

# Kinetics of Acetaldehyde Formation during the Staling of Lager Beer<sup>1</sup>

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## ABSTRACT

Using a gas-chromatographic headspace technique, acetaldehyde concentration was monitored during the staling of lager beer at air contents of 0.4 ml and 0.8 ml/12 oz at temperatures of 0°, 15.5°, 24°, and 38°C. Studies showed that the formation of acetaldehyde during staling follows first-order kinetics, the rate being dependent upon the air content and temperature.

*Key words: Flavor, Gas-chromatographic headspace technique, Rate of staling, Storage, Time-temperature-air effects.*

A cardboard/paper flavor has been associated with the staling of beer. This stale flavor has been attributed to the small concentrations of the higher aldehydes being formed during staling. Difficulties in measuring the specific aldehydes have led to indexing staling by indirect approaches. Two procedures have been introduced recently: the TBA method of Grigsby and Palamand (7), and the furfural method of Brenner and Khan (3). Data from recent studies of headspace volatile changes during storage of packaged beer indicated that acetaldehyde could also be used as an index to staling.

The increase in acetaldehyde concentration during warm storage of beer is well documented in the literature. Ahrenst-Larsen and Hansen (1) qualitatively found that acetaldehyde increased after storage for 3 weeks at 45°C. Engan (6) found acetaldehyde to increase during early stages of storage at 25° and 40°C and then decrease slightly. Baron and Wagner (2) found acetaldehyde to increase during storage at 30°C. Pessa (10) found acetaldehyde to increase and then decrease with time at 8°, 22°, and 40°C in pilsner beer with an abnormally high air content. He also found acetaldehyde to increase with time for two different air contents. It is also well established that the acetaldehyde concentration in beer does not appreciably change during storage at 0°C (2, 5, 6).

In a preliminary study, acetaldehyde concentration did not change appreciably during storage at 0°C and acetaldehyde increased asymptotically with time for beer stored at 38° and 24°C, in both cases approaching the same limit. In addition, the concentrations of the other headspace volatiles did not change appreciably during the formation of acetaldehyde.

The kinetics of acetaldehyde formation were then studied in more detail during staling of lager beer in the hope of finding another key to the staling process.

## EXPERIMENTAL

### Determination of Acetaldehyde

Acetaldehyde was determined gas-chromatographically in duplicate at various times during storage by the headspace technique of Hoff and Herwig (9), using a glass-lined injector. Results were reported as "Per cent of the Total Peak Area" (PTPA).

### Determination of Air

Twelve-ounce packages of fresh beer with two different air contents were obtained. The air contents were determined by the Zahm-Nagel technique on nine samples of beer at each air level within 6 hr after packaging. The mean air levels were 0.8 ml (high air) and 0.4 ml (low air), with a standard deviation of 0.1 ml.

### Storage

Beers of both air contents were then placed in environmental rooms maintained at 0°, 15.5°, 24°, and 38°C to simulate warehouse conditions at 32°, 60°, 75°, and 100° F, respectively.

## RESULTS AND DISCUSSION

### Acetaldehyde Concentration (PTPA) as a Function of Time

The initial concentration of acetaldehyde was 1.05 PTPA, and no appreciable change in acetaldehyde concentration was observed during 5 months of storage at 0°C, regardless of air content. Figure 1 suggests that, at the high air level, the acetaldehyde concentration at each temperature was an exponential function of time. The acetaldehyde concentration at the two higher temperatures approached a limiting value of 1.56. The study was not of sufficient duration to observe this phenomenon at 15.5°C. Figure 2 suggests that, at the low air level, the acetaldehyde concentration at each temperature was again an exponential function of time, but the study was not of sufficient duration to observe the asymptote, although a limiting value of 1.56 was intuitively evident at 38°C.

### Rate Constants

The determination of rate constants for a first-order reaction requires only the measurement of the ratios of the concentrations of the limiting reactant at two times as indicated in the following equation:

$$k = \frac{1}{t_2 - t_1} \ln \frac{C_1}{C_2}$$

where  $C$  is the concentration of the limiting reactant and  $k$  is the rate constant.

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Setting  $t_1 = 0$  and  $t_2 = t$  produces the following equation:

$$k = \frac{1}{t} \ln \frac{C_0}{C_t}$$

where  $C_0$  is the initial concentration and  $C_t$  is the concentration at time  $t$  of the limiting reactant.

