

A KINETIC MODEL DESCRIBING ACONITIC ACID ISOMERISATION AND SUBSEQUENT DECARBOXYLATION TO ITACONIC ACID UNDER FACTORY CONDITIONS

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Abstract

The measurement of the kinetics of isomerisation of *trans* to *cis* aconitic acid and subsequent decarboxylation to itaconic acid under different regimes have been completed. These include pH_{25} (4 to 8), temperature (70 to 110°C), ionic strength (0 to 150 mM) and cations (sodium, potassium, calcium and magnesium). Temperature and pH were found to be the most important factors. A model describing isomerisation as a function of temperature and pH was developed. Comparisons between factory and laboratory experiments based on factory materials are described.

Introduction

Previous work on the influence of temperature, pH, ionic strength and ionic composition on the isomerisation of aconitic acid in laboratory studies has been reported by Walford (1998). Variables included pH (5 to 8), temperature (70 to 97°C), buffer strength (0 to 150 mM) and selected cations (sodium, potassium, calcium and magnesium). The greatest influences on the rate of isomerisation were shown to be pH and temperature. Some decarboxylation of aconitic acid to itaconic acid was noted at pH 5. As some factory processes occur at higher temperatures than those considered, further investigation was undertaken at elevated temperatures (110°C) and low pH (4). From the completed data, a model is proposed describing the isomerisation and decarboxylation of aconitic acid as a function of temperature and pH.

Experimental

High performance liquid chromatography (HPLC) analysis conditions, reagents used and treatment of kinetic data have been described previously (Walford, 1998). Reactions at 110°C were carried out in a 400 ml teflon coated, brass pressure vessel (Schäffler, 1984). This vessel consisted of a well and top plate separated by an O-ring and held together by 10 mm allen screws. Four threaded orifices were machined into the top plate into which a threaded male nut and gasket were placed. This allowed insertion of a temperature probe, removal of sample through a sampling port sealed with a GC septum and addition of a pressure relief valve (set to 150 kPa). The fourth port was blanked off for these experiments. Reaction temperature was maintained by a hotplate stirrer which was controlled by an Omron E5CW PID temperature controller connected to a Pt100 probe in the reaction vessel. A schematic diagram of the system is shown in Figure 1.

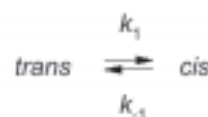
Buffer solutions were prepared at the required concentration and the pH measured and adjusted at room temperature. The

experimental procedure consisted of placing the buffer solution (298 ml) at the required concentration and pH into the pressure vessel with the temperature probe and magnetic stirrer. This was placed on the hotplate stirrer and heated until equilibrium at the desired temperature was achieved. A weighed sample of *trans* aconitic acid (15 mg) was dissolved in the buffer (2 ml) and immediately added to the solution vessel through the sampling port by means of a sampling syringe. After a period of half a minute for mixing, a 0,5 ml sample was removed, placed in an autosampler vial, crimped and immediately frozen. Samples were taken at 10 or 15 minute intervals and treated in the same manner. These samples were analysed off-line using the HPLC system.

Isomerisations at 97°C and pH 4 were carried out in phthalate buffer (10, 20, 25 and 50 mM) using the previously described equipment.

Results and Discussion

The isomerisation of *trans* to *cis* aconitic acid in solution can be described by :



where k_1 is the forward rate constant and k_{-1} the reverse rate constant. At the equilibrium of the isomerisation, the equilibrium constant K can be calculated from the ratio of the forward and reverse rate constants :

