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OLIGOMERIZATION OF SILICATE ANIONS IN PORTLAND CEMENT HYDRATION*

F. TAMÁS

(Research Group for Silicate Chemistry, Veszprém
University of Chemical Engineering)

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According to the classic theory of cement hardening, the strength of hardened cement is carried by non-chemical bonds. In this paper the importance of chemical bond formation during cement hardening is emphasized. In this process corner sharing (bridging) common oxygen ions serve as a bond between adjacent SiO_4-tetrahedra. From this point, cement hardening resembles the hardening of plastics: both processes can be described as polymerization reactions with the difference that -C-C-C-C- and Si-O-Si-O-Si- chains (or rings, and sheets etc.) are formed in the latter and former case, respectively. However, as the degree of polymerization in cements is low in contrast to plastics,the term "oligomerization" is suggested. The possible confirmation of the proposed theory and some practical results are outlined.

INTRODUCTION

Building materials can be classified by various principles: e.g. according to their resistance against the attack of water and behaviour to water during hardening (hydraulic and non-hydraulic binders): the system of SYČEV [1] classifies binders according to the process taking place during hardening and consequently divides binders into three classes: hardening by chemical processes (e.g. plastics, and water-glass binders); hardening by physico-chemical

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processes (e.g. portland cement or plaster of Paris);and hardening by physical processes (e.g. the initial period in the hardening of slaked lime).

A further basis of classification might be structural, according to the principal bond type. It is well known that the forces which bond the atoms or molecules of substances can be subdivided into two classes: chemical forces (ionic and covalent bonds) and non-chemical forces (van der Waals bonds, and hydrogen bonds). (The third type of bonding, namely the metallic bond can be disregarded from the point of this study).

Chemical forces are strong, their energy being some hundred kcal/mol.; non-chemical forces are all weak, the van der Waals forces are very weak, while hydrogen bonds somewhat stronger - as a fair approximation, the energy of non-chemical forces can be considered as being 10 kcal/mol.

In the development of the gross strength of a given substance the resultant joint effect of these forces should be taken into consideration: there may be high forces in one direction and the resultant strength is still low if the bonding forces are weak in an another direction: e.g. in the layer structure of orthoboric acid, H_3BO_3 strong chemical bonds exist within the layers, but the separate layers are bonded by van der Waals forces to each another. This is mirrored by the fact that crystals of H_3BO_3 can easily be pulled apart (cleaved) in a direction parallel to the layers.

Among binding materials, water-glass and phosphate base putties and plastics are characterized by the presence of mainly chemical bonds;on the other hand, the strength of plaster of Paris is supplied by the adhesion (i.e. non-chemical bond) developed between the felted gypsum crystals. In the view of POWERS [2] and BRUNAUER [3] non-chemical bonds are responsible for the strength of portland cement, the most important binder also, produced in vast quantities.

However, parallelities exist between the properties and structure of plastics and hardened portland cement, which justify a comparative study between the two groups of materials.

The most important element is C in plastics and Si in portland cement. Although both elements are tetravalent and in the same column of the periodic table, which would indicate similar chemical behaviour, some differences still exist. The most important difference is that no d orbitals exist in the valency shell (n = 2) of the carbon atom, but its ability to form π-bonds is responsible for most of the chemical properties of carbon. Si belongs to the next period (n = 3); silicon possesses d orbitals, but π-bonds do not exist. This is why most of the compounds of corresponding formula differ so characteristically in properties. A striking example: CO_2 and SiO_2. Carbon dioxide is composed of discrete molecules, containing C-atoms of digonal symmetry. However, the strong chemical bonding within the CO_2 molecule is useless, because the intermolecular bonding consists of weak forces. Therefore the thermal energy at $-78^{\circ}C$ supplies the separation of the molecules of solid CO_2, and it occurs as a gas at ordinary temperatures. SiO_2 on the other hand, is a solid of high strength and high refractoriness (m.p. = $1700^{\circ}C$). But SiO_2 contains Si atoms of tetrahedral symmetry, which form an infinite network in all the three dimensions of space; the Si atoms are linked through O-atoms shared always by two Si atoms, so finally the entire quartz crystal is one molecule, its formula being $SiO_{4/2}^{\infty\infty\infty}$. There is no difference between intramolecular and intermolecular bonds in quartz: the entire crystal is held together by strong chemical bonds.

However, the ability to form long chains by polymerization is common with C and Si, though the nature of the chains differ. Carboniferous chains are of -C-C-C-C- formula, but -Si-Si-Si-Si- chains do not exist in silicates: the bonding energy of Si-Si is too low (42 kcal/mol. as contrasted to the 83 kcal/mol. energy of the C-C bond); the Si-O bond on the other hand is strong (124 kcal/mol., the corresponding C-O bond being only 85 kcal/mol.). This suggests the possibility of the formation of stable, strong -Si-O-Si-O-Si-O- chains and its derivatives (double chains, rings, layers, and frameworks, etc.).

Formation of Bridging Oxygen Ions as Strength Carriers

In the formation of Si-O-Si chains, etc., the O-ions of the SiO_4^{4-} tetrahedra receive their energetically advantageous octett shell by utilizing their "internal" reserves: by the formation of bridging oxygen ions, belonging to two Si-ions simultaneously. So a common electron shell of octett symmetry surround the Si-O-Si complex. A stable octett, on the other hand can also be formed by "external help": by metal cations incorporated into the structure, which act as electron donors thus completing the electron-deficient shell. These incorporated ions however interrupt the continuity of the -Si-O-Si- chain, and thus decrease the strength.

A certain amount of energy is needed to break the -Si-O-Si-O- chain. In our view this is done during the burning of clinker (in this study formation of nonsilicate minerals during clinker burning is disregarded): the continuity of -Si-O-Si- chains in natural silicate polymers, e.g. quartz, is interrupted and Ca-ions are incorporated into the structure. The energy needed for this process is transmitted in the kiln. The resulting minerals are no longer polymers: C_2S* and C_3S both contain isolated, i.e. monomeric SiO_4-tetrahedra, as proved by X-ray diffraction. (Formerly O'DANIEL and HELLNER [4], proposed a structure of C_3S which would contain Si_3O_9 trimer rings; but careful later work, mainly by JEFFERY [5] also confirmed the presence of isolated, monomeric SiO_4 tetrahedra in C_3S).

