

Simulation and Computer Modelling of Carbonate Concentration in Brewery Effluent

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Abstract

The development of a mathematical model to predict the concentration of carbonates in effluent discharged from a brewery industry is the aim of this paper. This was achieved by obtaining effluent data for several years and using the method of least squares to develop the model. A mean deviation of 9% was observed by comparing the experimental data with the simulated results. The constituent parameter with the greatest influence on the simulated model was found to be sodium ion (Na^+) with a coefficient of 0.87642 while that with the least effect was the temperature with a coefficient of 0.0514255. In addition, a control model was developed to monitor the conversions of the effluent constituents in three Continuous Stirred Tank Reactors (CSTRs), some deviation was observed between the set-point values and the empirical values.

Keywords

Effluent, BOD, pH, brewery, ions, carbonate, model, simulation

Introduction

Recently, much attention has been focused on the development of accurate equations of state for the prediction of several process parameters. Much effort has also been applied to the development of several equilibrium calculation algorithms for handling some numerical

complexities that are inherent in the modeling of waste systems. Computing power, data acquisition, simulation, optimization and information systems have greatly improved effluent management over the recent years. To maintain set discharge standards, to the environment, it is imperative to adopt the most efficient effluent monitoring and management system available. In general, the optimization does not represent a radical change in operating procedures to maintain a safe discharge standard. Effluent monitoring systems provide accurate cause – and – effect relationships of a process. Obtained set point data are used by engineers as analytical tools to understand and improve the process (Luyben, 1995; Richardson and Peacock, 1994; Meyer, 1992a,b,c; Austin, 1984).

In Nigeria, the last two decades have marked the emergence of several indigenous and foreign breweries. The high demand for brewery products, as well as the technological advancement in this regards, have further accelerated the growth of this industries. In Nigeria, there are nineteen breweries, and the waste generated is one of the major sources of industrial waste hazards. Improper handling and disposal could easily constitute a problem to both the people and the environment. The solid waste could be a source and reservoir to epidemic disease such as cholera and typhoid fever. The liquid effluent, though less noticeable as a waste, constitutes more hazard than the easily noticeable solid waste. The liquid effluent, on percolation into shallow wells could be a direct source of contamination to portable water. When this reached into streams, the danger to public health is as a result of the consumption of polluted water by the unsuspecting public, the aquatic as well as the land animals. Polluted water could lead to the migration of fishes from streams and rivers or outright death of the fishes. The surviving ones may become sick and unpalatable, the result of which may have an economic impact on the surrounding communities. Even when aquatic life survives in the polluted stream, it is not a proof of pollution free environment as some aquatic animals such as shell-fish have been noticed to survive and even thrive in polluted waters. Some chemical constituents of brewery waste (e.g. Chromium) could be accumulated by plants and from there, enter the food chain and be consumed by humans, this could enhance the development of some terminal disease such as cancer (Eckenfelder, 1989; Nikoladze et-al, 1989; Welson and Wenetow, 1982; Suess, 1982; Kriton, 1980).

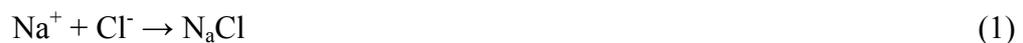
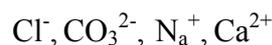
For brewery effluent, the prevailing pH value is the resultant of the disassociation of organic and inorganic compounds and their subsequent parameters are in principle targeted at measuring characteristics that could evaluate the extent or possibility of disassociation of

organic or inorganic compounds and their subsequent hydrolysis. In other words measured but are not additive functions. Effluents from breweries can be characterized based on the relative oxygen demand, expressed as biochemical oxygen demand (BOD) or chemical oxygen demand COD, suspended solids (SS), pH, Temperature and flow parameters (Odigure and Adeniyi, 2002; Luyben, 1995; Imre 1984, Suess 1982).

The aim of this paper is to develop a model equation to predict the concentration of carbonate ions (CO_3^{2-}) in brewery effluent, this would be achieved by utilizing, computer simulation techniques. In addition the paper seeks to monitor and control the concentration of CO_3^{2-} in 3 CSTRs connected in series.