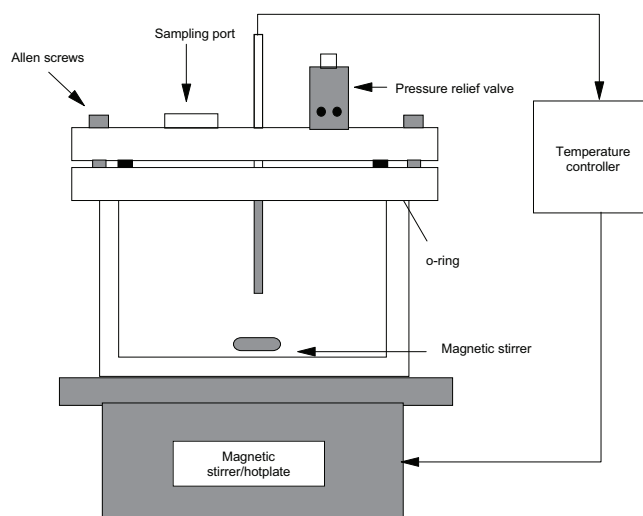


Figure 1. Schematic of reaction vessel used for determining reaction rates at temperatures greater than 100°C.

Table 1. Calculated rate constants ($s^{-1} \times 10^{-5}$) for the cis-trans isomerisation of aconitic acid at increasing temperature, pH and buffer ionic strength.

Temp °C	Buffer conc (mM)	pH4		pH5		pH6		pH7		pH8	
		k_2	k_{-1}	k_1	k_{-1}	k_1	k_{-1}	k_1	k_{-1}	k_1	k_{-1}
70	0			0.14	0.29	0.08	0.23	0.01	0.06		
	25			0.41	0.90	0.17	0.61	0.03	0.21		
	50			0.50	1.24	0.31	1.89	0.03	0.19		
	75			0.94	2.40	0.43	1.76	0.05	0.38		
	150			1.68	4.32	0.64	3.05	0.11	0.83		
80	0			0.45	1.06	0.09	0.29	0.03	0.18		
	25			0.91	2.19	0.30	1.07	0.06	0.44		
	50			1.62	3.68	0.30	1.50	0.08	0.59		
	75			2.41	5.72	0.78	3.24	0.15	1.10		
	150			3.22	7.70	1.50	6.71	0.22	1.53		
90	0			0.99	2.03	0.17	0.46	0.04	0.23		
	25			1.95	4.32	0.44	1.42	0.08	0.50		
	50			3.17	7.23	1.29	4.65	0.12	1.09		
	75			3.74	8.87	1.59	6.03	0.17	1.18		
	150			6.11	10.51	2.99	12.64	0.31	2.17		
97	0	3.69	4.68	0.83	1.95	0.41	0.97	0.11	0.58	0.05	0.42
	25 (10)	5.30	7.92	2.33	5.90	1.02	2.97	0.20	1.22	0.07	0.51
	50 (20)	7.06	10.90	3.99	9.55	2.26	7.37	0.49	3.03	0.08	0.64
	75 (25)	7.16	10.82	6.19	14.13	2.59	9.25	0.52	3.24	0.09	0.64
	150 (50)	9.01	15.89	11.42	26.07	5.20	22.35	0.78	5.59	0.10	0.76
110	0			0.98	1.77	1.16	3.03	0.10	0.62		
	25			4.38	8.00	2.62	7.61				
	50			9.73	19.50	6.56	21.44	0.50	3.02		
	75			11.21	22.40	8.38	27.45	1.07	6.04		
	150			42.18	83.89	13.46	47.96	1.95	11.38		

*Values in parenthesis refer to phthalate buffer concentration at pH 4. All others refer to acetate buffer (pH 5) and phosphate buffer (pH 6 to 8). Values in italics (0 mM) are extrapolated

$$\frac{k_1}{k_{-1}} = K$$

The calculated rates of aconitic acid isomerisation for all experiments are summarised in Table 1 (part of this table has been reproduced from previous studies). The values at 0 mM ionic strength are extrapolated from the data in the tables using the previously described equation (Walford, 1998).

Effect of temperature

The rate of most chemical reactions will increase with increasing temperature. From the data presented in Table 1, the isomerisation of aconitic acid follows the same trend. The relationship between temperature and reaction rate can be expressed in the form of the Arrhenius equation. This was reported previously (*ibid*, 1998). Average values of the two factors used in the equation (activation energy and pre-exponential factor) can be calculated for the pH 5,6 and 7 data (Table 2) and used in the development of the isomerisation model. The higher value recorded for the forward reaction implies that more en-

Table 2. Average activation energy (E_a) and pre-exponential factor ($\log A$) from the cis-trans isomerisation data at pH 5,6 and 7 and increasing buffer solution concentrations.