During the reaction of C_2S and C_3S with water the Ca-ions incorporated into the silicate by external energy are expelled from the structure and precipitated as CaO or more correctly $Ca(OH)_2$. This means that the octett-shell, maintained by "external help", i.e. electron donor cations will be replaced by an internal octett shell of bridging O-ions again, and the energy, invested during clinker burning will be regained. This is one of the preconditions for the formation of a stable hardened cement, as only

*Cement chemical notation system is used, together with the conventional system. C = CaO, S = SiO_2.

processes where the free energy is decreased can proceed without external excitation.

The stoichiometry of the hydration reactions, according to BRUNAUER and co-workers [6] in the case of C_3S:

$$2\ Ca_3SiO_5 + 6\ H_2O \rightarrow Ca_3Si_2O_7.3\ H_2O + 3\ Ca(OH)_2$$

and in the case of C_2S

$$2\ Ca_2SiO_4 + 4\ H_2O \rightarrow Ca_{3.3}Si_2O_{7.3}.3.3\ H_2O + 0.7\ Ca(OH)_2$$

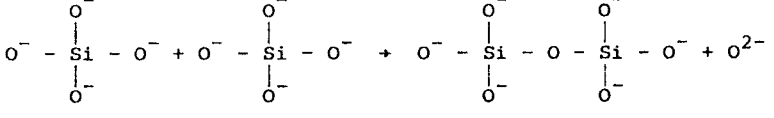
The product is very poorly crystalline, whose structure resembles to that of natural tobermorite. Its Ca/Si ratio may vary over a wide range; but this is always lower than in the parent product, being about 1.5 instead of 3.0 in case of C_3S and about 1.65 instead of 2 in case of C_2S.

These phenomena can be well interpreted by the polymerization (or, more correctly, oligomerization, as only products of limited chain lengths are formed) of the monomer C_2S and C_3S. The essence of the reactions in both cases consists of the disproportionation of O-ions:

$$2\ O^- \rightarrow O^0 + O^{2-}$$

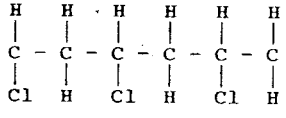
where O^- represents O-ions held by Si on one side only (e.g. one of the O-ions in C_2S); O^0 represents an O-ion held by Si on both sides (i.e. a bridging O-ion); and O^{2-} is an O-ion where both valencies are neutralized by a cation.

In our special case, the first equation by Brunauer can be interpreted in such a way that C_2S is dimerized, one of its 8 O^- ions is degraded to O^0; and this counteracted by the formation of one O^{2-}, which latter is bonded to the expelled Ca-ion. Dimerization means that a two-link chain is formed:



Obviously polymerization may proceed further on, longer chains, and by their linkage, rings, sheets, and space frameworks

may develop. In well-crystallized substances definite complexes are present: e.g. $K_2O.2\ PbO.2\ SiO_2$ is purely dimer, its correct formula being $K_2Pb_2Si_2O_7$ (NÁRAY-SZABÓ and KÁLMÁN [7]). In amorphous or ill.crystallized products, on the other hand (as e.g. in silicate glass, and hydrated portland cement), the concept of equilibria between various complexes of different degrees of polymerization is of utmost importance. The theory of these equilibria is well established for silicate glass (BALTĂ and BALTĂ [8], MASSON [9]), but the concept is similar for hardened portland cement, where C_2S (or C_3S), containing isolated SiO_4 tetrahedra are the monomers, and these become oligomerized during hardening. The process itself resembles the hardening of plastics, e.g. where poly(vinyl chloride):



is formed by the polymerization of the monomer vinyl chloride, $CH_2{=}CHCl$.

As stated earlier, complexes of different polymerization degree exist in amorphous or ill-crystallized silicates. The average degree of polymerization can be characterized by:

$$p = \frac{\sum_{x=1}^{\infty} f_x n_x}{2\ n_M}$$

where x is the number of units (in the case of silicates, the number of the SiO_4 groups) in the complex, f_x is the number of linkages (in our case the number of bridging O-ions), n_x is the number of the x-membered complexes, while n_M in the denominator is the number of the monomer mols. Index p may vary between 0 and 1, the first limit being the absence of polymerization, the second complete polymerization into one giant molecule. The summation in the numerator indicates clearly that the formula always gives an average. Thus, from Brunauer's stoichiometry one may think that the hydrate resulting from C_3S is purely dimer, with p = 0.25; but

the same Ca/Si ratio of 1.5 and consequently p = 0.25 may come e.g. also from the equilibrium of 40 % still monomeric and 60 % hexameric complexes.

The following changes occur during the polymerization of C_2S while p changes from 0 to 1:

1. The molecular weight of the complex increases from 172 to ∞.

2. The O/Si ratio changes from 4 to 2.

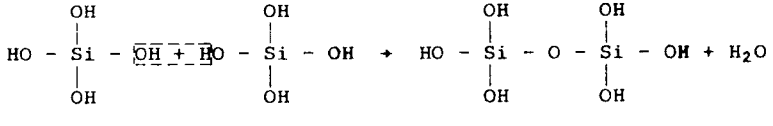
3. The Ca/Si ratio changes from 2 to 0.

However, the process of polymerization is discontinued after a time, the limit being approx. p = 0.35 or slightly beyond.

The SiOSiOSiO chain, formed during this polymerization is one of the principal conditions to develop the strength of cement. A second important condition is the cross-linkage of these chains, because the linear polymer molecules (linear here obviously means unbranched, not cross-linked complex, with a zig-zag axis, corresponding to the 140° valency angle of the SiOSi bond) could be easily pulled apart by external load along the weak intermolecular bonds, similarly to H_3BO_3, examined earlier.