Conceptualization and Model Development

In the effluent stream, the components of consideration are



The liquid effluent from the brewery is charged into a series of 3 CSTR, where product B is produced and reaction A is consumed according to the first order reaction, occurring in the fluid. The feed back controller used for this system, is a Proportional and Integral controller (PI). The controller looks at the product concentration leaving the third tank (C_{A3}) and makes adjustments in the inlet concentration to the first reaction C_{A0} in order to keep C_{A3} near its desired set point value C_{A3}^{set} (Levenspiel, 1997; Fogler, 1997; Luyben, 1995; Richardson and Peacock, 1994; Smith, 1981).

The variable C_{AD} is the disturbance concentration, and the variable C_{AM} is the manipulated concentration that is changed by the controller. From the system, it can be postulated that:

$$C_{A0} = C_{AM} + C_{AD} \quad (3)$$

The controller has proportional and integral action; it changes C_{AM} , based on the magnitude of the error (the difference between the set point concentration and C_{A3}) and the integral of this error.

$$C_{AM} = 0.8 + K_c(E + 1/\tau_i \int E(t) dt) \quad (4)$$

where:

$$E = CA_3^{\text{set}} - CA_3 \quad (5)$$

K_c = Feed back Controller gain

T_f = Feed back Controller space- time constant (minutes).

The 0.8 term is the bias value of the controller, that is, the value of C_{AM} at time equal zero. Numerical values of $K_c = 30$, $T_f = 5$ minutes are used (Perry and Green, 1997; Luyben, 1995; Himmelblau, 1987; Imre, 1986).

The industrial brewery effluent, has the following measured parameters; potency of hydrogen (pH), temperature (TEMP), total dissolved solid (TDS), biochemical oxygen demand (BOD), carbonate ions (CO_3^{2-}), calcium ions (Ca^{2+}), sodium ions (Na^+) and chloride ions (Cl^-).

Let $\text{pH} = P$, $\text{Temp} = T_1$, $\text{TDS} = T_2$, $\text{BOD} = B$, $\text{CO}_3^{2-} = C$, $\text{Ca} = C_1$, $\text{Na} = N$, $\text{Cl} = C_2$

To develop a model for the concentration of CO_3^{2-} ion as a function of the other parameters in the effluent we have:

$$C = f(P, T_1, T_2, B, C_1, N, C_2) = f(aP, bT_1, cT_2, dB, eC_1, fN, gC_2) \quad (6)$$

where C is the dependent variable, a, b, c, d, e, f and g are the coefficients, which should be determined, while $P, T_1, T_2, B, C_1, N, C_2$ are the independent variables of the equation.

To develop the model the linear regression techniques (least square method) was applied (Stroud, 1995a,b; Carnahan *et-al*, 1969). Let Z represent the square of the error, between the observed value and the predicted value. Mathematically:

$$Z = \text{Observed value} - (aP + bT_1 + cT_2 + dB + eC_1 + fN + gC_2)^2 \quad (7)$$

For n experimental values of $P, T_1, T_2, B, C_1, N, C_2$ we have:

$$nZ = \sum (V_i - (aP_i + bT_{1i} + cT_{2i} + dB_i + eC_{1i} + fN_i + gC_{2i}))^2 \quad (8)$$

We could minimize the error of this regression, by finding the derivative of nZ with respect to the constant a, b, c, d, e, f, g and equating to zero.

$$\begin{aligned} \partial(nz)/\partial a &= -2\sum P_i(V_i - (aP_i + bT_{1i} + cT_{2i} + dB_i + eC_{1i} + fN_i + gC_{2i})) = 0 \\ \partial(nz)/\partial b &= -2\sum T_{1i}(V_i - (aP_i + bT_{1i} + cT_{2i} + dB_i + eC_{1i} + fN_i + gC_{2i})) = 0 \\ \partial(nz)/\partial c &= -2\sum T_{2i}(V_i - (aP_i + bT_{1i} + cT_{2i} + dB_i + eC_{1i} + fN_i + gC_{2i})) = 0 \\ \partial(nz)/\partial d &= -2\sum B_i(V_i - (aP_i + bT_{1i} + cT_{2i} + dB_i + eC_{1i} + fN_i + gC_{2i})) = 0 \\ \partial(nz)/\partial e &= -2\sum C_{1i}(V_i - (aP_i + bT_{1i} + cT_{2i} + dB_i + eC_{1i} + fN_i + gC_{2i})) = 0 \\ \partial(nz)/\partial f &= -2\sum N_i(V_i - (aP_i + bT_{1i} + cT_{2i} + dB_i + eC_{1i} + fN_i + gC_{2i})) = 0 \\ \partial(nz)/\partial g &= -2\sum C_{2i}(V_i - (aP_i + bT_{1i} + cT_{2i} + dB_i + eC_{1i} + fN_i + gC_{2i})) = 0 \end{aligned} \quad (9)$$