	Forward (trans to cis)	Reverse (cis to trans)
E_a (kJ.mol ⁻¹)	77.78	72.45
log A	6.21	5.93

ergy is required to convert the *trans* isomer to the *cis* form than *vice versa*. However, the average difference between the forward and reverse activation energies is 5,3 kJ mol⁻¹ showing that it is relatively easy to convert between the two isomers. For a 10°C rise in temperature the isomerisation rate approximately doubles.

Effect of pH

The effect of pH can be seen in the calculated isomerisation rates (Table 1) and subsequently in the isomerisation equilibrium constant K (Table 3). It can also be seen that increasing buffer solution concentration leads to increasing isomerisation rates. Although the buffer solutions at different pH values were prepared at the same concentration, the ionic strength of these solutions is not equivalent due to differing charges and number of ions in each buffer reagent. Consequently the rates at any particular equivalent buffer concentration cannot be compared. To eliminate this effect, the isomerisation rates and

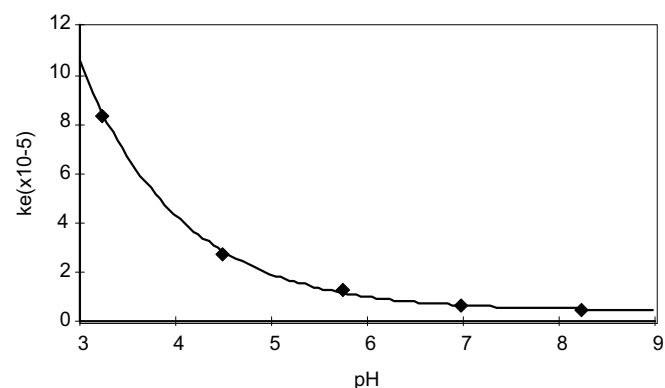


Figure 2. pH-rate profile for the isomerisation of trans to cis aconitic acid at 97°C and 0 mM buffer concentration.

Table 3. Calculated equilibrium constants for the *cis-trans* isomerisation of aconitic acid at increasing temperature, pH and buffer ionic strength.

Temp	Buffer conc (mM)*	pH4	pH5	pH6	pH7	pH8
70	0		<i>0.47</i>	<i>0.34</i>	<i>0.13</i>	
	25		0.45	0.28	0.14	
	50		0.41	0.26	0.14	
	75		0.39	0.24	0.14	
	150		0.39	0.21	0.14	
80	0		<i>0.43</i>	<i>0.31</i>	<i>0.14</i>	
	25		0.42	0.28	0.14	
	50		0.44	0.25	0.14	
	75		0.42	0.24	0.14	
	150		0.42	0.22	0.14	
90	0		<i>0.49</i>	<i>0.37</i>	<i>0.15</i>	
	25		0.45	0.31	0.15	
	50		0.44	0.28	0.15	
	75		0.42	0.26	0.15	
	150		0.41	0.24	0.15	
97	0	<i>0.79</i>	<i>0.43</i>	<i>0.45</i>	<i>0.19</i>	<i>0.13</i>
	25 (10)	0.67	0.44	0.35	0.17	0.13
	50 (20)	0.65	0.42	0.31	0.16	0.13
	75 (25)	0.67	0.44	0.28	0.16	0.13
	150 (50)	0.57	0.44	0.23	0.14	0.13
110	0		<i>0.55</i>	<i>0.38</i>	<i>0.16</i>	
	25		0.55	0.34		
	50		0.50	0.31	0.17	
	75		0.50	0.31	0.18	
	150		0.50	0.28	0.17	

* Values in italics (0 mM) are extrapolated

equilibrium constants were calculated at 0 mM buffer concentration, which is equal to zero ionic strength (figures in italics in Tables 1 and 3). The resultant relationship between pH and rate (pH-rate profiles) is best viewed graphically. The combined rate equation ($k_e = k_f + k_{-f}$) is plotted against pH (Figure 2). The rate is plotted at the measured pH of isomerisation.