Possible Proofs of the Theory

1. The direct determination of the mean molecular weight, e.g. by cryoscopic methods, in a suitable solvent. C_2S and most of its hydration products are soluble in acids; but at the same time an instantaneous condensation may take place which, in turn, means that the original anionic structure is not preserved. E.g. the orthosilicic acid may condensate according to the formula below:



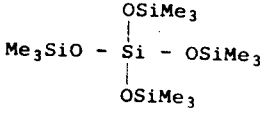
to pyrosilicic acid or even beyond, finally $SiO_2 \cdot n\ H_2O$ will form. The danger of instantaneous condensation can be reduced by using

weak acids and a low temperature dissolution. Obviously a compromise should be sought, because these measures slow down the dissolution process, which brings the same danger again. The use of organic acids of known molar melting point depression is recommended.

2. Instead of molecular weight determination a corresponding property may be examined, e.g. the reactivity of the solution. WIEKER and associates [10] have shown that the reaction rate between silicic acids and molybdate solutions depends on the anionic structure of the silicic acid. The concentration of the product silicomolybdate can easily be measured photometrically. By this method, not only the molecular weight, but also the shape (linear, or ring, etc.) of the molecules can be determined (by calibration with substances of known structures). However, an important limitation: obviously only in cases of a uniform structure. Using a mixture of silicic acids of different molecular size an average value will be obtained.By this method the gradual decrease of the reactivity, i.e. an increase of its molecular weight of the liberated silicic acids as a function of hydration time has been verified [11].

3. The silicic acids, described in the previous paragraph can be separated by paper chromatography [10], thus the individual factors of the average can be studied.

4. The instantaneous condensation mentioned under 1. can be eliminated according to the proposal of LENTZ [12] in such a way that acid dissolution is ensured in the presence of silylating agents, e.g. trimethyl chlorosilane. In this case the original anionic structure remains intact, because the reactive OH or H groups at the end are blocked by the Me_3Si-radical (Me = methyl). E.g. the trimethyl silyl derivative of the orthosilicic acid:



is not capable of instantaneous polymerization, because of the absence of the reactive end groups. The molecular weight or a functional property (e.g. refractive index) of the end-blocked solution can be measured. This method also gives an average only.

5. The end-blocked silicic acid solution can also be separated, e.g. by gas chromatography [12] or by mass spectrometry [13].

6. The proceeding of polymerization can also be determined by indirect methods. For example, by measuring the change in the Ca/Si ratio during hardening (obviously after the selective dissolution of the free lime) Brunauer proved the decrease of this ratio during proceeding hydration. This result accords with the suggested polymerization mechanism of hardening, although Brunauer interprets his results by a different approach.

The formation of cross-links, mentioned earlier, takes place instantaneously during the hardening of silicate cements. The factors influencing the increase of the polymerization degree and cross-linked framework formation are not yet known, although their knowledge would constitute a milestone towards stronger, higher quality binders. An analog example from the history of organic polymers: the technical significance of latex, which contains linear chains of poly(isoprene) is negligible, while cross-linked poly(isoprene) is the polymer, manufactured and utilized in vast quantities: rubber.

By this analogue we endeavoured to affect the hydration of cement so as to produce, in addition to Si - O - Si bonds, cross-linked Si - S - Si bonds too. This can be achieved, e.g. by the addition of compounds containing active sulphur ($SOCl_2$, S_2Cl_2) in such a way that its incorporation into the structure should outpace its decomposition by water. Final strength of cement pastes and concretes produced by this patented method [14] may increase by 40-60 % in contrast to the untreated cement; a further advantage being that the hardening of concrete can be effectively accelerated by steam curing without a loss in final strength.

The endeavour to develop and prove the polymerization mechanism of cement hardening is also significant from a side point: mathematical methods, some practical results, even measurement techniques of the highly advanced theory of organic polymers might be adapted. This will certainly reduce the extent of the fundamental and methodological research needed. Improved knowledge of the

hardening process of cement will constitute a basis for the planned development of new types of cements, having predetermined, controlled properties that are significantly higher than at the present time.

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РЕЗЮМЕ

Согласно классической теории твердения цемента прочность затвердевшего цемента обусловливают нехимические связи. В этой статье автор обращает внимание на тот факт, что в процессе твердения цемента важную роль играет также и образование химических связей. В данном процессе общие мостовые кислородные ионы обеспечивают связь между тетраэдрами SiO_4, соединяя вершины многогранников. В таком смысле твердение цемента подобно твердению пластмасс с той лишь разницей, что в последнем случае образуются цепи C-C-C-C, а в первом - цепи (и затем, при дальнейшей полимеризации, кольца, слои и т.д.) Si-O-Si-O. Однако, ввиду того, что при твердении цемента имеет место полимеризация значительно меньшей степени, чем в случае пластмасс, автор предлагает использовать здесь понятие "олигомеризации". Данная статья знакомит также с возможностями доказательства предлагаемой теории и представляет практически важные выводы.

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STUDIES ON HOMOGENEOUS OLEFIN DISPROPORTIONATION CATALYSTS

L. BENCZE, Á. RÉDEY and L. MARKÓ

(Department of Organic Chemistry, Veszprém University of Chemical Engineering)

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Carbon monoxide increases the activity of catalysts composed of tungsten and molybdenum halide complexes and $EtAlCl_2$ for the disproportionation of olefins. Hexacarbonyls as final products and halo carbonyls as intermediates were isolated from the reaction mixtures.

INTRODUCTION

The disproportionation of olefins has undergone a very fast but contradictory development during the last 12 years since the first patent application. The heterogeneous propylene disproportionation is already at present an industrial process, while the disproportionation of longer chain olefins will still remain at the level of laboratory experiments for probably a long time, because of the simultaneous double bond isomerization leading to a low selectivity of the reaction. An increase of catalyst selectivity by the blocking of acidic centres is accompanied with a rapid decrease in activity [1, 2].

The development of the homogeneous catalytic process seems to be somewhat faster; the disproportionation of terminal and internal olefins has been achieved in the last few years [3, 4, 5]. Numerous new catalytic combinations and metals (Ti, Rh, Fe, Co,

etc.) [6, 7] have been reported, in addition to those based on molybdenum and tungsten which were applied from the beginning. However, although a large number of active catalysts are already known, only a few investigations on the catalytic mechanism have so far been reported.