Dividing both sides by -2 and rearranging, we obtain:

$$\begin{aligned}\sum P_i V_i &= a \sum p_i^2 + b \sum T_i P_i + c \sum T_{2i} P_i + d \sum B_i P_i + e \sum C_i P_i + f \sum N_i P_i + g \sum C_{2i} P_i \\ \sum T_{1i} V_i &= a \sum p_i T_i + b \sum T_{ii}^2 + c \sum T_{2i} T_{1i} + d \sum B_i T_{1i} + e \sum C_{1i} T_{1i} + f \sum N_i T_{1i} + g \sum C_{2i} T_{1i} \\ \sum T_{2i} V_i &= a \sum p_i T_{2i} + b \sum T_{ii} T_{2i} + c \sum T_{2i}^2 + d \sum B_i T_{2i} + e \sum C_{1i} T_{2i} + f \sum N_i T_{2i} + g \sum C_{2i} T_{2i} \\ \sum B_i V_i &= a \sum P_i B_i + b \sum T_{1i} B_i + c \sum T_{2i} B_i + d \sum B_i^2 + e \sum C_{1i} B_i + f \sum N_i B_i + g \sum C_{2i} B_i \\ \sum C_{1i} V_i &= a \sum P_i C_{1i} + b \sum T_{1i} C_{1i} + c \sum T_{2i} C_{1i} + d \sum B_i C_{1i} + e \sum C_{1i}^2 + f \sum N_i C_{1i} + g \sum C_{2i} C_{1i} \\ \sum N_i V_i &= a \sum P_i N_i + b \sum T_{1i} N_i + c \sum T_{2i} N_i + d \sum B_i N_i + e \sum C_{1i} N_i + f \sum N_i^2 + g \sum C_{2i} N_i \\ \sum C_{2i} V_i &= a \sum P_i C_{2i} + b \sum T_{1i} C_{2i} + c \sum T_{2i} C_{2i} + d \sum B_i C_{2i} + e \sum C_{1i} C_{2i} + f \sum N_i C_{2i} + g \sum C_{2i}^2\end{aligned}\quad (10)$$

The following values were obtained from mathematical calculation (Stroud, 1995a,b; Carnahan *et-al*, 1969):

