

The Chemical Destruction of Sucrose, Fructose, and Glucose in Hot Alkaline Process Juices and Liquors

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Introduction

Most recently, the destruction of sucrose in hot alkaline synthetic process juices has been investigated by Pieck (5)² and Carruthers (1).

The measurement technique pursued by these investigators involved the separate measurement of the rate of formation of invert in a hot alkaline buffered solution containing sucrose and the rate of invert destruction in a buffered solution under similar conditions of temperature and pH. In both cases pure sucrose and invert solutions in conjunction with appropriate buffers were used. Having obtained the formation rate of invert from sucrose and the independent rate of destruction of invert, it was possible to determine the amount of sucrose destroyed at any given process condition. All reactions were found to be of the first order with respect to invert formation and invert destruction. Carruthers (1) intimated the existence of steady state with respect to the transient reaction intermediate invert. Pieck (5) enlarged on the steady state invert concept by measuring invert concentrations under various pH and temperature conditions.

It is the intention of this paper to utilize the kinetic concept of steady state. By doing so, it is possible to solve for the first order reaction rates describing the destruction of sucrose, glucose and fructose, and the concentrations of glucose and fructose within the steady state invert level.

Theory

Steady state as opposed to dynamic state can be explained in a graphic form. Figure 1 denotes the concentration of sucrose (A), invert (B), intermediates (C) and terminal acidic end products (D). These concentrations are plotted with respect to time. In this model, sucrose concentration is approximately equivalent to the other reactants. Reaction rates K_A , K_B and K_C are all high in numerical magnitude. This set of conditions precludes the existence of steady state. Concentrations of all reactants involved in the irreversible reaction are subject to

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² Numbers in parentheses refer to literature cited.

constant change. Fortunately, dynamic state does not exist in hot alkaline process juices and liquors. Any measurement of reaction rates in a dynamic state reaction is extremely difficult.

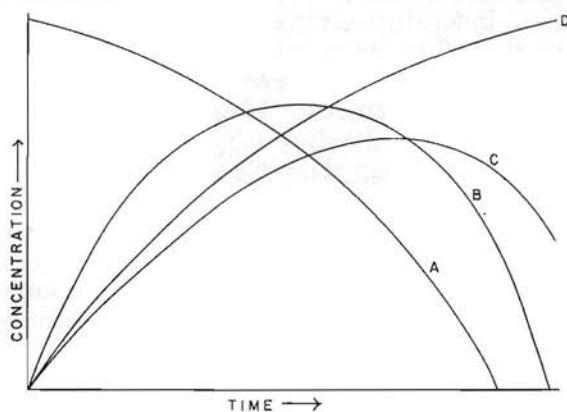
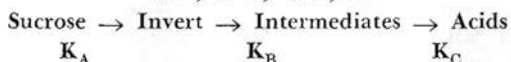


Figure 1.—Dynamic state sucrose destruction.



The graphic model, Figure 2, simulates steady state conditions existent in actual hot alkaline process liquors and juices. In this case the concentration of sucrose exceeds that of invert

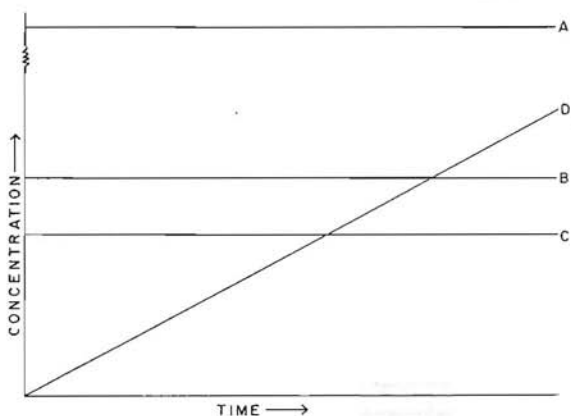
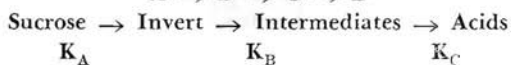


Figure 2.—Steady state sucrose destruction.



by a factor of 300. The first order reaction rate describing the destruction of invert exceeds the reaction rate of sucrose by a factor of 1000. Thus, all products of sucrose destruction with the exception of the acidic end products are in steady state with respect to their individual concentrations in solution. In time, usually more than five hours, a slight deviation in the steady state invert concentration may be noted due to a small decrease in the primary reactant sucrose. This may be predicted in accordance with equations developed by Giddings (3).

