gas stream flowing through the catalyst bed is not constant but cyclically reversed, and
- the catalyst bed is placed between two layers of ceramic filling which accumulate the heat at the two successive changes of the gas stream direction.

With this scheme the catalyst bed is buffered from the cooling effect of the incoming gas stream. Heat transferred from the centrally heated catalyst bed is recovered by the ceramic filling on the downstream side of the catalyst (Figure 2). The gas flow through the unit is reversed when heat breaks through the downstream ceramic filling. Upon flow reversal, the function of the two ceramic fillings are reversed: the previous heat sink becomes a heat source for the gas stream and catalyst, and the previous source becomes a sink for cooling the purified effluent

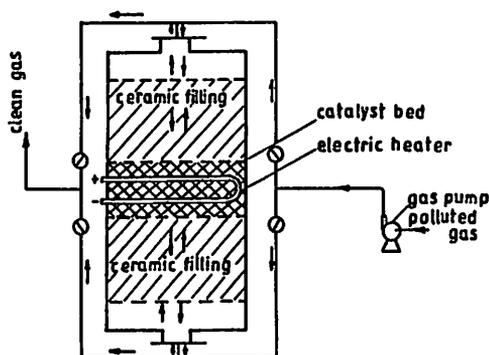


Fig. 2. Diagram of Swingtherm process.

stream. The only external energy required is that needed to maintain the catalyst temperature at 190°C.

The process described above has been incorporated into Swingtherm (8,9). The name expresses the main feature of the process: rhythmical displacement of heat in the reactor. The temperature rise in the catalyst bed depends on:

- physical and thermal properties of the filling and of the catalyst,
- incoming gas temperature and space velocity of the gas flowing through the reactor,
- quantity of heat supplied to the middle part of the reactor,
- frequency of changes of the gas flow direction in the reactor.

The temperature distribution in the Swingtherm reactor is shown schematically in Figure 3. The difference between the temperatures of the inlet and outlet gases is $\Delta T'$. This difference changes with time. The minimal value occurs at the beginning of the cycle and the maximal value occurs at the end of the cycle. The difference between the maximum temperature in the catalyst bed and the inlet gas temperature is $\Delta T''$.

When designing the Swingtherm reactors it is of importance to know the ratio $\Delta T''/\Delta T'$. The ratio $\Delta T''/\Delta T' = A$ is the thermal efficiency coefficient of the Swingtherm reactor. This coefficient determines the heat efficiency of the Swingtherm process as compared with a reactor in which the gas stream passes the catalyst bed without the change in direction. The value of coefficient A varies from 10 to 20 in reactors used for industrial pollution control and from 30 to 75 for the reactors installed in the fruit storages. The value of this ratio, characteristic in a certain range for a given construction of the

- a. temperature of inlet gas
- b. temperature of outlet gas
- c. temperature of ceramic filling

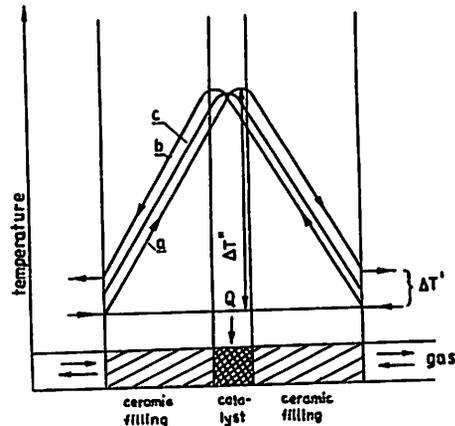


Fig. 3. Temperature profile in Swingtherm reactor.

reactor, depends on the following parameters of the process:

- intensity of gas flux through the reactor,
- amount of heat supplied to the middle part of the reactor,
- concentration of the pollutants (ethylene),
- frequency of changes of the gas stream direction.

If the gas flux intensity and the impurity (ethylene) concentration are constant, the ratio $\Delta T''/\Delta T'$ depends upon the amount of heat supplied from outside and on the frequency of gas flow reversal. The design values of the parameters are chosen to maintain the desired temperatures in the catalyst bed.