It is apparent that the rate increases as the pH decreases suggesting that a change in the nature of the aconitic acid occurs with pH. Aconitic acid is a tricarboxylic acid which undergoes ionisation in the pH range studied. The degree of ionisation is dependent on the pH of the solution. This can be visualised by plotting a distribution of the aconitic acid - conjugate base species against pH (Figure 3). The pH-rate profile (Figure 2) is overlaid onto this plot for comparison purposes. A good correlation is apparent between the rate profile and the unionised and mono-ionised forms of the aconitic acid. Isomerisation

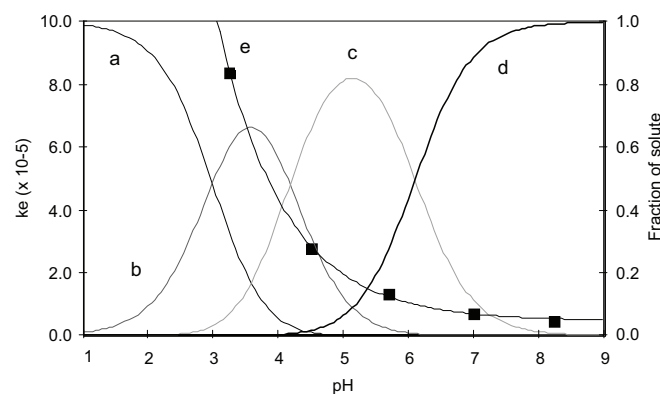


Figure 3. Composition of aconitic acid as a function of pH, overlaid with the *cis-trans* isomerisation rate k_e . a = H_3A , b = H_2A^- , c = HA^{2-} , d = A^{3-} , e = k_e .

Table 4. Summary of average K for isomerisation of aconitic acid as a function of pH.

pH	Average K
4	0.64
5	0.43
6	0.27
7	0.15
8	0.13

would therefore appear to be dependent on the presence of the unionised or singly charged forms of the acid and is thus pH dependent. Isomerisations of this nature are well documented (Finar, 1977).

The increase in isomerisation rates with pH has an effect on the equilibrium ratio and can therefore be used to introduce isomerisation as a function of pH into the model (Table 4). The increase in K as the pH drops is proportional to the degree of ionisation of the *trans* isomer. Subsequent isomerisation is easier and the concentration of the *cis* isomer increases. This data can be summarised in an exponential form for the modeling process as a function of pH as:

$$K = 3.47 \exp(-0.4225 * pH)$$

Decarboxylation of aconitic acid

Scrutiny of the raw data at 110°C at pH 5 and 97°C at pH 4 showed that the isomerisation did not reach a final equilibrium value. The total aconitic acid concentration decreased with time, indicating a further reaction was taking place. An unknown compound appeared on the chromatograms with a con-

Table 5. Mass balance of *cis-trans* isomerisation and subsequent decarboxylation to itaconic acid at pH 4 and 97°C.

Time (min)	<i>Cis</i> (mM)	<i>Trans</i> (mM)	Itaconic (mM)	CO ₂ (mM)	Total Conc (mM)
0	0.002	0.312	0.001	0.001	0.316
15	0.024	0.289	0.001	0.001	0.315
30	0.042	0.267	0.001	0.001	0.312
45	0.057	0.252	0.002	0.002	0.313
60	0.068	0.240	0.003	0.003	0.314
80	0.080	0.224	0.005	0.005	0.314
100	0.087	0.212	0.006	0.006	0.312
120	0.093	0.201	0.008	0.008	0.311
150	0.099	0.191	0.011	0.011	0.312
180	0.101	0.180	0.014	0.014	0.309
240	0.103	0.167	0.020	0.020	0.309
300	0.099	0.156	0.025	0.025	0.306
360	0.096	0.148	0.031	0.031	0.305
420	0.092	0.140	0.036	0.036	0.304
510	0.084	0.128	0.043	0.043	0.299
1455	0.031	0.047	0.091	0.091	0.259
1815	0.019	0.033	0.098	0.098	0.248
1940	0.016	0.030	0.100	0.100	0.246