$$\begin{aligned}\sum P_i^2 &= 12276.64 \cdot 10^{-8}; \quad \sum P_i T_i = 2845.59 \cdot 10^{-4}; \quad \sum T_{2i} P_i = 930.88 \cdot 10^{-4}; \\ \sum B_i P_i &= 0.254900000; \quad \sum C_{1i} P_i = 928.8557 \cdot 10^{-4}; \quad \sum N_i P_i = 841.99000 \cdot 10^{-4}; \\ \sum C_{2i} P_i &= 174.6000 \cdot 10^{-4}; \quad \sum P_i T_{1i} = 2845.59 \cdot 10^{-4}; \quad \sum T_{ii}^2 = 94740.84 \cdot 10^{-4}; \\ \sum T_{2i} T_{1i} &= 2377.36 \cdot 10^{-4}; \quad \sum B_i T_i = 0.708970000000; \quad \sum C_{1i} T_{1i} = 2641.97 \cdot 10^{-4}; \\ \sum N_i T_i &= 2340.830 \cdot 10^{-4}; \quad \sum C_{2i} T_{1i} = 441.74 \cdot 10^{-4}; \quad \sum C_{1i} T_2 = 845.600000 \cdot 10^{-4}; \\ \sum N_i T_{2i} &= 760.7 \cdot 10^{-4}; \quad \sum C_{2i} T_{2i} = 157.500000 \cdot 10^{-4}; \quad \sum C_{1i} B_i = 0.23145000; \\ \sum N_i B_i &= 0.20413000000; \quad \sum C_{2i} B_i = 39.34 \cdot 10^{-3}; \quad \sum N_i C_{1i} = 764.2002 \cdot 10^{-4}; \\ \sum C_{2i} C_{1i} &= 156.458 \cdot 10^{-4}; \quad \sum C_{2i} N_i = 142.9500 \cdot 10^{-4}; \quad \sum T_i^2 = 10179.2 \cdot 10^{-8}; \\ \sum T_{1i}^2 &= 94740.84 \cdot 10^{-4}; \quad \sum B_i^2 = 762.864 \cdot 10^{-6}; \quad \sum C_i^2 = 10124.38 \cdot 10^{-8}; \\ \sum N_i^2 &= 7144.814 \cdot 10^{-8}; \quad \sum C_{2i}^2 = 351.7600 \cdot 10^{-8}; \quad \sum P_i V_i = 924.2800 \cdot 10^{-4}; \\ \sum T_{1i} V_i &= 2568.1 \cdot 10^{-4}; \quad \sum T_{2i} V_i = 839.400 \cdot 10^{-4}; \quad \sum B_i V_i = 0.2297000; \\ \sum C_{1i} V_i &= 838.86 \cdot 10^{-4}; \quad \sum N_i V_i = 763.3 \cdot 10^{-4}; \quad \sum C_{2i} V_i = 156.33 \cdot 10^{-4}.\end{aligned}\quad (11)$$

Substituting the values obtained into the equation, we have:

$$\begin{aligned}a(12276.64 \cdot 10^{-8}) + b(2845.59 \cdot 10^{-4}) + c(930.88 \cdot 10^{-4}) + d(0.2549) \\ + e(928.86 \cdot 10^{-4}) + f(841.99 \cdot 10^{-4}) + g(174.60 \cdot 10^{-4}) = 924.28 \cdot 10^{-4} \\ a(2845.59 \cdot 10^{-8}) + b(94740.84 \cdot 10^{-8}) + c(2377.74 \cdot 10^{-4}) + d(0.709) \\ + e(2641.97 \cdot 10^{-4}) + f(2340.83 \cdot 10^{-4}) + g(441.74 \cdot 10^{-4}) = 2568.1 \cdot 10^{-4} \\ a(930.88 \cdot 10^{-4}) + b(2377.36 \cdot 10^{-4}) + c(10179.2 \cdot 10^{-8}) + d(0.2326) \\ + e(845.6 \cdot 10^{-4}) + f(760 \cdot 10^{-4}) + g(157.5 \cdot 10^{-4}) = 839.4 \cdot 10^{-4} \\ a(0.2549) + b(0.709) + c(0.2326) + d(762.864 \cdot 10^{-6}) \\ + e(0.23145) + f(0.20413) + g(39.34 \cdot 10^{-3}) = 0.2297\end{aligned}\quad (12)$$

$$\begin{aligned}
& a(928.86 \cdot 10^{-4}) + b(2621.97 \cdot 10^{-4}) + c(845.6 \cdot 10^{-4}) + d(0.23145) \\
& + e(10124.38 \cdot 10^{-8}) + f(764.202 \cdot 10^{-4}) + g(156.458 \cdot 10^{-4}) = 838.86 \cdot 10^{-4} \\
& a(841.99 \cdot 10^{-4}) + b(2340.83 \cdot 10^{-4}) + c(760.7 \cdot 10^{-4}) + d(0.20413) \\
& + e(764.202 \cdot 10^{-4}) + f(7144.814 \cdot 10^{-8}) + g(142.95 \cdot 10^{-4}) = 763.3 \cdot 10^{-4} \\
& a(174.60 \cdot 10^{-4}) + b(441.74 \cdot 10^{-4}) + c(157.5 \cdot 10^{-4}) + d(39.34 \cdot 10^{-3}) \\
& + e(156.458 \cdot 10^{-4}) + f(142.95 \cdot 10^{-4}) + g(351.76 \cdot 10^{-8}) = 156.33 \cdot 10^{-4}
\end{aligned}$$

