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ACETYLSALICYLIC ACID CRYSTALLIZATION:
HYDRODYNAMICS OF THE FLUIDIZED BED

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Hydrodynamics of fluidized bed at acetylsalicylic acid crystallization from acetic acid solution is studied and a modified form of Re number is proposed.

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Introduction

Crystallization in fluidized bed is a variety of acetylsalicylic acid (AAS) continuous crystallization. Only few data refer to fluidized bed crystallization. GLASBY [1] reported about crystallization (of AAS) from 23-40% alcoholic solutions at 29-49 °C with the growing of crystals from mean sizes of 500 μm to that of 1250 μm. He determined the mass transfer coefficients from crystallization rate and obtained an activation energy of crystallization of 91 kJ mol^{-1}, which suggested the incorporation of molecule to the crystal network as the rate-limiting step.

Crystallization from solutions of 96% ethanol was studied by F. MATZ (F. F. Bayer) [2] who gave diagrams for the determination of porosity vs. flow rate in the field of Re < 2. The precision of the diagrams, 1-10% is much smaller than that corresponding to the relation $\varepsilon = k\,(\mathrm{Fr/Re})^b$.

The present paper is an attempt to establish an analytical method for determining the real porosity of the fluidized bed, on the basis of mentioned criterial relation, amending Re number for the case of acetylsalicylic acid crystallization from saturated acetic solutions, at 25 °C and for crystal dimensions of 100-1600 μm. These experiments are connected to the elaboration of a continuous crystallization procedure[3].

Experimental

Acetylsalicylic acid crystals produced by SINTEZA - Oradea are divided into dimensional classes by sieving on a set of standard sieves of: 1600, 1250, 1000, 800, 630, 500, 400, 315, 200 and 160 μm. Saturated solutions of acetylsalicylic acid in pure acetic acid (analytical grade, Reactivul) have been used as fluidisation media.

The experimental set-up consists of a fluidisation column, a 10 dm^3 reservoir for the saturated solution and a collecting drum for the solution. The glass column has an i.d. of 33 mm and is provided with a triple bed of ceramic filling (30 mm height), 1-2 mm size sand (20 mm height) and 0.5-1 mm sand (10 mm height) at the bottom, in order to realise a uniform flow rate across the column section.

The mass of known size crystals is placed in the column and the latter is filled with solution. Under the action of compressed air, the solution flows through the column at a controlled flow rate so that the initial crystal bed height, h_o, increases to the value h. When steady-state conditions are attained the solution volume and elapsed time are measured.

The real porosity is $\varepsilon_r = 1 - 40(1-\varepsilon_0)/h$, the Re_w number results from the fictional flow rate and the Re_r number from the criterial equation:

$$\mathrm{Re}_r = \left[-9 \pm \left(81 + \mathrm{Ar}\cdot 0.36\cdot \varepsilon^{4.761}\right)^{0.5}\right] / 0.36$$

Correlation and the statistical analyses have been made with the program Table curves.

Table 1 Porosity of the layer as a function of mean microscopic size (width)

Sieve holes dimensions, µm	Mean size (d), mm	Porosity (ε_0)
630	0.67	0.65
500	0.50	0.60
400	0.42	0.55
315	0.31	0.50
200	0.20	0.40
100	0.14	0.30