Following the first successful disproportionation experiments a trans alkylidenation mechanism was proposed for propylene disproportionation

$$\begin{matrix} CH_3 - CH = CH_2 \\ CH_3 - CH = CH_2 \end{matrix} \rightleftharpoons \begin{matrix} CH_3 - CH \\ \| \\ CH_3 - CH \end{matrix} + \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \qquad (1)$$

This general scheme was confirmed by the disproportionation of 2-propene-^{14}C [9]. However, it still remained a problem, that the "quasi cyclobutane intermediate" state proposed for this reaction requires thermaly forbidden electron transitions according to the HOFFMAN–WOODWARD rule [10]. This problem could be solved by the assumption that since the trans alkylidenation has to take place partly or entirely within the co-ordination sphere of the transition metal, the d orbitals of the transition metal also have to be considered in these calculations. The Hoffman–Woodward rule extended in this sense was found to be applicable for the disproportionation of olefins: the process can be described by the combination of the d orbitals of one transition metal and the pi orbitals of two olefins [11].

The homogeneous catalysts used for the disproportionation of olefins are generally composed of a transition metal compound (such as WCl_6) and a cocatalyst such as $EtAlCl_2$ or BuLi [12]. The cocatalyst probably functions partly to produce free co-ordination sites which can be used by the olefin molecules and partly to maintain the necessary electron concentration for the reaction. According to the proposed mechanism, at least two co-ordination sites are required on the transition metal. The experimental observations that disproportionating activity is shown by catalyst combinations with an Al(Li)/W(Mo) ratio of ≥ 2 are in accordance with this theory.

Very little is known about the formation of the catalytically active species. Suggestions for this process were first made by MENAPACE et al. [12] for the two component WCl_6 + BuLi catalyst system:

$$W^{VI}Cl_6 + 2\ R^-Li^+ \longrightarrow W^{IV}R_2Cl_4 + 2\ LiCl \qquad (2)$$

$$\begin{array}{l} W^{IV}R_2Cl_4 \xrightarrow{-2\ R^\cdot} W^{IV}Cl \\ \qquad\qquad\qquad\quad \Big\Updownarrow 2\ \text{olefin} \\ \qquad\quad \Big\downarrow \xrightarrow[-2\ R^\cdot]{2\ \text{olefin}} W^{IV}(\text{olefin})_2Cl_4 \end{array} \qquad (3)$$

$$W^{IV}(\text{olefin})_2Cl_4 \rightleftharpoons W^{IV}Cl_4 + \text{products} \qquad (4)$$

$$\Big\uparrow \text{2 new olefin} \Big\downarrow$$

According to the schema above, the free co-ordination sites are formed by the decomposition of dialkyltungsten tetrachloride. Following this the trans alkylidenation takes place by an intramolecular transformation of the bis olefin complex. Some suggestions were made regarding the oxidation and co-ordination states of the transition metal in Equations (2)-(4), but no experimental proof was presented. The experiments described in this paper were directed towards the isolation of stable derivatives of these intermediates to elucidate some steps of the disproportionation mechanism.

RESULTS AND DISCUSSION

For all experiments cis,trans-2-pentene was chosen as model olefin. Using CALDERON's WCl_6 + EtOH + $EtAlCl_2$ catalyst it was observed that this was very sensitive to air and moisture, whereas Ar, N_2, H_2 or CO and small quantities of PPh_3 or pyridine did not alter its activity appreaciably and CO even increased its selec-

tavity [13]. It was, therefore, concluded that CO, phosphines and pyridine may function as ligands of the transition metal in these catalytic systems.

In order to eliminate the moisture sensitive WCl_6 at first Mo and W compounds were sought that were not sensitive to air and which combined with $AlEtCl_2$ would give active disproportionation catalysts. When 2-pentene was added to the benzene solution of a $AlEtCl_2$ and a ML_2Cl_4 type compound (where L = Py, PPh_3 or 1/2 $C_2H_4(PPh_2)_2$; M = Mo or W) the olefin was consumed by a Friedel--Crafts type reaction for the alkylation of benzene in a few minutes and the disproportionation reaction could not be studied under such conditions [14]. However, using chloro benzene as a solvent (which is more difficult to alkylate than benzene), a homogeneous master solution could be prepared which had the desired disproportionating catalytic activity and was not disturbed by the alkylation of the aromatic ring. The activity of these catalysts significantly increased under CO and approached that of the CALDERON system [15].

Investigating the WPy_2Cl_4 + $EtAlCl_2$ + 2-pentene + chloro benzene reaction mixture by IR spectroscopy, a very strong, sharp absorption band could be observed at 1980 cm^{-1} in addition to some smaller peaks in the ν_{CO} range. This strong band indicated the presence of $W(CO)_6$ which was proved by the subsequent isolation of $W(CO)_6$ from these reaction mixtures. The yield of $W(CO)_6$ reached about 30 per cent and thus surpassed the yield of some of the previously known high pressure syntheses.

By comparing the $W(CO)_6$ content and the catalytic activity of catalyst master solutions (Fig.1) it was shown that an increase of $W(CO)_6$ leads to a decrease of activity. The increase of catalytic activity under carbon monoxide could not, therefore, be attributed to the $W(CO)_6$ formed in the reaction mixture,but to tungsten derivatives having oxidation states between IV and O. It was assumed that the formation of the free sites necessary for co-ordination of olefin (in the catalytic reaction) or carbon monoxide (in metal carbonyl formation) to the metal atom is a result of alkylation (5) and the subsequent decomposition of metal alkyls (6):

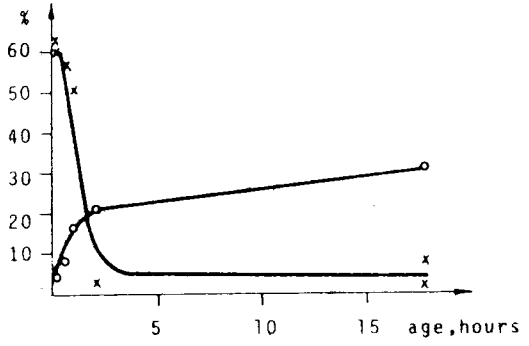

Fig.1. Yield of $W(CO)_6$ and disproportionation activity as functions of the age of the catalyst master solution. o - yield of $W(CO)_6$; x - conversion of 2-pentene in 3 minutes reaction time

$$ML_2Cl_4 + 2\ EtAlCl_2 \rightarrow MEt_2L_2Cl_2 + AlCl_3 \qquad (5)$$

$$MEt_2L_2Cl_2 \xrightarrow{\text{solvent (S)}} ML_2Cl_2S_n + 2\ Et^{\cdot} \qquad (6)$$