The steady state kinetic principle may be defined as follows:

In any hot alkaline process liquor or juice maintained at constant pH and temperature, there exists a steady state glucose and fructose concentration. Under steady state conditions, the rate of formation of glucose and fructose from sucrose equals the rate of glucose and fructose degradation in solution. Under these conditions the concentration of both glucose and fructose remains constant.

Procedure and Equipment

A graphic example of a typical process juice run is shown in Figure 3. Upon establishing steady state invert concentration, a weighed dry increment of pure fructose is added to the reaction mixture. Two or three minutes are allowed for complete mixing of the fructose in the reactor, before a small sample is withdrawn and cooled immediately in an ice bath. The time of withdrawal is noted. The fructose concentration in excess of the steady state invert level is determined with triphenyl-tetrazolium chloride reagent. At given time intervals, after the initial sampling, the fructose concentration is determined. Usually four to five separate fructose determinations are required. In approximately two hours (time for reaction is dependent on solution tempera-

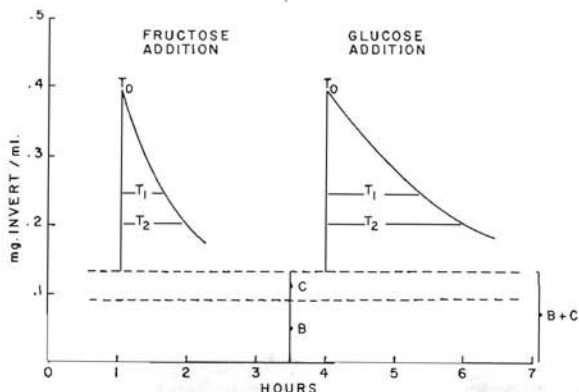
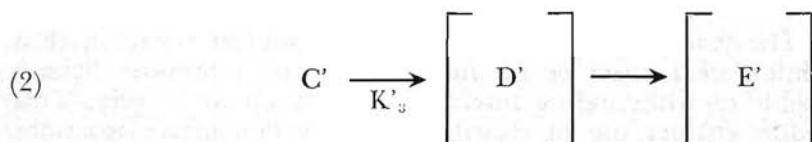
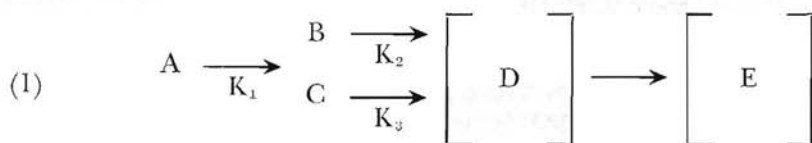


Figure 3.—Steady state model.

ture and solution pH), essentially all fructose will be degraded and steady state conditions will be restored. The same procedure is duplicated with the addition of a weighed glucose increment to the reaction solution.

During the course of the reaction the solution pH must be maintained at some control value. Runs conducted on thin juice and high brix liquors have displayed typical pH decrease characteristics. The pH of the reaction is maintained with a few potassium hydroxide pellets mixed in a small volume of juice from the reaction vessel. Small additions of this solution throughout the run effectively maintain a constant pH.

Reaction system—(1) shows the accepted pathway for sucrose destruction under hot alkaline conditions at steady state.



Reaction system—(2) shows the addition of an increment of fructose to the steady state system (1).

A = Sucrose	D = Intermediates	K_1 = Sucrose Reaction Rate
B = Glucose	E = Acidic end Product	K_2 = Glucose Reaction Rate
C = Fructose		K_3 = Fructose Reaction Rate

As indicated in Figure 3, any deviation from steady state invert concentration is due to the dynamic degradation of the added fructose. Calculation of K_1 , K_2 , K_3 in conjunction with concentrations of (C) and (B) within the steady state, are performed in the following manner.

1. Solve first order reaction rate constants K_2 and K_3 for B and C (4).

$$K_2 = \frac{2.3}{T} \cdot \log \frac{(B)}{(B - X)}$$

$$K_3 = \frac{2.3}{T} \cdot \log \frac{(C)}{(C - X)}$$

X = the amount of B or C left after time T.