Since the limiting reactant is unknown, its concentration cannot be measured. The acetaldehyde concentration can, however, be measured to obtain a quantity which is proportional to the concentration of limiting reactant. This can more easily be seen in Fig. 3, where  $Acet_m$  is the concentration of acetaldehyde at the completion of the reaction,  $Acet_t$  is the concentration of acetaldehyde at time  $t$ , and  $Acet_0$  is the initial concentration of acetaldehyde. The quantity  $(Acet_m - Acet_0)$  is proportional to the total amount of acetaldehyde which will be formed during the reaction and is proportional to the initial concentration of the limiting reactant. The quantity  $(Acet_m - Acet_t)$  is proportional to the amount of acetaldehyde yet to be formed during the reaction and is proportional to the concentration of the limiting reactant at time  $t$ . Substitution of these quantities into the rate equation produces the following equation:

$$k = \frac{1}{t} \ln \frac{(Acet_m - Acet_0)}{(Acet_m - Acet_t)}$$

Conversion to common logarithms and algebraic manipulation produces the following equation useful in determining rate constants.

$$\log (Acet_m - Acet_t) = \frac{-kt}{2.303} + \log (Acet_m - Acet_0)$$

Therefore, a plot of  $\log (Acet_m - Acet_t)$  vs.  $t$  should yield a straight line with slope  $= -k/2.303$ .

The half-life is found as follows:

$$t_{0.5} = \frac{2.303}{k} \log \frac{1}{0.5} = \frac{0.693}{k}$$

The maximum acetaldehyde PTPA was approximately 1.56 for the beer with the high air level at 38° and 24° C as well as for the beer with the low air level at 38° C (see Figs. 1 and 2). Therefore, for the calculation of rate constants, the assumption was made that the acetaldehyde concentration would approach a limit of 1.56 in all cases.

Figures 4 and 5 show the plots of  $\log (Acet_m - Acet_t)$  vs. time at 28°, 24°, and 15.5° C for the high and low air contents, respectively. Straight lines were observed in all cases. Table I shows the slopes, rate constants, and half-lives for all cases, as well as the corresponding correlation coefficients for the regression lines. In all instances, the correlation coefficient indicated good linearity suggesting that the reactions follow first-order kinetics. Closer examination revealed that the rate constants were approximately doubled and half-lives approximately halved on doubling the air level at all three temperatures.

To corroborate these findings (based on an acetaldehyde maximum concentration of 1.56 PTPA), rate constants were also estimated by the method of Guggenheim (4, 8), where neither an infinite time value nor a zero time value is needed. The following derivation of the rate equation is useful for determining the rate constants using Guggenheim's method:

$$\log (Acet_2 - Acet_1) = \frac{-kt}{2.303} + \log [(Acet_m - Acet_0) (1 - e^{-k\Delta t})]$$

The data were obtained from the smooth curves of acetaldehyde PTPA vs. time drawn with the aid of the computer (see Figs. 1 and 2). For each observation, the acetaldehyde PTPA at time  $t$  ( $Acet_t$ )

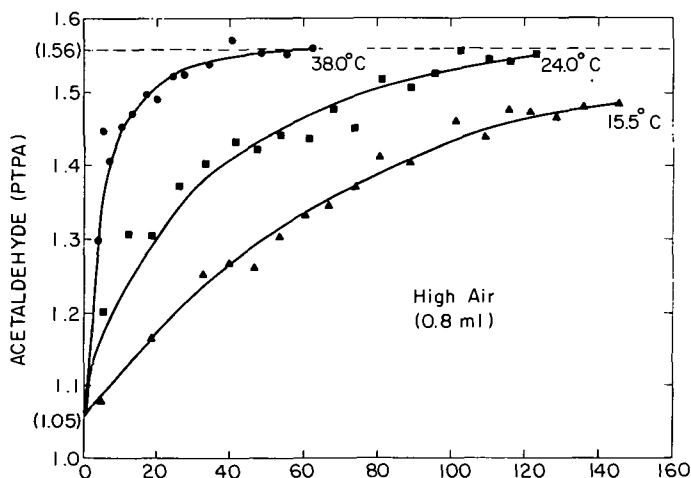


Fig. 1. Time-temperature effects on the formation of acetaldehyde at an air content of 0.8 ml/12-oz package.

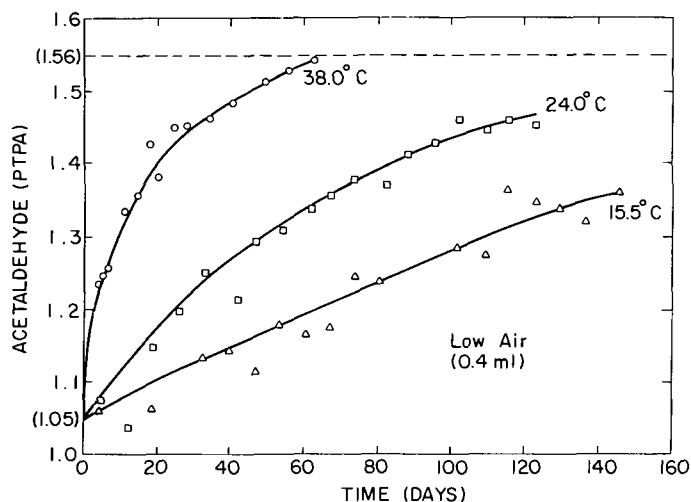


Fig. 2. Time-temperature effects on the formation of acetaldehyde at an air content of 0.4 ml/12-oz package.