A computer program, coded in C++ was developed to solve the 7×7 matrices and the resulting model is:

$$\begin{aligned}
C = & 0.163488P + 0.0514255T_1 + 0.166722T_2 + 0.0596487B \\
& + 0.182077C_1 + 0.87642N + 0.821217C_2
\end{aligned} \tag{13}$$

Results and Discussion

The effluent from the brewery was discharged at different points such as the tank cellars, bottling hall, brew house and filter-room. The effluent analyzed in this study was however obtained from the combined effluent discharge collection point. The analytical results are presented in Tables 1, 2 and 3.

Table 1. Analysis of effluent discharge from brewery industry (1999)

	pH	TEMP (°C)	TDS (kg/dm ³)	BOD (kg/dm ³)	CO ₃ ²⁻ (kg/dm ³)	Ca ²⁺ (kg/dm ³)	Na ⁺ (kg/dm ³)	Cl ⁻ (kg/dm ³)
Jan	9.60	27.60	8.211	2.35·10 ⁻³	13.8421	8.480	8.106	1.477
Feb	9.00	28.20	8.120	2.30·10 ⁻³	13.6687	8.146	8.125	1.523
Mar	9.50	26.50	8.000	2.35·10 ⁻³	14.9868	8.742	8.636	1.612
Apr	9.20	26.00	9.512	2.40·10 ⁻³	14.8273	8.102	8.064	1.585
May	9.30	26.00	8.167	2.30·10 ⁻³	13.9182	8.261	8.093	1.532
Jun	9.40	24.50	8.000	2.00·10 ⁻³	13.7231	7.992	7.602	1.632
Jul	9.40	26.00	8.261	2.30·10 ⁻³	13.5698	8.266	8.611	1.723
Aug	9.10	26.50	8.082	2.35·10 ⁻³	14.8955	8.361	8.626	1.439
Sep	9.00	24.00	8.664	2.44·10 ⁻³	14.0688	8.073	8.0423	1.321
Oct	9.00	24.00	8.164	2.40·10 ⁻³	13.5890	8.042	7.110	1.732
Nov	9.20	26.00	9.026	2.40·10 ⁻³	13.9936	8.364	8.210	1.521
Dec	9.10	24.50	8.164	2.33·10 ⁻³	13.9814	8.772	8.116	1.621

The effluent was analyzed based on several parameters of pH, temperature and ionic content (CO_3^{2-} , TDS, Ca, Na, Cl, BOD). From the empirical results presented on Tables 1 to 3, it was observed that the determinant ion is CO_3^{2-} , because of its high concentration and its high acidity.

Table 2. Analysis of effluent discharge from brewery industry (2000)

	pH	TEMP (°C)	TDS (kg/dm ³)	BOD (kg/dm ³)	CO_3^{2-} (kg/dm ³)	Ca^{2+} (kg/dm ³)	Na^+ (kg/dm ³)	Cl^- (kg/dm ³)
Jan	9.40	26.50	8.575	$2.37 \cdot 10^{-3}$	13.0842	8.183	8.105	1.532
Feb	9.10	26.00	8.324	$2.33 \cdot 10^{-3}$	13.9271	8.176	8.173	1.561
Mar	9.70	27.00	8.175	$2.40 \cdot 10^{-3}$	13.9866	8.233	8.621	1.663
Apr	9.30	24.00	8.025	$2.30 \cdot 10^{-3}$	13.1182	8.136	7.189	1.419
May	9.10	25.00	8.000	$2.36 \cdot 10^{-3}$	13.3970	8.491	7.326	1.567
Jun	9.10	28.00	8.000	$2.37 \cdot 10^{-3}$	13.774	8.247	7.961	1.668
Jul	9.20	26.30	8.232	$2.40 \cdot 10^{-3}$	13.0736	8.566	6.119	1.589
Aug	9.40	24.50	8.727	$2.20 \cdot 10^{-3}$	13.0180	8.373	6.327	1.772
Sep	9.00	23.00	8.632	$2.25 \cdot 10^{-3}$	13.0000	8.392	6.331	1.699
Oct	9.30	26.00	8.442	$2.40 \cdot 10^{-3}$	13.2941	8.626	6.861	1.427
Nov	9.10	28.00	8.665	$2.35 \cdot 10^{-3}$	13.5084	8.286	7.544	1.489
Dec	9.10	24.00	8.361	$2.33 \cdot 10^{-3}$	13.5126	8.725	7.612	1.551