The volumetric rate of ethylene removal from a storage chamber during continuous Swingtherm operation is expressed in the following rate equation:

volumetric rate of change of ethylene in chamber	=	volumetric rate of ethylene production by fruit	-	volumetric rate of ethylene conversion by Swingtherm
$V \frac{dc}{dt} = rm - \eta FC \quad (1)$				

Where:

V = volume of atmosphere in storage chamber, m³
 C = concentration of ethylene, ppm
 r = rate of ethylene production by fruit, m³ton⁻¹hr⁻¹
 M = mass of fruit in storage chamber, tons
 η = converter efficiency, assumed independent of C
 F = gas flow through converter, m³hr⁻¹
 t = time, hr.
 d = derivative

The time required for the ethylene concentration in the chamber to change from some initial value C_i at t = 0 to a value of C_t is found by integration:

$$t = \int_{C_i}^{C_t} \frac{V}{\eta F} \frac{dc}{\left(\frac{rm}{\eta F} - C\right)} = \frac{V}{\eta F} \ln \frac{C_i - \frac{rm}{\eta F}}{C_t - \frac{rm}{\eta F}} \quad (2)$$

For values of C_i and C_t >> $\frac{rm}{\eta F}$, $t \approx \frac{V}{\eta F} \ln \frac{C_i}{C_t}$ (3)

During continuous use of the converter the equilibrium ethylene concentration, C_e, in the storage chamber is reached when the rate of ethylene production by the apples equals the rate of conversion by the Swingtherm. Under these conditions:

$$rm = \eta FC_e \text{ or } C_e = \frac{rm}{\eta F} \quad (4)$$

The gas flow through the converter necessary to achieve equilibrium is:

$$F = \frac{rm}{C_e \eta} \quad (5)$$

The conversion efficiency of the Swingtherm was determined experimentally by measuring the incoming and outgoing ethylene concentration of the gas stream through the catalyst. The efficiency is:

$$\eta = 1 - \frac{C_2}{C_1} \quad (6)$$

Where C₁ = C at entrance
 C₂ = C at exit

The equilibrium rate of ethylene production by the fruit is calculated from the storage chamber ethylene concentration at equilibrium. This value is:

$$r_e = \frac{C_e \eta F}{M} \quad (7)$$

Since η , F and M are constant for a given chamber and Swingtherm configuration, the volume of ethylene produced by the apples and removed by the Swingtherm may be easily determined by measuring C_e and solving equation (7) for r_e . The volume of ethylene produced per unit time at equilibrium is identical to the volumetric conversion rate for the scrubber:

$$V = r_e M = \eta F C_e \quad (8)$$

In the 1981-82 season the Swingtherm process was experimentally adapted to ethylene removal from apple storage chambers in Poland. Following this research the Polish-Italian Company COMINDEX started production of the Swingtherm Ethylene Converters (Table 1).

Table 1. "Swingtherm E", manufacturer's specification for ethylene converters produced by Polish-Italian Company COMINDEX.

Type	Energy consumption (kW)	Flow rate (m ³ /h)	Weight (kg)	Width (m)	Depth (m)	Height (m)
E - 50	1.1	50	180	1.4	0.85	1.2
E - 150	1.3	150	250	1.4	0.85	1.2
E - 300	1.8	300	360	1.4	0.85	1.2
E - 500	2.0	500	480	2.0	1.2	1.3
E - 750	2.8	750	650	2.0	1.2	1.3

One of these converters, Swingtherm E-150, was connected to a 120 ton McIntosh CA chamber 35 days after filling the chamber with apples. The free volume of gas in the chamber was ca. 380 m³. The O₂ concentration was held at 3-3.5% and CO₂ at 4-5%. The CO₂ concentration was regulated by an activated carbon absorber. The initial concentration of ethylene in chamber was 202 ppm.

The comparison of calculated and measured data (Figure 4) shows that the real time for decreasing of the ethylene concentration in the storage chamber was over 3 times longer than the theoretical time calculated by the ethylene mass balance equation. The difference may have been caused by incomplete mixing of gas in storage chamber. Practical experience with CO₂ scrubbing and N₂ flushing of commercial storage chambers, however, lead us to conclude that this was not the case. The ethylene conversion in the catalyst bed was higher at the very beginning than at the end of the test. This can be explained by the fact that the rate of catalytic oxidation of ethylene (and hence η) was lower at the low concentrations of

ethylene experienced nearer the end of the test.