Table 2 Correlation of Re number at fluidization

Crystal characteristics	ε_r	Re_w	Re_r	R
$d = 0.14$ $\varepsilon_0 = 0.30$ $Ar = 2.9$	0.530	0.065	0.00784	8.29
	0.680	0.140	0.0257	5.45
	0.720	0.158	0.0337	4.69
	0.750	0.200	0.0409	4.89
	0.820	0.280	0.0625	4.48
$d = 0.20$ $\varepsilon_0 = 040$ $Ar = 8.5$	0.790	0.480	0.153	3.18
	0.760	0.410	0.127	3.21
	0.740	0.380	0.112	3.38
	0.630	0.240	0.0525	4.59
	0.530	0.170	0.0230	7.39
	0.500	0.120	0.0175	6.84
$d = 0.31$ $\varepsilon_0 = 0.50$ $Ar = 32$	0.610	0.450	0.168	2.67
	0.616	0.570	0.176	3.22
	0.630	0.590	0.196	3.00
	0.634	0.630	0.202	3.11
	0.661	0.870	0.247	3.52
	0.670	0.950	0.263	3.61
	0.780	1.130	0.539	2.10
	0.800	1.320	0.607	2.17
	0.820	1.500	0.683	2.195
$d = 0.42$ $\varepsilon_0 = 0.55$ $Ar = 68$	0.880	2.560	1.980	1.29
	0.850	2.100	1.690	1.245
	0.830	1.900	1.510	1.26
	0.760	1.500	1.003	1.49
	0.730	1.200	0.831	1.44
	0.670	1.100	0.555	1.98
	0.680	0.970	1.110	0.874
$d = 0.50$ $\varepsilon_0 = 0.60$ $Ar = 128$	0.760	1.910	2.010	0.950
	0.800	2.170	2.340	0.743
	0.830	2.450	2.770	1.600
	0.850	3.200	3.080	1.030
	0.880	3.800	3.610	1.050
$d = 0.67$ $\varepsilon_0 = 0.65$ $Ar = 161$	0.720	2.800	1.810	1.54
	0.760	3.200	2.310	1.38
	0.800	4.300	2.920	1.47
	0.820	5.000	3.260	1.53
	0.860	6.200	4.030	1.54

Results and Discussions

Continuous crystallization studies have been made in a cascade of two perfectly stirred tank reactors, in semi-continuous system with discontinuous evacuation in perfectly stirred tank reactor and in fluidised bed.

Real porosity of acetylsalicylic acid crystal layer has been determined by means of direct measurements of bulk volume and of saturated solution volume needed for complete immersion of crystals. The results are given in *Table 1*.

For other dimensions, the following correlation applies:

$$\varepsilon_0 = 0.93 - 0.238 / \sqrt{d}\ ;\ n=6;\ r=0.999;\ s=0.09;\ F=961$$

Crystals of a given size obtained by sieving on a standard set of sieves, are placed in a glass column measuring the initial height after immersion in a saturated acetic solution. In order to obtain the real porosity (ε_r) of the bed, the bed is fluidized by recycled saturated solution.

Theoretical porosity is computed from the criterial relation $Ar = Ga \cdot \Delta p / \rho$:

$$\varepsilon_t = \left[\left(18 \cdot Re + 36 \cdot Re^2\right) / Ar\right]^{0.21}$$

The mean size taken into account is the microscopic mean width (*Table 1*) as the crystals are far from being sphere-shaped and because d_{ech} correlates much better with microscopic mean width ($r = 0.954$, $s = 0.080$, $F = 37$) than with mean granulometric size ($r = 0.4$, $s = 0.23$, $F = 0.7$) for a set of 30 samples obtained by crystallization.

Determination of the real porosity by the use of the equivalent diameter (d_{ech}) computed from the real mean volume determined by microscopic individual measurements delivered weaker results.

Table 2 shows some of the resulting data. The Re_r number calculated from real porosity values is far from those determined by means of fictional flow rate (Re_w). The ratios of the two Re values tend to a constant for a given size of crystals. This ratio (R) increases as crystal size is smaller and the two Re numbers get close to each other only for the size of 0.5 mm, that is the one accepted by US Pharmacopeia 1993.

Large deviations can be observed at low flow rates and at low porosity compact beds. It is the case of crystallization start in fluidised bed. On the other hand, high flow rates are not recommended because of the mechanical erosion of crystals that leads to both unwanted increase of "powder" (microcrystalline form) proportion and rounded forms of crystal clusters, thus decreasing the commercial acceptance of the final product. In addition, adsorption of microcrystals on cluster surface gives them the non-commercial opaque look ("aged" crystals).