2. Determine the concentration of (B) and (C) contained within the steady state invert level.

$$(B) = \frac{K_3}{K_2 + K_3} \cdot (B) + (C)$$

$$(C) = \frac{K_2}{K_2 + K_3} \cdot (B) + (C)$$

When glucose and fructose are produced in equimolar amounts, as from sucrose, their concentration within the steady state concentration (B) + (C) is indirectly proportional to the individual rate constants involved.

3. Solve for reaction rate constant K_1 describing destruction of (A) in solution.

$$K_1 (A) = K_2 \cdot (B) \cdot f + K_3 \cdot (C) \cdot f$$

$$K_1 = \frac{K_2 \cdot (B) \cdot f + K_3 \cdot (C) \cdot f}{(A)}$$

f = factor converting B and C to A equivalents.

4. Solve for percent sucrose destroyed in time (T)

$$\% = \frac{K_1 \cdot (A) \cdot T}{(A)} \cdot 100$$

The reaction vessel designed for this project consisted of a stainless steel vessel of 1.5 liter capacity with pressure fittings capable of withstanding internal pressures up to 75 psig. This feature enables the investigator to study destructive reactions at temperatures far above those obtainable at atmospheric pressure. The reaction vessel was fitted with an internal stirrer, pressure pH electrodes, electric temperature control, pressure equalized burret for reagent addition, sample outlets, and standard temperature and pressure gauges.

Results

The concept of steady state invert concentration was investigated using first carbonation clarifier juice. Figure 4 demonstrates a logarithmic increase in steady state invert concentration as the juice temperature decreases. The function is linear, which enables extrapolation of invert concentrations to include higher or lower temperature ranges.

Figure 5 indicates the variation of the specific reaction constants K_2 and K_3 of glucose and fructose at different process temperatures. A temperature range of 70°C to 90°C was used as this range amply covers temperatures maintained in the first carbonation clarifier. The linear function found for both glucose and fructose is in accordance with the Arrhenius equation which describes the influence of temperature on reaction velocity (2).

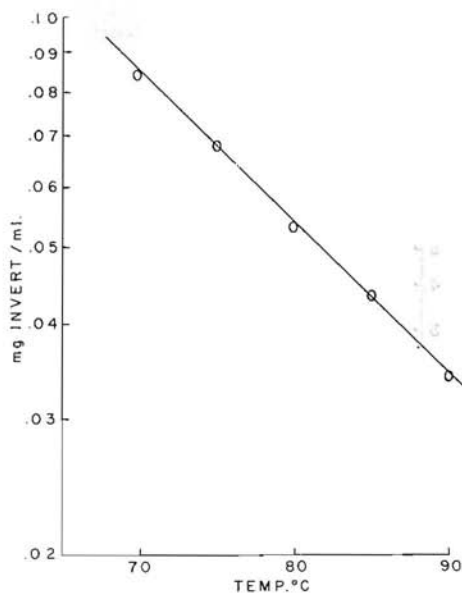


Figure 4.—Clarifier steady state invert concentration vs. temperature at a constant pH of 9.70 measured at 20°C.

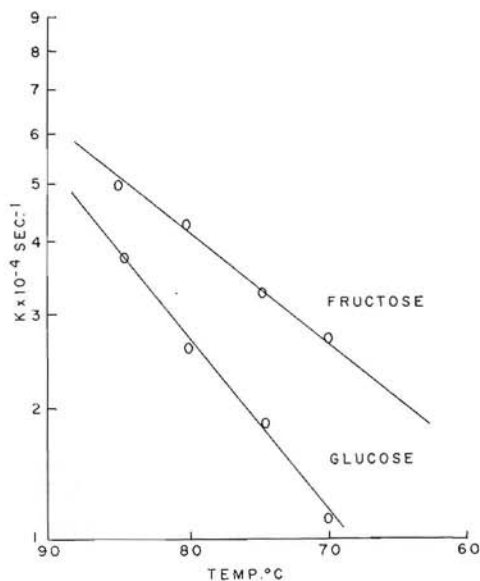


Figure 5.—Reaction rates vs. temperature at a constant pH of 9.70 measured at 20°C.

The difference in reaction constants between glucose and fructose indicates that only 36.5% of any steady state invert concentration

at 80°C and 9.70 pH will consist of fructose. Referring to Figure 4, it is noted that the steady state invert concentration at 80°C is 0.055 mg invert/ml solution. Thus within this level 0.020 mg/ml is fructose and the remaining 0.035 mg/ml is glucose.