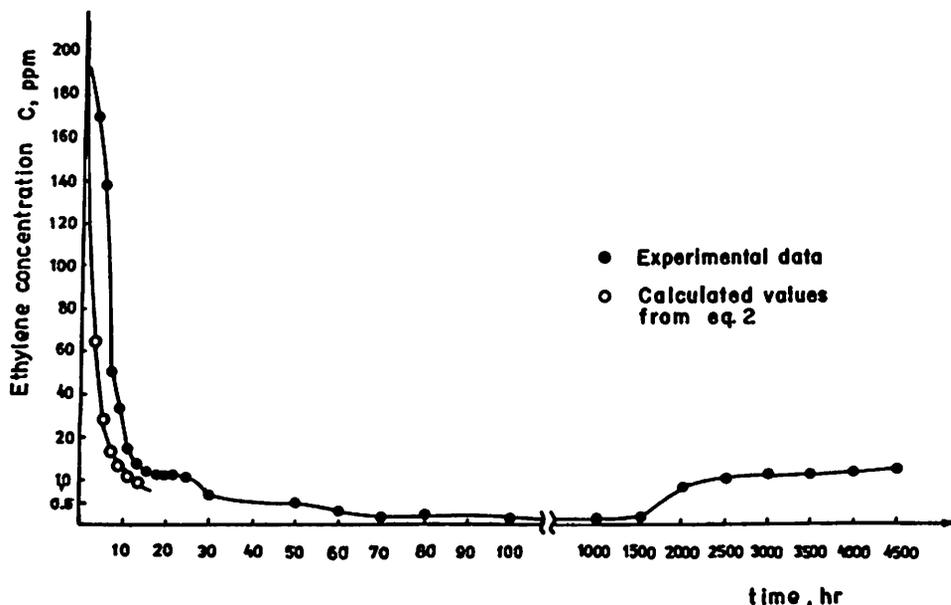


Fig. 4. Ethylene concentration in a CA room during non-stop Swingtherm E-150 operation.

A Swingtherm E-500 ethylene converter was used to remove ethylene from a 200 ton 'McIntosh' CA room during the 1983-84 storage season in New York. The ethylene concentration in the CA room was maintained in the range equilibrium of 1-2 ppm, with a few higher concentrations (up to 6 ppm) being recorded after periods of higher than desirable oxygen concentrations. The close relationship between rate of ethylene conversion and the ethylene concentration in the CA room is shown in Figure 5. Within the range of ethylene concentrations observed (1-6 ppm), the converter efficiency averaged 0.85.

The Swingtherm E-500 was used again from January to March of the 1984-85 storage season in New York. The ethylene in the CA room, which held 200 tons of 'Empire' and 'Delicious' apples, varied from 0.4 to 1.4 ppm and the average efficiency of conversion was 0.87. A study of the relationship between catalyst temperature and ethylene conversion by this scrubber (Fig. 6) supported the earlier observation that the catalyst temperature should be maintained at 160-200°C (Figure 6).

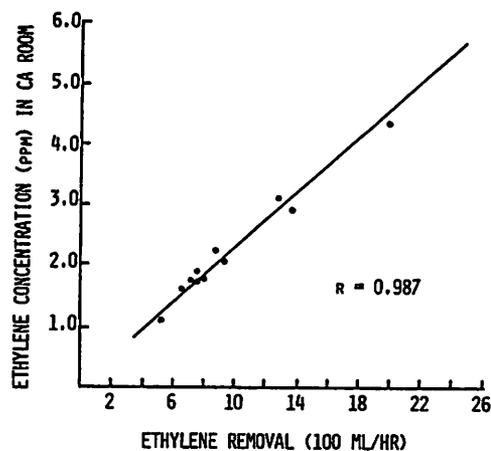


Fig. 5. Rate of ethylene removal by Swingtherm E-500 operated with 200 ton 'McIntosh' CA room.

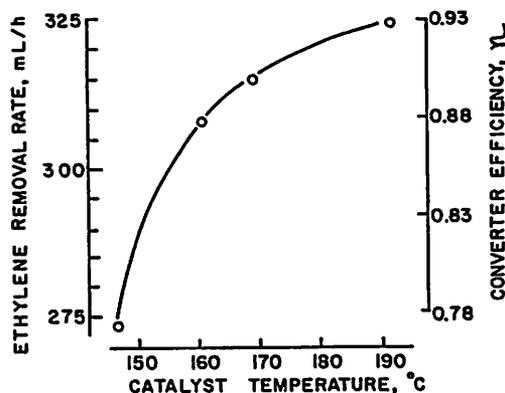


Fig. 6. Effect of catalyst bed temperature on ethylene conversion by Swingtherm E-500 operated with 200 ton 'Empire' low ethylene CA room.