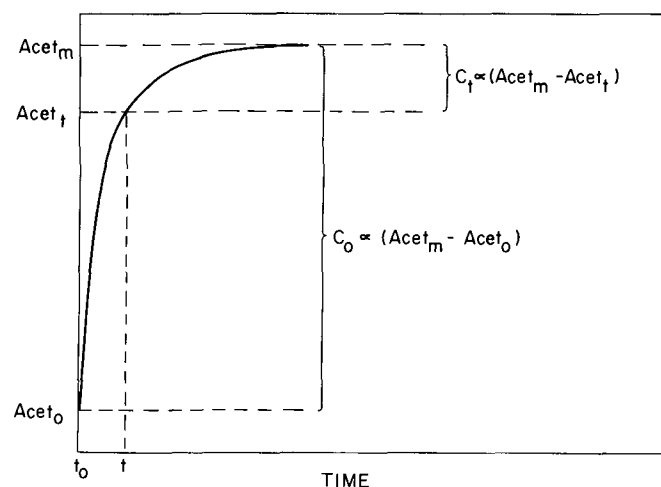


Fig. 3. Hypothetical plot of acetaldehyde formation exemplifying quantities which are proportional to the concentrations of limiting reactant.

and the acetaldehyde PTPA at time  $t + \Delta t$  ( $\text{Acet}_2$ ) are obtained where  $\Delta t$  is some fixed time interval (usually one-half the duration of the experiment). If the reaction follows first-order kinetics, a plot of  $\log (\text{Acet}_2 - \text{Acet}_1)$  vs.  $t$  will yield a straight line of slope  $= -k/2.303$ .

Straight lines were observed in all cases. The rate constants obtained by the Guggenheim approximation and the assumption of 1.56 PTPA as the limiting concentration of acetaldehyde are compared in Table II. Agreement is good, and examination of the intercepts obtained by the Guggenheim method showed that the acetaldehyde concentration would have approached a concentration of 1.56 PTPA as a limit in each case.

The influence of temperature on the rate constant is important; since the temperature range is not great, the dependence of rate constants on temperatures can be represented by the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

where  $E_a$  is the activation energy for the reaction,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $A$  is commonly referred to as the frequency factor and is a measure of the frequency of collision between the reactants.

Conversion to common logarithms and algebraic manipulation gives the more useful form of the equation:

$$\log k = \frac{-E_a}{2.303R} \cdot \frac{1}{T} + \log A$$

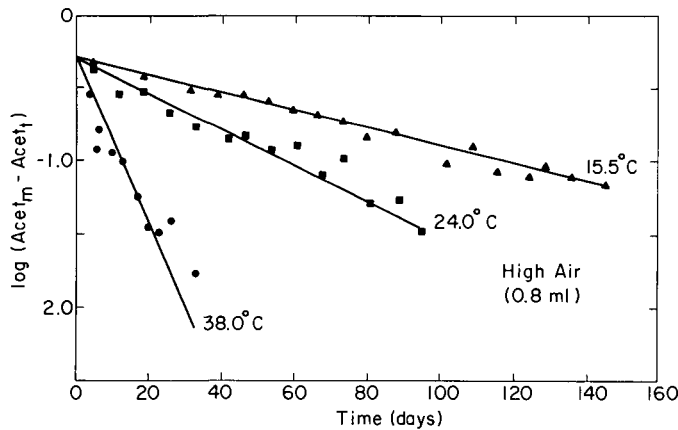


Fig. 4. Plot of  $\log (\text{Acet}_m - \text{Acet}_t)$  vs. time for three temperatures at an air content of 0.8 ml/12-oz package.