These free co-ordination sites can then be occupied either by olefins:

$$ML_2Cl_2S_n + 2\ \text{olefin} \rightleftharpoons ML_2(\text{olefin})_2Cl_2 + n\ S \qquad (7)$$

or by carbon monoxide:

$$ML_2Cl_2S_n + 2\ CO \rightleftharpoons ML_2(CO)_2Cl_2 + n\ S \qquad (8)$$

If olefin and CO is also present at the same time the following equilibrium must be taken into account:

$$ML_2(\text{olefin})_2Cl_2 + 2\ CO \rightleftharpoons ML_2(CO)_2Cl_2 + 2\ \text{olefin} \qquad (9)$$

Such types of VIb metal-halo-carbonyls are already known. Some of these derivatives (like L = PPh_3) are "CO carriers" [16]:

$$M(PPh_3)_2(CO)_2Cl_2 + CO \rightleftharpoons M(PPh_3)_2(CO)_3Cl_2 \qquad (10)$$

To confirm the probability of the above reactions $ML_2(CO)_2Cl_2$ or rather $ML_2(CO)_3Cl_2$ type complexes had to be detected during the disproportionation reaction carried out under carbon monoxide. Although the formation of such compounds was observed in the WPy_2Cl_4 containing systems, their isolation in a pure state failed. Efforts were more successful in the case of the catalyst composed of $Mo(PPh_3)_2Cl_4$ and $AlEtCl_2$:

$$Mo(PPh_3)_2Cl_4 + 2\ EtAlCl_2 \xrightarrow[\text{olefin, solvent}]{CO} Mo(PPh_3)_2(CO)_3Cl_2 \quad (11)$$

The isolation of these complexes supports the assumption that the active catalyst combination contains a low (but not 0) oxidation state transition metal atom having available co-ordination sites. However, the formation of free co-ordination sites does not require the presence of olefins, since the appropriate halo carbonyl complexes can also be prepared from the CO-treated catalyst master solutions in the absence of olefin with good yield.

The halo molybdenum and tungsten carbonyls were prepared previously only by the oxidative transformation of the corresponding carbonyls. Our qualitative observations have been developed to a preparative method which enables the preparation of halo carbonyls by reductive carbonylation with 30-35 per cent yields.

Based on these results, the method described above was also applied in the study of the highly active catalysts derived from $WOCl_4$ or WCl_6 and $AlEtCl_2$ at a molar ratio of W/Al = 1/4. The formation of intermediate unsubstituted halo carbonyls and $W(CO)_6$ was also observed here. $W(CO)_4Cl_2$ was isolated from these reaction mixtures in the form of its stable triphenylphosphine derivative $W(PPh_3)_2(CO)_3Cl_2$. Molybdenum halides reacted similarly [17].

As a matter of fact, all of these results confirm the Menapaces hypothesis and complete it by the reactions occurring under CO atmosphere:

$$W(olefin)_2Cl_4 \xrightarrow[olefin]{CO} W(CO)_2Cl_4 \xrightarrow{PPh_3} W(PPh_3)_2Cl_4 \quad (12)$$

$$W(CO)_2Cl_4 \xrightarrow[olefin]{EtAlCl_2} W(CO)_2(olefin)_2Cl_2 \qquad (13)$$

$$\uparrow\downarrow +CO \quad -olefin$$

$$W(CO)_6 \xleftarrow[CO]{EtAlCl_2} W(CO)_4Cl_2 \xrightarrow[acetone]{PPh_3} W(PPh_3)_2(CO)_3Cl_2 + CO$$

Carbon monoxide is generally known as a catalyst poison and behaves here similarly: it expels the olefins from the catalyst. Despite this the rate of disproportionation is increased in its presence, which suggests the $M(PPh_3)_2(CO)_nCl_2$ (n = 2, 3) type compounds ("the poisoned catalysts") formed in these reaction mixtures are also good catalysts in combination with $EtAlCl_2$ or $AlCl_3$. This assumption was confirmed experimentally: the mixtures of $ML_2(CO)_nCl_2$ (where L = PPh_3 or $AsPh_3$ and M = Mo or W) and $EtAlCl_2$ or $AlCl_3$ (Al/M = 4/1) in chlorobenzene solvent catalyzed the disproportionation of 2-pentene present in a 2-500 fold excess of the equilibrium olefin mixture within 3-5 min [18].

EXPERIMENTAL

General. All manipulations were carried out under Ar or CO at room temperature. Hexane, benzene and cis, trans-2-pentene (Fluka) were distilled from K-Na alloy, chlorobenzene and methylene chloride (Reanal) from phosphorous pentoxide before use. All were stored under Ar.

Molybdenum and tungsten complexes were prepared from purum WCl_6 and $MoCl_5$ (Koch-Light)(Fluka) as described in literature [19, 20]. $EtAlCl_2$ was prepared from Et_3Al and $AlCl_3$ and purified by distillation [21].

The IR spectra were recorded on a double-beam Carl Zeiss UR 20 spectrophotometer.