Figure 6 shows the Arrhenius temperature vs. reaction rate relationships. The reaction rate of sucrose is not greatly affected by increases in temperature at a constant pH of 9.70.

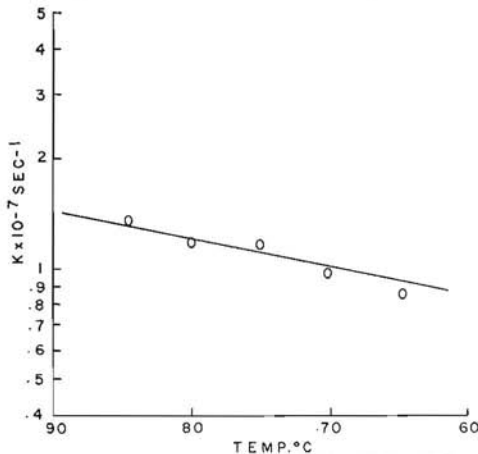


Figure 6.—Sucrose reaction rate vs. temperature at a constant pH of 9.70 measured at 20°C.

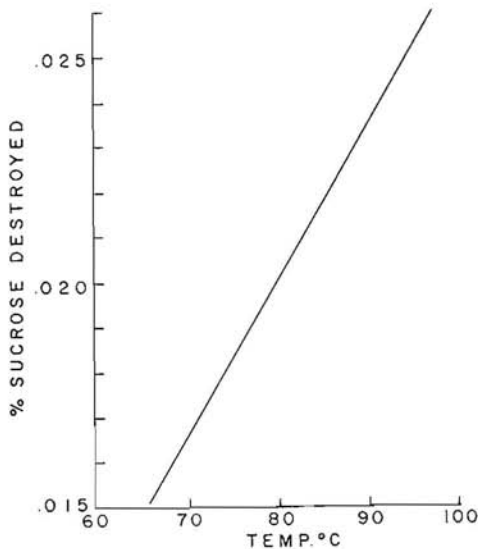


Figure 7.—Clarifier sucrose destruction vs. temperature at a constant pH of 9.70 measured at 20°C. Clarifier retention time is constant at 30 minutes.

Figure 7 indicates the actual percent loss of sucrose, which would be expected, in a clarifier after 30 minutes juice retention time at a pH of 9.70. This pH corresponds to an alkalinity of .070. It is evident that sucrose destruction in a clarifier approximates only .022% of the sucrose introduced. This loss may be considered negligible.

Figure 8 shows the graphic interpretation of sucrose destruction in the high green storage tank under various conditions. Data were arrived at by application of the steady state method at the four different pH levels indicated. This interpretation indicates that if the recirculation load is high, the temperature high, storage long, and high green pH low, significant losses of sucrose due to destruction may occur. It should be pointed out that any loss of sucrose in the process contributes nonsugar breakdown products which in turn are of a melassigenic nature.

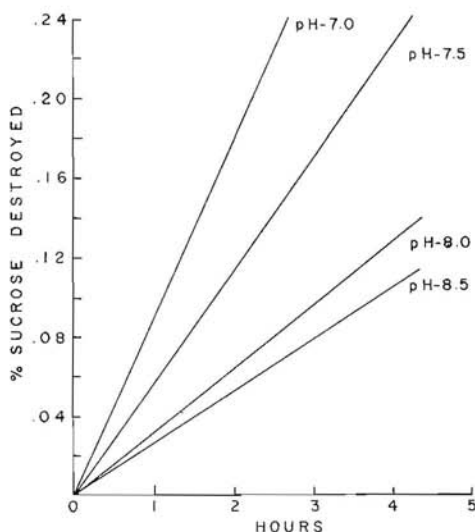


Figure 8.—High green sucrose destruction vs. time at a constant temperature of 100°C. All pH measurements were made at 20°C.

Summary

A new kinetic method has been presented which is dependent on the steady state kinetic concept. The equations developed in this paper enable an investigator to obtain the following information.

1. The steady state invert concentration of any hot alkaline process liquor or juice.
2. The concentration of glucose and fructose contained within the steady state invert level.
3. The first order reaction rate constants for sucrose, glucose and fructose.
4. The percent sucrose destroyed per unit time in any hot alkaline process juice or liquor.

Acknowledgment

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