comitant decrease in the amounts of the *cis* and *trans* isomers being reported. Aconitic acid has been shown to decarboxylate producing itaconic acid (propylenedicarboxylic acid) on heating (Chu and Clydesdale, 1976). The unknown peak eluted at the same retention time as itaconic acid on two different HPLC eluent systems. Calibration of the chromatograph with this acid allowed calculation of the concentration present in the isomerisation solutions. Applying a mass balance to the system and including the theoretical concentration of carbon dioxide produced gave reasonably accurate total mass balances (Table 5) for the first fifteen hours of the isomerisation. A concentration profile for this data is shown in Figure 4.

With extended times the mass balance is inaccurate. Unknown peaks appear in the chromatogram indicating that further reactions begin to occur (Figure 5). Other unsaturated compounds that may also form will not be detected by the UV chromatographic system used. In all instances when itaconic acid was found, there appeared to be a time lag between start of the isomerisation and appearance of itaconic acid. This paralleled the appearance and increase in *cis* aconitic acid. It was therefore assumed that the itaconic acid originated from decarboxylation of the *cis* isomer.

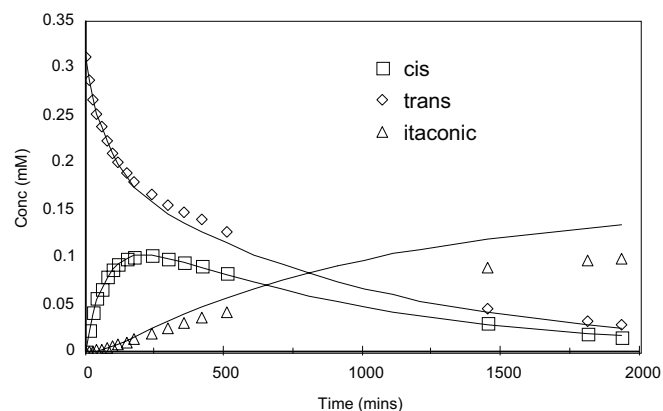
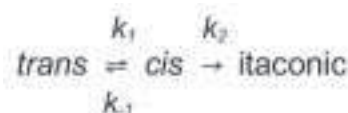


Figure 4. Measured vs calculated concentration profile of the *cis-trans* aconitic acid isomerisation with subsequent itaconic acid formation (data from Table 5). Drawn lines from calculated rate constants.

The following reaction scheme for the isomerisation / decarboxylation can be written:



The rate law for each of the species can be written:

$$-\frac{d[\text{trans}]}{dt} = k_1[\text{trans}] - k_{-1}[\text{cis}]$$

$$\frac{d[\text{cis}]}{dt} = k_1[\text{trans}] - k_{-1}[\text{cis}] - k_2[\text{cis}]$$

$$\frac{d[\text{itaconic}]}{dt} = k_2[\text{itaconic}]$$

where [] is the concentration of the individual species. For the case where the initial concentration $[\text{cis}]^0 = [\text{itaconic}]^0 = 0$ (the case studied here), the concentrations at any time t for the three species are given by (Fersht and Jencks, 1970) :

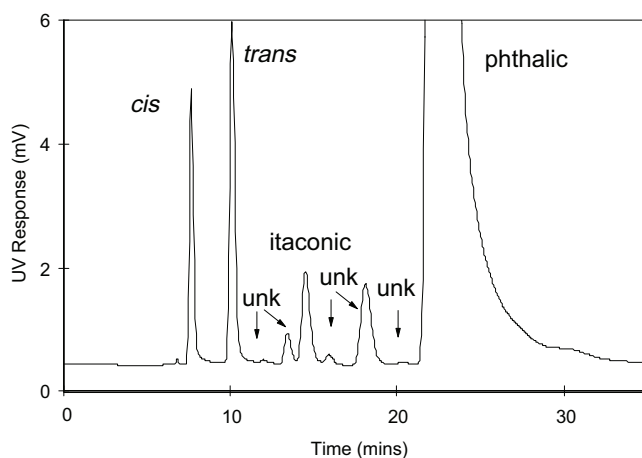


Figure 5. Chromatogram of *cis-trans* aconitic acid isomerisation after 510 minutes at 97°C and pH₂₅ 4 showing formation of itaconic acid and unknown (unk) compounds. Also shown are the *cis* and *trans* isomers and phthalic acid peak from the phthalate buffer.