Catalytic experiments

a) A solution (5 ml) of cis-2-pentene in n-pentane (1/1) and 0.05 ml $EtAlCl_2$ was added to a suspension of 29 mg WPy_2Cl_4 in 5 ml chlorobenzene. After 1 hour, the mixture was hydrolyzed and analyzed by GLC. Based on the quantity of cis-2-pentene introduced, the reaction product contained 14.1 per cent cis, trans-2-butene, 45.7 per cent cis, trans-2-pentene and 27.3 per cent cis, trans-3--nexene. The rest of the olefins were converted to polymers.

b) Several parallel runs were performed with the above catalyst under Ar and CO. After a 15 minute reaction, the conversions of 2-pentene ranged between 7-22 per cent under Ar and 48-51 per cent under CO; since the equilibrium composition was reached under carbon monoxide, the rate of reaction must have been rather high. This was confirmed by utilizing even shorter reaction times: conversion of 2-pentene was 40.6 per cent after 1 minute, 41.8 per cent after 3 minutes and 47.2 per cent after 5 minutes.

c) To study the connection between $W(CO)_6$ content and catalytic activity, a master solution was prepared from 300 mg WPy_2Cl_4, 0.9 ml $EtAlCl_2$ and 50 ml chlorobenzene. This was stirred under CO and samples were taken at certain intervals. 5 ml of the sample was given to 5 ml of a mixture of n-pentane and 2-pentene (1/1) and the conversion of 2-pentene after 3 minutes reaction time was used as a measure of the activity. The concentration of $W(CO)_6$ was determined in another part of the sample by IR spectroscopy and an extinction vs. concentration curve using the extinction measured at 1980 cm^{-1}.

d) $W[C_2H_4(PPh_2)_2]_2Cl_3$, $W[C_2H_4(PPh_2)_2]Cl_4$ and $Mo(PPh_3)_2Cl_4$ behaved similarly to WPy_2Cl_4 under the conditions of a), b) and c).

e) 5 ml of a solution of cis-2-pentene in pentane (1/1) containing 0.05 ml $EtAlCl_2$ was added to a suspension of 0.05 g $W(PPh_3)_2(CO)_3Cl_2$ in 5 ml chlorobenzene under Ar. A homogeneous solution was formed. After 1 hour, the reaction mixture was hydrolyzed and GLC analysis indicated the presence of 13.4 per cent 2-

-butenes, 49.7 per cent 2-pentenes, 26.2 per cent 3-hexenes and traces of higher olefins.

Preparative Experiments

f) The master solutions made according to c) were steam distilled after 2-3 hours reaction time. $M(CO)_6$ (M = Mo or W) precipitated on the wall of the condenser in the form of white crystals, before an appreciable distillation of chlorobenzene has started. Yield 10-30 per cent.

g) A solution of 0.05 ml $EtAlCl_2$ in 3 ml 2-pentene was given to a solution of 190 mg $Mo(PPh_3)_2Cl_4$ in 3 ml chlorobenzene. Rapid disproportionation reaction was observed. Adding pentane (5-10 ml) a precipitate formed due to the diminished solubility of the complexes. This solid portion of the product was separated and dissolved in a small quantity of acetone upon which 20-30 mg $Mo(PPh_3)_2(CO)_3Cl_2$ precipitated.

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РЕЗЮМЕ

Окись углерода в реакции диспропорционирования олефинов увеличивает активность используемого катализатора, состоящего из галогенидных комплексов вольфрама и молибдена и из $EtAlCl_2$. Из реакционной смеси были выделены в качестве конечных продуктов гексокарбонилы и в качестве интермедиеров галогенокарбонилы.

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STUDIES ON GRANULATION IN A FLUIDIZED BED III.

CALCULATION OF THE FEED RATE OF GRANULATING LIQUID

Z. ORMÓS, K. PATAKI and B. CSUKÁS

(Research Institute for Technical Chemistry of the
Hungarian Academy of Sciences, Veszprém)

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In granulation in a fluidized bed, the appropriate selection of the feed rate of the granulating liquid is very important since this parameter, in addition to its effect on the formation of the granulates, considerably influences the capacity of the apparatus. The results of experiments on the effect of the feed rate of granulating liquid on the physical properties of the granulates formed in a fluidized bed (average particle size, the relative amount of the particles not granulated, wear strength, and the inhomogeneities of the binder distribution) are given. On the basis of the heat and liquid balances of the process, correlation is given for the maximum and equilibrium liquid feed rates.

A very important process parameter of the batch granulation in a fluidized bed is the feed rate of the granulating liquid. To attain the optimum average particle size, a well defined quantity of the given binder solution is needed. The liquid can be sprayed in the fluidized bed at different feed rates, i.e. during various lengths of time. Thus the appropriate choice of the feed rate of the granulating liquid, basically determines the duration of the granulation and hence the capacity of the apparatus.

In the first paper of this series [1] - where the relationships between the amount of the binder and the physical properties

of the formed granulates were dealt with - the effect of the feed rate on the physical properties of the granulates was also touched upon to ensure the completeness of the paper. The results of other authors - RANKELL and all. [2], MÖBUS [3] and DAVIES and GLOOR [4] were also given. It was pointed out that the results were evaluated in literature in two different ways. Some authors changed the feed rate while keeping the duration of the spraying at a constant value [2, 3], while others kept the quantity of the granulating liquid constant [4] - hence the results are difficult to compare.

On the basis of the experimental results it was deduced that the average diameter and average porosity and the particle size distribution of the formed granulates were only slightly influenced by the variation within certain limits of the feed rate of the granulating liquid, provided that the overall amount of the binder was kept constant. Therefore, the influence of the feed rate was neglected in addition to those parameters that had greater effects on the above mentioned properties of the granulates.

In the present paper the influence of the feed rate of the granulating liquid on the average particle size, the relative amount of the particles not granulated, the wear strength and the homogeneity of the binder distribution will be dealt with in details. On the basis of the heat and liquid balances of the process, correlations were derived for the upper limit of the liquid feed rate and for the approximately optimum feed rate.

EXPERIMENTAL APPARATUS AND METHODS

The experimental laboratory granulating apparatus and the applied experimental methods will not be described here in detail, since they do not depart from those described in the previous paper of this series [1].The 0.1-0.2 millimetre fraction of quartz sand was used as basic material and an aqueous gelatine solution of a concentration of $c' = 60$ kilograms per cubic metre was used as the granulating liquid. In the experiments dealt with in this

paper, the concentration of the granulating liquid, the mass of the material to be granulated, the relative expansion of the fluidized bed, the temperature of the air at the inlet and the distance between the atomizer and the underplate were kept at constant values, in addition to the characteristics of the apparatus and the basic material and the binder. The air feed rate of the atomizer was increased with the feed rate of the granulating liquid to ensure a nearly identical liquid dispersion throughout the measurements, so that the specific air consumption was always about 2.5 kilograms air per kilogram liquid.

The test and calculation methods for the physical properties of the granulates formed were summarized in the previous paper of this series [1] while the test methods were detailed in the first paper [5].