Ethylene Removal By Chemisorption

Ethylene may be oxidized at standard conditions by potassium permanganate according to this reaction:



Practically, potassium permanganate is incorporated into beads of activated alumina (Al_2O_3). The efficiency of various types of ethylene chemisorption beads (ECB) as well as the influence of temperature, humidity, carrier material and size, etc. upon the rate of ethylene removal have been reported (1,2,4).

To use ECB for removal of ethylene from a large commercial CA storage it is necessary to construct a scrubber cabinet which is filled with ECB and located outside the CA room (2). It was observed that the ethylene scrubbing efficiency of external scrubbers filled with ECB was initially quite high, but decreased rapidly with time (Table 2).

Table 2. Performance of ethylene chemisorption beads (85 kg) held in 10 cm X 0.9m² bed. Atmosphere from 200 ton CA Empire' apple room pumped through the bed (475m³/hr). March 1985.

Elapsed days	Ethylene		
	At scrubber inlet (ppm)	Conversion efficiency	Removal (ml/hr)
"Purafil"			
1	2.6	.73	885
2	1.1	.46	238
3	1.2	.42	238
7	1.7	.38	300
11	3.3	.21	324
16	4.4	.07	143
"Ethysorb"			
1	1.4	.88	557
2	2.0	.33	314
6	1.7	.13	109
7	2.6	.12	147
12	2.5	.08	95

A series of experiments were conducted to explain this phenomenon. One gram of "Ethylsorb" ECB was placed into a 17 mm diameter glass tube. Air containing 50 ppm ethylene was passed through the tube at the rates 10, 15, and 20 l/hr. A gas chromatograph was used to determine the ethylene concentration entering and leaving the tube. The curve for the data (Fig. 7) is expressed in the equation:

$$t = 1 - 3\left(1 - \frac{C_2}{C_1}\right)^{2/3} + 2\left(1 - \frac{C_2}{C_1}\right) \quad (9)$$

where C_1 = ethylene concentration at inlet
 C_2 = ethylene concentration at outlet of tube

Equation (9) indicates that the reaction of ethylene oxidation is controlled by ash layer diffusion (4). When the gas-solid reaction is controlled by ash layer diffusion it is very difficult to keep high conversion of gaseous reactant without high excess of solid reactant.

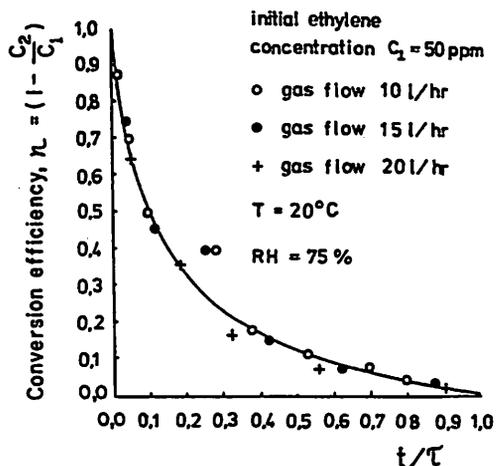


Fig. 7. Ethylene conversion on lg "Ethysorb".

From the chemical engineering point of view there are four possible models of flow through an ECB scrubber:

- batch of beads contacted with gas (Fig. 8a),
- concurrent flow of gas and beads (Fig. 8b),
- counter-current flow (Fig. 8c),
- cross-current flow (Fig. 8d).