Better correlation between hydrodynamic conditions and mean size of the crystals that form the fluidised bed was possible when the Re number was corrected according to the ratio $R = Re_w/Re_r$. ($Re_{cor} = R \cdot Re_w$) Correlation of the correction ratio with crystal size has the following form:

$$R_1 = 10.4 - 49.8 \cdot d + 44.4\, d^{1.5},$$

$$n = 37,\ r = 0.994,\ s = 0.27,\ F = 122 \qquad (1)$$

$$R_2 = 16.9 + 30.5 \cdot d - 43.8\, d^{0.5},$$

Table 3 Computing errors (%) for Re_{cor} values

Crystal characteristics	Re_r	$R_1 = 1.590$		$R_2 = 1.380$		$R_3 = 1.368$	
		Re_{cor}	ε,%	Re_{cor}	ε,%	Re_{cor}	ε,%
$d = 0.42$ mm	1.980	1.610	-18.6	1.957	-1.1	1.871	-5.5
Ar = 68	1.690	1.321	-21.8	1.605	-5.0	1.536	-9.2
$\varepsilon_0 = 0.55$	1.510	1.194	-20.9	1.453	-3.8	1.388	-8.0
	1.003	0.943	-5.9	1.147	14.0	1.096	9.3
	0.831	0.755	-9.3	0.917	10.4	0.877	5.5
	0.555	0.692	24.0	-	-	-	-

$$n = 26, r = 0.994, s = 0.2, F = 119 \qquad (2)$$

$$R_3^2 = -0.78 + 0.468\, d^{-2},$$

$$n = 21, r = 0.997, s = 0.12, F = 607 \qquad (3)$$

where d is given in mm and Re<2.

Correlation of all obtained data leads to *Eq.(1)*. This gives errors up to 97% at flow rates close to the critical fluidisation flow rate and/or when $\varepsilon < 2\,\varepsilon_0$.

Increase of precision can be attained by eliminating results obtained at low flow rates. Thus obtained correlation *Eq.(2)* limits errors at less than 25%. Since this correlation is altered by the presence of large size crystals (Ar < 150; $d > 0.5$ mm) and because these sizes are not commercial and require high energy consumption for fluidisation, for a technical crystallization they can be discarded. Under these circumstances one can obtain correlation *Eq.(3)* when errors are systematically in the range of 10%. *Table 3* gives the errors that affect the determination of R ratios for a given crystal size.

In conclusion, crystal mean dimensions and real porosity and height of the fluidised bed can be calculated on a theoretical basis if the Re number is corrected as shown $Re_{cor} = d_{cor}w\rho / \eta = dw\rho / R\eta = Re_w / R$, where d is microscopic mean width.

Conclusion

For the particular case of a fluidised bed of acetylsalicylic acid, crystals in mother liquor hydrodynamic equations are applied by the use of corrected mean dimensions. The correction factor is predictable and depend on mean width of crystals, which is easy to determine.

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SYMBOLS

Ar	Archimedes number, $Ar = Ga \cdot \Delta p / \rho$
d	microscopic mean size (width)
d_{col}	column diameter
d_{cor}	corrected mean size
d_{ech}	equivalent diameter of crystal
F	Fisher test
Fr	Froude number, $Fr = w^2 / g \cdot d_{col}$
Ga	Galilei number, $Ga = Re^2 / Fr$
h	crystal bed height on flow
h_0	initial crystal bed height
n	number of data
r	correlation coefficient
R	correction number, $R = Re_w / Re_r$
R_i	determinated correction number
Re	Reynolds number, $Re = wdg/\eta$
Re_{cor}	corrected Re, $Re_{cor} = Re_w / R_i$
w	fictional rate of flow
Re_r	real Re, calculated
Re_w	fictional Re, calculated from w
s	standard deviation
Δp	pressure fall

Greek Letters

ε	porosity
ε_0	initial measured porosity
ε_r	real porosity, calculated from h
ε_t	theoretical porosity, calculated
η	dynamic viscosity of liquor
ρ	density of liquor

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