In some cases the relative humidity of the air at the outlet and the liquid content of the bed were determined several times during the granulation at various liquid feed rates. The liquid content of the bed was determined by drying the samples taken from the bed in a drying oven until constant weight. The relative humidity of the air at the outlet was measured by an ASSMANN psychrometer redesigned to this purpose. These measurements had two objectives: they provided data for the establishment of the heat and liquid balances of the process and helped in deciding whether the change of state of the air flowing through the apparatus is really adiabatic as suggested in literature [2, 6].

At the two extreme values of the feed rate of the granulating liquid, the concentration of the binder was determined as a function of the size of the granulates. The average binder content of the granulates was determined by dissolving NaCl in the granulating liquid. Having concluded the granulation, the dry product was fractioned and from the average samples of identical mass, the labelled binder was extracted by hot distilled water. The conductivity of thermostated solutions of identical volumes of the samples were measured by bell-shaped electrodes. In the knowledge of the relationship between the conductivity and concentration of the NaCl solution, the binder content was determined from the measured conductivity.

EXPERIMENTAL RESULTS

The effects of the feed rate on the physical properties of the granulates were studied by altering the feed rate at four different values of the relative amount of the granulating liquid (V'/V = 5; 10; 20; 30 vol per cent) while keeping the other parameters at constant values. The studied feed rates were as follows: w' = (2.5; 4.2; 5.9; 7.6 and 9.2) $\times 10^{-5}$ kilogram per second. When the feed rate is changed while the relative amount of the granulating liquid is kept constant, the duration of the granulation also changes,with smaller feed rate it is longer, and with greater feed rate is shorter. Because of the repeatability of the experimental results [1] three parallel experiments were carried out in every case so the dots in the following Figures correspond to the average value of three parallel experiments.

The average diameter of the granulates is plotted against the feed rate of the granulating liquid in Fig.1. The average particle size tends to be decreased by the increase of the feed rate, though the dots are rather scattered.(The straight lines in the Figure do not show anything more than the tendencies of the changes!) When the relative amount of the granulating liquid is greater, the decrease of the particle size is greater. While at a relative liquid amount of

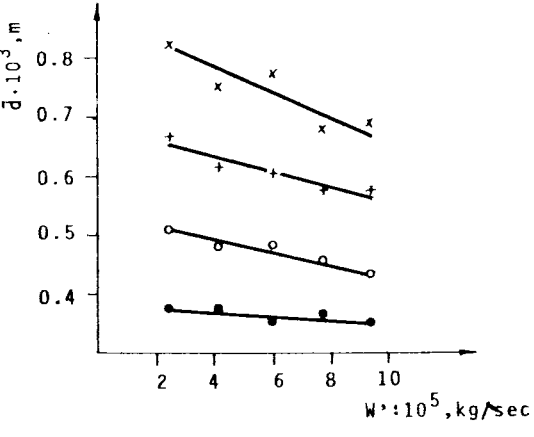

Fig.1. x - V'/V = 30 vol. per cent
+ - V'/V = 20 vol. per cent
o - V'/V = 10 vol. per cent
• - V'/V = 5 vol. per cent

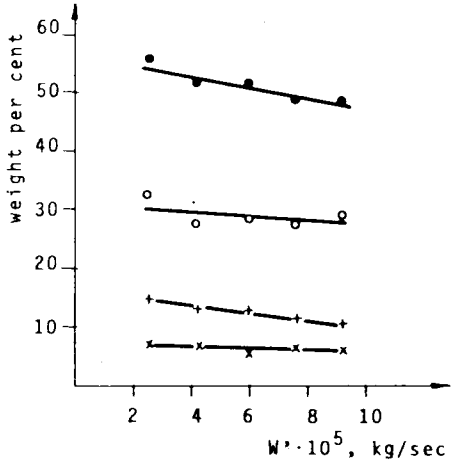

Fig.2. d = (0.1 - 0.2)x10^{-3} m
•-V'/V = 5 vol. per cent
o-V'/V = 10 vol. per cent
+-V'/V = 20 vol. per cent
x-V'/V = 30 vol. per cent

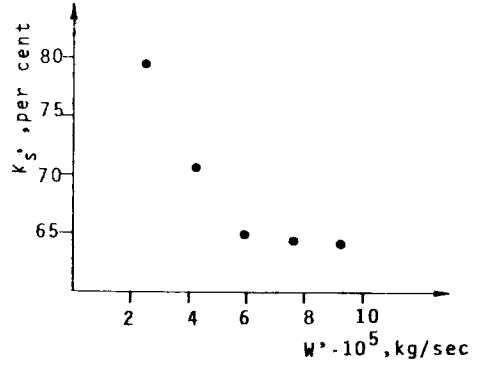

Fig.3. V'/V = 20 vol. per cent

V'/V = 5 vol.per cent, the increase of the feed rate by about four times decreases the average particle size by only about 7 per cent at a relative liquid amount of V'/V = 30 vol. per cent this change is almost 16 per cent.

In Fig. 2 the weight fraction of the particles not granulated is plotted against the feed rate at four different values of the relative amount of the granulating liquid. With the increase of the feed rate there is a slight decrease of this weight fraction. The greatest effect was found at the smallest liquid amount (V'/V = 5 vol. per cent), where the amount of the particles not granulated decreases by about 7 weight per cent when the feed rate is increased from 2.5x10^{-5} kilogram per second to 9.2x10^{-5} kilogram per second, which represents a relative decrease of 12.5 per cent.

In Fig. 3 a more profound change is shown, the wear strength is plotted

against the feed rate of the granulating liquid. After an initial sharp drop, the wear strength approaches a lower limit with the increase of the feed rate, despite the fact that the amount of the binder does not vary.

In Fig. 4 the binder content is plotted against the particle size at two different feed rates. The tendencies are identical in both cases, the binder content at first increases with the particle size, but later it attains a nearly constant value. From the Figure it is clear that if a given amount of the binder solution is sprayed in the bed with high velocity, that is during a short time, there are greater differences between the binder content of the particles of different size than in the case of granulation with small feed rates.