$$\begin{aligned}
 [\text{trans}]_t &= \frac{k_1[\text{trans}]^0}{\lambda_2 - \lambda_3} \left\{ \frac{\lambda_2 - k_1}{\lambda_2} \exp(-\lambda_2 t) - \frac{\lambda_2 - k_1}{\lambda_3} \exp(-\lambda_3 t) \right\} \\
 [\text{cis}]_t &= \frac{k_1[\text{trans}]^0}{\lambda_2 - \lambda_3} (\exp(-\lambda_3 t) - \exp(-\lambda_2 t)) \\
 [\text{itaconic}]_t &= [\text{trans}]^0 \left\{ 1 + \frac{\lambda_2}{\lambda_2 - \lambda_3} \exp(-\lambda_2 t) - \frac{\lambda_2}{\lambda_2 - \lambda_3} \exp(-\lambda_3 t) \right\}
 \end{aligned}
 \tag{1}$$

where

$$\begin{aligned}
 \lambda_2 &= \frac{1}{2}(\rho + q) \\
 \lambda_3 &= \frac{1}{2}(\rho - q) \\
 \rho &= k_1 + k_{-1} + k_2 \\
 q &= \sqrt{(\rho^2 - 4k_1k_2)}
 \end{aligned}$$

Any one of the concentrations measured can be fitted to the equation. From the calculated parameters (k_1 , λ_2 , λ_3), the constituent rate constants can be obtained. The *cis* concentration data were fitted to equation 1. Calculated rate constants for this scheme at 97°C and pH 4 are :

$$\begin{aligned}
 k_1 &= 5.333 \times 10^{-3} \text{ s}^{-1} \\
 k_{-1} &= 5.964 \times 10^{-3} \text{ s}^{-1} \\
 k_2 &= 2.561 \times 10^{-3} \text{ s}^{-1}
 \end{aligned}$$

These rate constants were used to calculate the theoretical concentrations as a function of time (Figure 4). The apparent difference in calculated and observed values for itaconic acid toward the end of the measuring period can be attributed to further reaction of this acid. The reaction scheme shown does not take this into account but assumes itaconic acid will accumulate. In reality the concentration reaches some plateau and then tails off, forming other compounds. There is evidence of this occurring in the reactions at 100°C. This was not considered in the kinetic treatment, resulting in the observed differ-

ence. Although of interest from a kinetic viewpoint, this line of enquiry was not pursued further since sugar process technologists aim to minimise sucrose inversion which would occur at these pH's and temperatures. In the initial investigation of aconitic acid concentrations present in factory streams, no itaconic acid was found. Consequently decarboxylation of aconitic acid to itaconic was not used in this kinetic model

Development of the isomerisation model

A model can be developed using the isomerisation rates and equilibrium ratios as a function of temperature and pH to predict the equilibrium value of the isomerisation. This can be applied to the major factory processes to determine the relative concentrations of the isomers present. Factory parameters that are easily measured are time, pH and temperature. The model must therefore express the equilibrium ratio as a function of these variables.

Given that the relationship developed earlier between equilibrium ratio K and pH is :

$$K = 3.47 \exp(-0.4225 * \text{pH})$$

and for the average activation energy E_a and pre-exponential factor A (Table 2), the rate equations can be written:

$$k_1 = A \exp(-E_a/RT) = 10^{6.21} \exp(-75480/8.314 * T)$$

$$k_{-1} = A \exp(-E_a/RT) = 10^{5.85} \exp(-71890/8.314 * T)$$

$$k_a = k_1 + k_{-1}$$

for any particular value of T (Kelvin).