The data presented are combined effluent discharge data for three different years (1999, 2000, and 2001), in all cases the carbonate ion was observed to dominate in concentration. Therefore part of the aims of this work is to develop appropriate techniques to conveniently reduce the concentration of this ion. The process chosen for this task was characterized by two neutralization reactions occurring simultaneously in the reaction vessel as given by Equation 1 and 2. (Meyer, 1992a,b,c; Luyben, 1990, Austin, 1984).

The principal reactions of consideration are Equation 1, where the model equation is represented as:



where A is Calcium ion; B is Carbonate ion; C is Calcium carbonate.

The limiting reactant is B and its conversion is of interest in this research work. Appropriate software coded in Visual Basic was developed to monitor the concentration of the carbonate ions in the system, the results are presented on Tables 7, 8 and 9. From the Tables it was observed that there was a change in concentration (conversion) across the tanks in series, this change was attributed to the reaction given by Equation 1.

Table 3. Analysis of effluent discharge from brewery industry (2001)

	pH	TEMP (°C)	TDS (kg/dm ³)	BOD (kg/dm ³)	CO ₃ ²⁻ (kg/dm ³)	Ca ²⁺ (kg/dm ³)	Na ⁺ (kg/dm ³)	Cl ⁻ (kg/dm ³)
Jan	9.70	28.00	8.164	2.30·10 ⁻³	13.973	8.274	7.994	1.6114
Feb	8.90	28.30	8.180	2.30·10 ⁻³	13.083	8.354	8.074	1.6114
Mar	9.60	26.00	7.990	2.40·10 ⁻³	14.886	8.399	8.883	1.7390
Apr	9.10	24.00	9.410	2.44·10 ⁻³	12.818	7.832	6.495	1.5650
May	9.30	26.40	8.082	2.36·10 ⁻³	12.545	8.286	6.514	1.4450
Jun	9.40	24.00	7.999	1.71·10 ⁻³	14.922	8.626	9.061	1.7390
Jul	9.70	27.90	7.999	2.30·10 ⁻³	14.367	8.399	8.291	1.5890
Aug	9.00	26.40	8.263	2.35·10 ⁻³	13.262	8.399	8.291	1.6114
Sep	8.80	22.50	9.163	2.33·10 ⁻³	12.471	8.853	6.119	1.5470
Oct	9.10	24.90	8.090	2.41·10 ⁻³	12.584	8.286	6.514	1.5730
Nov	9.30	26.30	9.412	2.37·10 ⁻³	12.604	8.286	6.317	1.4320
Dec	8.90	23.10	8.131	2.35·10 ⁻³	13897	8.626	8.488	1.2920

For the first case the feed enters the first reactor with the following concentrations: C_{A2} at 10 kg/dm³, C_{A3} at 0.1 kg/dm³ while C_{AM} is at 0.8 kg/dm³ (which is the bias value of the controller at time zero, $T = 0$), the feedback controller used for this process has proportional and integral action (PI controller), it changes C_{AM} based on the magnitude of the error. The value of the set point, C_{A3}^{set} was at 0.1 kg/dm³, the controller looks at the product concentration leaving the third Tank, C_{A3} , and makes adjustments in the inlet concentration to the first reactor, C_{A0} , in order to keep C_{A3} near its set point C_{A3}^{set} . The variable C_{AD} is the disturbance concentration and the variable C_{AM} is the manipulated concentration that was changed by the controller (Equation 3).