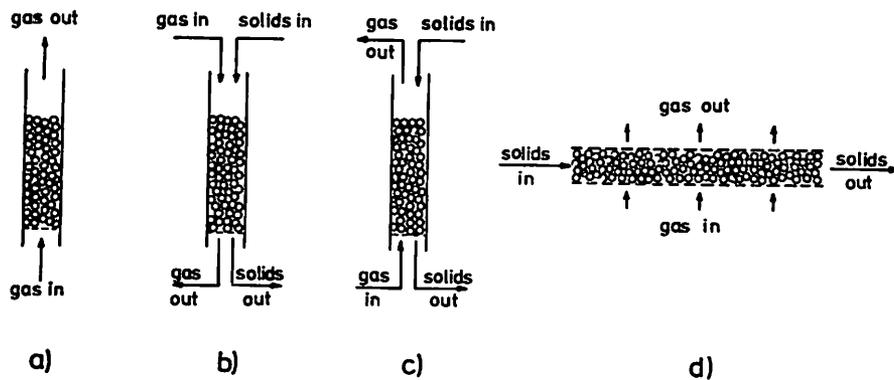


Fig. 8. Several models for gas flow through ethylene chemisorbant beads.

Cross-current flow through a shallow ECB bed appeared to be the best scheme to minimize electric costs for gas pumping. A shallow ECB bed was used for tests shown in Table 2 and for cost calculations which follow.

Estimated Costs

The scrubber should be designed to maintain the equilibrium ethylene concentration in the storage chamber at or below 1 ppm for the duration of the CA storage period. The critical design condition must be based upon late season conditions when apples are producing ethylene at an accelerating rate. For the purpose of comparing estimated costs for heated catalyst conversion and chemisorption of ethylene, we have assumed that $1 \mu\text{l kg}^{-1}\text{hr}^{-1}$ ($1 \text{ ml ton}^{-1}\text{hr}^{-1}$) will be the maximum rate of ethylene production. We also assume the apples will produce $0.1 \text{ ml ton}^{-1}\text{hr}^{-1}$ from harvest to mid-January, after which the rate will increase linearly to 1.0

Table 3. Some characteristics of ethylene removal by heated catalyst conversion (Swingtherm) and by chemisorption ("Purafil"). 400 tons of apples producing $0.1 \mu\text{l ethylene kg}^{-1}\text{hr}^{-1}$ from harvest to mid-January and then increasing linearly to $1.0 \mu\text{l ethylene kg}^{-1}\text{hr}^{-1}$ at day 270 (6480 hrs total).

No.	Compared parameter	Heated catalyst conversion	Chemisorption
1	Total ethylene produced (l)	969	969
2	Gas flow thru scrubber (m^3/hr)	444 ^a	1333 ^b
3	Type of equipment	Swingtherm E-500	homemade
	investment cost (U.S.\$)	9000	850
	chemical usage per season (kg)		
	catalyst	6.7 ^c	0
	KMnO_4 beads	0	1101 ^d
	heat introduced to CA room (Kcal hr^{-1})	1590 ^e	1692 ^f
	electrical usage (kw)		
	additional refig. ^g	0.51	.53
	fan	0.82	1.86
	heater	2.60	0
	total	3.93	2.39
4	Total energy consumption (kW hr)	25,466	15,487
5	Annual operating costs (U.S.\$)		
	catalyst ($\$35 \text{ kg}^{-1}$)	233	0
	KMnO_4 beads ($\$5 \text{ kg}^{-1}$)	0	5,505
	electricity ($\$0.10 \text{ kW hr}$)	2,547	1,549
	maintenance (6% of equipment cost)	540	51
	equipment depreciation (10%/yr.)	900	85
	interest (10%) on average equipment cost	450	43
	total cost each season	4,670	7,233
	cost per kg (bu.) of apples	0.012(0.21)	0.018(0.33)

a. Calculated using eq. 5 for average 0.9

b. Calculated using eq. 5 for average 0.3

c. 20 kg catalyst replaced every 3 yrs.

d. based on total chemisorption $0.881 \text{ l of ethylene kg beads}^{-1}$

e. calculated using equation $Q = F \cdot \tau C_p$ for average $\tau = 10^\circ\text{C}$

f. see above for $\tau = 4^\circ\text{C}$

g. 1 kW of refrigeration = $3,210 \text{ kCal heat added hr}^{-1}$

ml/ton⁻¹hr⁻¹ at the end of the 270 day storage period. These assumptions are based on F. W. Liu's ethylene production rate measurements, which are presented elsewhere in this publication.

The cost comparisons summarized in Table 3 are based on the assumptions described above. These data indicated that under the operating conditions described, the cost of chemisorption of ethylene is almost 50 percent higher than the cost of heated catalyst conversion of ethylene.

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