Given $K = \frac{[\text{cis}]^{\text{eq}}}{[\text{trans}]^{\text{eq}}}$ and $[\text{cis}]^{\text{eq}} = [\text{trans}]^0 - [\text{trans}]^{\text{eq}}$, as-

Table 6. Comparison of measured and calculated isomerisation equilibrium constants for different stages in the sugar factory.

Stage	Initial K	Time in stage (min)	Average pH of stage	Average temperature of stage (°C)	Increase in K across stage	Calculated K at output	Actual K at output
Extraction Diffuser to MJ	0.03	15	6	85	0.01	0.04	0.05
Clarification MJ to CJ	0.05	30	7	95	0.02	0.07	0.07
Evaporation							
1st effect	0.07	5	7.0	115	0.01	0.08	
2nd effect	0.08	20	6.8	103	0.02	0.10	
3rd effect	0.10	10	6.6	98	0.01	0.11	
4th effect	0.11	16	6.4	82	0.01	0.12	
5th effect	0.12	20	6.4	60	0.00	0.12	
Syrup							0.11
Syrup to sugar							
A-pan	0.11	180	6.1	65	0.02	0.13	
A-crystaliser	0.13	480	6.1	55	0.03	0.16	
A sugar							0.19
B+C masscutes to molasses							
Pans	0.16	900	5.9	60	0.07	0.23	
crystalisers	0.24	2700	5.8	50	0.08	0.31	
C molasses							0.28

suming no further reaction, these can be combined to give:

$$[trans^{eq}] = \frac{[trans^0]}{(1+K)} \quad (2)$$

Which can be combined with the combined rate equation to give the value of the *trans* concentration at any time *t* (in seconds)

$$[trans^t] = [trans^{eq}] + ([trans^0] - [trans^{eq}]) \exp[-(k_e)t] \quad (3)$$

Assuming no other aconitic reactions occur, the *cis* isomer concentration can be calculated from:

$$[cis^t] = [trans^0] - [trans^t] \quad (4)$$

And the *cis/trans* ratio at time *t* as

$$K_t = \frac{[cis^t]}{[trans^t]} \quad (5)$$

By substitution of 2 into 3 and 4 and subsequently into 5, the equilibrium ratio at any time *t* can be expressed as a function of pH, temperature and time, independent of any measured aconitic acid concentration. This can be written :

$$K_t = \frac{1 - \left(\frac{1}{1+K}\right) - \left(1 - \frac{1}{1+K}\right) \exp(-k_e t)}{\left(\frac{1}{1+K}\right) + \left(1 - \frac{1}{1+K}\right) \exp(-k_e t)} + K_{initial}$$

K, *k_e* and *t* are the equilibrium constant, combined reaction rate constant and time in seconds respectively. If the initial *K* is known for the solution before further isomerisation occurs this can be added to the calculated *K*. This gives an additive effect to predict the correct ratio for any particular part of the factory. These equations are only valid for the isomerisation reaction. At higher temperatures the decarboxylation of the aconitic acid to itaconic acid may introduce small errors. Using this model theoretical *cis/trans* ratios were calculated and compared to those measured in the factory (Table 6).

The model describes the actual factory values well. The figure for A molasses is slightly less than the actual value (0.16 vs. 0.19 found in A-sugar). This can be attributed to the recycling of B- and C-sugars in the factory back to the A-pans. These sugars will contain *cis* and *trans* isomers from the back of the factory which have not been accounted for in the model. In general a slight overestimation occurs toward the back-end of

the factory. Again no recycle streams have been considered. The times and pH values used in the model are average values and overestimation of especially crystalliser retention times is possible. It is pleasing to confirm the adequate explanation of the equilibrium increase found across the evaporator stage in earlier studies. Knowing the ratios of isomers present in a particular process stream could help in further investigation into calcium-magnesium aconitate and oxalate scales (Walford, 1998).

Conclusions

The isomerisation of aconitic acid entering the mill is influenced mainly by temperature and pH. At higher temperatures and lower pH values, decarboxylation occurs, producing itaconic acid. A kinetic model has been developed which can adequately explain the isomerisation found to occur across the unit processes in the mill. It includes the rates of isomerisation as a function of pH and temperature but excludes the effect of decarboxylation.

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