For this particular simulation (applying Equations 3 and 4), the following values were used; K_c at 30, τ_f at 5minutes. Critical observation shows that the output concentration of the system (C_{A3}) approaches the set point concentration (C_{A3}^{set}), as shown Table 7 to 9. The difference between the set point value and C_{A3} in each case is small, this was attributed to the reactor design specification and reactor operating condition (Luyben, 1990; Himmelblau, 1987). Generally, the whole essence of the process set-up is to neutralize the concentration of the carbonate ions to values low enough, so as not to be toxic to the environment, and to a reasonable extent this was achieved.

Tables 1-3 gives the analysis of the effluent discharge from the brewery industry for three consecutive years.

The pH values for the years are slightly high, with a minimum of 9.00 for the first two years and 8.90 for the third year. On the general the pH were mostly alkaline from the discharge. The temperature was within the set limits by the Federal Environmental Protection Agency (FEPA). The limits of the other parameters were also within the acceptable limits. The facts is that all these compounds present in the effluent could be hydrolyzed by water, that is, the ions of these compounds could be exchanged with water molecules (Odigure and Adeniyi, 2002; Karapetyant and Drakin, 1981). The carbonate ions concentrations from Table 1-3 are relatively higher than the other parameters.

Comparative values for the concentration of carbonate between the empirical and simulation are presented in Tables 4 to 6.

The highest deviation for 1999 was 8.70%, for 2000 was 5.50% and 1.70% for 2001. The deviation of the simulated values from that of the empirical could be attributed to certain limitations placed during model development.

Table 4. Comparative values for empirical and simulation of CO_3^{2-} (1999)

	Empirical (kg/dm^3)	Simulated (kg/dm^3)	Deviations	%Errors
Jan	13.8421	14.2193	-0.3772	2.73
Feb	13.6687	14.1303	-0.4616	3.38
Mar	14.9868	14.6850	0.4129	2.76
Apr	14.8273	14.4144	0.4129	2.78
May	13.9182	14.0744	-0.1562	1.12
Jun	13.7231	13.5885	0.1346	0.98
Jul	13.5698	14.7508	-1.181	8.70
Aug	14.8955	14.4622	0.4333	2.91
Sep	14.0688	13.7540	0.3148	2.24
Oct	13.5890	13.1848	0.4042	2.97
Nov	13.9936	14.3135	-0.3199	2.29
Dec	13.9814	14.1535	-0.1689	1.21

That is, apart from these seven parameters considered there could be other factors, which contributed to the level of carbonates in the effluent. One is the interactions, which the effluents would have undergone during the process of flowing through the discharge path.

Table 5. Comparative values for empirical and simulation of CO_3^{2-} (2000)

	Empirical (kg/dm ³)	Simulated (kg/dm ³)	Deviations	%Errors
Jan	13.0842	12.7240	0.3602	2.75
Feb	13.9271	14.0867	-0.1596	1.15
Mar	13.9866	14.7578	-0.7712	5.50
Apr	13.1182	13.0387	0.0795	0.60
May	13.3970	13.3595	0.0375	0.30
Jun	13.7740	14.1089	-0.3349	2.40
Jul	13.0736	12.4553	0.6183	4.70
Aug	13.0180	12.7754	0.2426	1.90
Sep	13.0000	12.5641	0.4359	3.40
Oct	13.2941	13.0194	0.2747	2.10
Nov	13.5084	13.7144	-0.2060	1.50
Dec	13.5126	13.6484	-0.1358	1.00

Table 6. Comparative values for empirical and simulation of CO_3^{2-} (2001)

	Empirical (kg/dm ³)	Simulated (kg/dm ³)	Deviations	%Errors
Jan	13.973	14.2132	-0.2373	1.70
Feb	13.083	12.9527	0.1303	1.00
Mar	14.886	14.9830	-0.097	0.65
Apr	12.818	12.6945	0.1235	0.96
May	12.545	12.6300	-0.085	0.68
Jun	14.922	15.0447	-0.1227	0.82
Jul	14.367	14.4452	-0.0782	0.54
Aug	13.262	13.3709	-0.1089	0.82
Sep	12.471	12.3688	0.1022	0.82
Oct	12.584	12.6266	-0.0426	0.34
Nov	12.604	12.6633	-0.0593	0.47
Dec	13.897	14.0094	-0.1124	0.81

Consequently, pollutants present in water could seriously affect the resultant carbonate concentration. The extent of acidification or alkalization of the solution by pollutants is dependent, on not only the chemical nature of the compounds present, but also the prevailing technological conditions (Odigure and Adeniyi, 2002). From the calculated coefficients, it could be seen that the carbonate concentration is most affected by the sodium ions and least by the temperature.