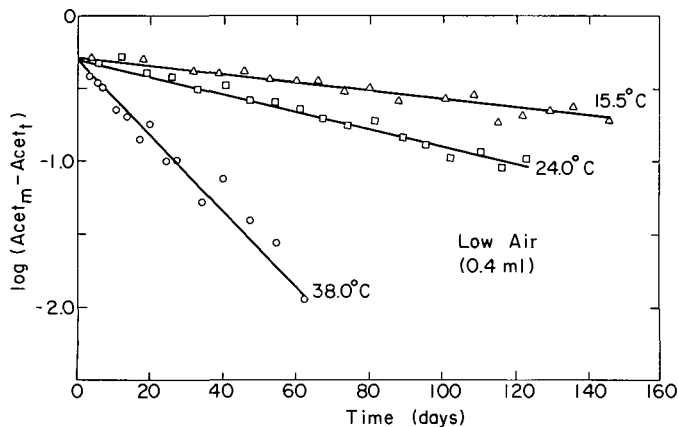


Fig. 5. Plot of  $\log (\text{Acet}_m - \text{Acet}_t)$  vs. time for three temperatures at an air content of 0.4 ml/12-oz package.

where a plot of  $\log k$  vs.  $1/T$  will produce a straight line of slope  $= -E_a/2.303R$  and intercept  $\log A$ . Figure 6 shows the Arrhenius plot for both air contents. Straight lines were obtained in both cases, and the slopes did not differ appreciably.

Substituting the mean slope and calculated intercepts into the Arrhenius equation produces the following equations:

$$\log k = \frac{-3523}{T} + 10.37 \text{ for } 0.8 \text{ ml air}$$

$$\log k = \frac{-3523}{T} + 10.06 \text{ for } 0.4 \text{ ml air}$$

TABLE I  
Critical Values for Beer Stored with Varied Air Content at Various Temperatures

Temperature °C	Air ml	n	Slope $\times 10^3$	$k \times 10^3$	r	$t_{1/2}$
38.0	0.8	11	-43.2	99.7	-0.954	6.95
38.0	0.4	15	-24.2	55.7	-0.980	12.5
24.0	0.8	15	-12.2	28.2	-0.965	24.6
24.0	0.4	19	-6.15	14.2	-0.987	48.8
15.5	0.8	19	-6.18	14.2	-0.986	48.8
15.5	0.4	19	-2.99	6.89	-0.964	101

TABLE II  
Comparison of Rate Constants

Temperature °C	Air ml	Rate Constants ( $\text{days}^{-1}$ ) $\times 10^3$	
		Guggenheim approximation	Acetaldehyde assumption
38.0	0.8	96.5	99.7
38.0	0.4	52.5	55.7
24.0	0.8	25.1	28.2
24.0	0.4	14.2	14.2
15.5	0.8	14.4	14.2
15.5	0.4	4.61	6.89

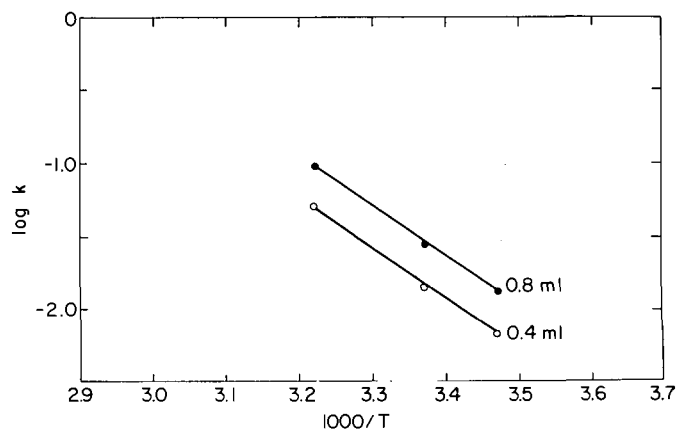


Fig. 6. Arrhenius plots for each air content.

Since other parameters which could affect  $E_a$  and  $A$ , such as antioxidant concentration and type, are constant for the beer under investigation,  $\log A$  becomes a function of the air content, and a general equation of the following form could be developed:

$$\log k = \frac{-3523}{T} + f(\text{air})$$

More observations are necessary to find a reliable  $f(\text{air})$ , and a study incorporating several air levels is under current investigation. Once  $f(\text{air})$  is determined for this particular beer, a rate constant and half-life can be calculated for any temperature and air content within their normal ranges.

### SUMMARY

The formation of acetaldehyde during the staling of lager beer is a complex reaction and appears to follow first-order kinetics. Holding other parameters constant, the rate of acetaldehyde formation seems to be dependent upon air content and temperature. The amount of acetaldehyde formed seems to be influenced by an unknown limiting reactant whose concentration probably varies across beer brands, as well as beer types. Using the PTPA method of Hoff and Herwig (9), it was found in all six cases that at the same time the acetaldehyde concentration became significantly different from that found in beer stored at 0°C, a triangular taste panel also found a significant difference at a risk of 0.05 or less. Regression analysis showed a linear relation between acetaldehyde concentration (PTPA) and organoleptic quantitation of stale flavor.<sup>2</sup> These observations, and the evidence supporting

first-order kinetics presented here, indicate that acetaldehyde could be of value as an index to staling. These theories will be expounded upon by investigating more air levels and by investigating the concentration effects of antioxidants on the rate of acetaldehyde formation.

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