Tables 7- 9 gives the time-concentration value from simulation of the months of January, March and June of the year 2001.

Table 7: Time – Concentration data from simulation (Jan. 2001)

Run	Time (min)	C _{A1} (kg/dm ³)	C _{A2} (kg/dm ³)	C _{A3} (kg/dm ³)	C _{AM} (kg/dm ³)
1	0.00	13.0830	10.0000	0.1000	0.8000
2	0.50	1.7949	7.5767	1.8086	53.3328
8	3.51	9.2574	1.9208	1.6843	48.9541
12	5.51	1.0135	2.9864	1.1401	32.2791
19	9.01	7.1980	1.2045	0.3007	13.1300
20	9.51	5.6166	2.0257	0.1556	3.2070

From Table 7 at time zero, the conversion of CO₃²⁻ was 0.8 kg/dm³ (which is the bias value of the controller), at T=0.5 minutes, the conversion was 53.33278 kg/dm³, showing that with increase in time the manipulated variable concentration decreases proportionately toward the set point. The same pattern was observable in Table 8 and 9.

Table 8: Time – Concentration data from simulation (Mar. 2001)

Run	Time (min.)	C _{A1} (kg/dm ³)	C _{A2} (kg/dm ³)	C _{A3} (kg/dm ³)	C _{AM} (kg/dm ³)
1	0.00	14.8860	10.0000	0.1000	0.8000
2	0.50	2.8012	7.8471	1.8242	54.3856
8	3.51	9.1626	2.1493	1.7621	50.7102
12	5.51	0.7137	3.1506	1.1611	32.9314
19	9.01	7.4191	1.1768	0.3364	14.0958
20	9.51	5.9060	2.0619	0.1355	0.5531

Table 9: Time – Concentration data from simulation (Jun. 2001)

Run	Time (min.)	C _{A1} (kg/dm ³)	C _{A2} (kg/dm ³)	C _{A3} (kg/dm ³)	C _{AM} (kg/dm ³)
1	0.00	14.9220	10.0000	0.1000	0.8000
2	0.50	2.8213	7.8525	1.8431	54.4067
8	3.51	9.1607	2.1539	1.7638	50.7430
12	5.51	0.7078	3.1538	1.1655	32.9445
19	9.01	7.4236	1.1762	0.3371	14.1151
20	9.51	5.9118	2.0626	0.1351	0.5648

Table 10 gives the percentage error deviation analysis of the simulated concentration for the third tank to that of the set point. This gives the deviation error analysis for the process control model. The highest deviation was 38% at the fifth run.

Table 10: Error deviation analysis for process control model

Run	C_{A3}	C_{A3}^{set}	Error Deviation	% Error Deviation
1	0.14565	0.1	0.04565	31
2	0.15564	0.1	0.05560	36
3	0.13548	0.1	0.03550	26
4	0.15852	0.1	0.05852	37
5	0.16156	0.1	0.06156	38
6	0.13508	0.1	0.03510	26
7	0.14126	0.1	0.04130	29
8	0.15357	0.1	0.05360	35

Conclusions

From the empirical model developed, the constituent parameter with greatest influence was Na^+ with a coefficient of 0.87642, while that with the least influence, was the temperature with a coefficient of 0.0514255. This study, in addition, seeks to reduce the concentration of carbonate ion to an acceptable degree, so as not to degrade the environment. To some extent, this could be said to have been achieved, since the concentration was lowered from 13.973 to 0.145648108458162 in the first case. Under ideal operating conditions, the output concentration from the system should converge at the set point (i.e. $C_{A3}=C_{A3}^{set}$). In such a case, no error is generated, but because of differences in the design specifications and process parameters, such errors are inevitable as shown in the results presented. Thus the proposed model could be used to predict the concentration of carbonate ions from brewery effluent with similar operating conditions.

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