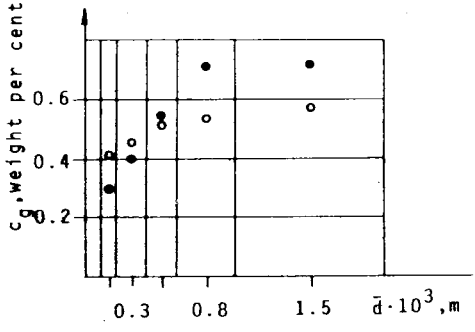

Fig.4. • - w' = 8.4×10^{-5} kilogram per second; o - w' = 3.4×10^{-5} kilogram per second; V'/V = 20 vol. per cent

The temperature and relative humidity of the air was measured at the inlet and at the outlet. In the Mollier diagram of the humid air, the point corresponding to the measured relative humidity of the air at the outlet was determined from the conditions of the air at the inlet, supposing an adiabatic drying process. The dry bulb temperature corresponding to this point is the "adiabatic temperature", (T_a''). The comparison of T_a'' and the measured temperature at the outlet makes it possible to see how the process approaches the ideal adiabatic one. The differences between the measured temperatures and those obtained from the psychrometric diagram are plotted against the measured temperatures in Fig. 5. The discrepancies between the temperature of the air at the outlet

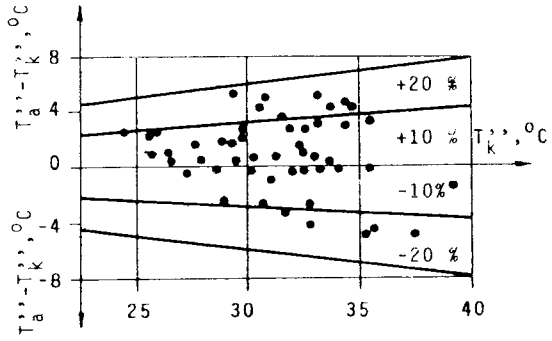

Fig. 5

and the adiabatic temperature were in every case less than ± 20 per cent and in 75 per cent of the cases the differences were not greater than ± 10 per cent.

DISCUSSION

According to Fig. 1, 2, 3 and 4 the changes in the physical properties of the granulates due to the increase of the feed rate of the granulating liquid are not of the type that would make it possible to determine a well defined optimum value of the feed rate. The increase of the feed rate is undesirable on the one hand, because of the worse binder distribution and because of the decrease in the wear strength, while it is desirable on the other hand, because of the greater capacity and because a slight decrease in the amount of the particles not granulated.

The feed rate of the granulating liquid cannot be selected arbitrarily. Both the experimental results and the theoretical considerations show that there is a maximum value of the feed rate above which granulation in a fluidized bed cannot be realized.This

greatest feasible value of the feed rate is determined by the air velocity corresponding to the required bed expansion and by the air temperature at the inlet; after a certain feed rate, the heat content of the air flow is insufficient for the removal of the liquid sprayed in. In such cases, the amount of the granulating liquid retained in the bed continuously increases and at a critical liquid content characteristic of the given system, the fluid movement of the bed cannot be maintained even by a further increase of the air velocity.

The maximum liquid feed rate can easily be determined from the liquid mass balance of the process, in the knownedge of the critical liquid content of the bed.

The liquid mass balance:

$$w't'\left(1 - \frac{c'}{\rho'}\right) - F\rho''(x_k'' - x_b'') \int_0^{t'} u''(t)dt - V_p''t'(x_k'' - x_b'') = x_r G \quad (1)$$

Equation (1) can be reduced by the introduction of the average gas velocity (integral mean); the air flow of the atomizer should be expressed as the product of the liquid feed rate and the specific air requirement of the atomizer:

$$w't'\left(1 - \frac{c'}{\rho'}\right) - F\rho''(x_k'' - x_b'')\,\bar{u}''t' - kw't'(x_k'' - x_b'') = x_r G \quad (2)$$

The results on the changes of the velocity of the air required for the movement of the fluidized bed, with respect to time, and the method for the determination of the average air velocity will be published in a following paper on the fluidization properties of the granulates.

Taking the critical liquid content as the liquid content of the bed ($x_r = x_{rk}$), Equation (2) gives the maximum feed rate:

$$w_M' = \frac{x_{rk} G + F\rho''(x_k'' - x_b'')\,\bar{u}''t'}{t'\left(1 - \frac{c'}{\rho'}\right) - kt'(x_k'' - x_b'')} \quad (3)$$

The liquid content of the bed attains the critical value at which the movement of the bed stops, just by the end of the spraying (during a time interval of t') if the feed rate is that corresponding to Equation (3). The correlation helps in finding the feasible range of feed rates, that extends in theory from a feed rate of zero to w'_M. In practice the lower limit is the lowest feed rate where the precondition of the formation of the liquid bonds does not exist because of the very small wetting. In such cases the atomized granulating liquid becomes partly dry before getting in the bed (drying with atomization), and partly it dries on the surface of the particles without the formation of either liquid or solid bonds.

The heat balance of the batch granulation in a fluidized bed with spraying can be used for the determination of the equilibrium liquid feed rate (w'_e). The latter is the feed rate at which the heat content lost by the flowing gas is equal to the heat required for the evaporation of the solvent sprayed in.

The heat balance:

$$F\rho''c''_p(T''_b - T''_k)\int_o^{t'} u''(t)dt = [w't'(1 - \frac{c'}{\rho'}) - G\int_o^{t'} x_r(t)dt]r' + Q_v \qquad (4)$$

The term on the left hand side of Equation (4) can be reduced by the introduction of the average gas velocity ($\bar{u}''$); moreover, the Q_v heat loss can be neglected in the case of appropriate heat insulation, since the temperature of the bed does not differ significantly from the room-temperature.

$$F\rho''c''_p(T''_b - T''_k)\bar{u}''t' = [w't'(1 - \frac{c'}{\rho'}) - G\int_o^{t'} x_r(t)dt]r' \qquad (5)$$

The liquid feed rate can be equated to that of the equilibrium liquid feed rate defined above. In that case there is no accumulation of the liquid in the bed, so the equation reduces once again:

$$F\rho''c''_p(T''_b - T''_k)\bar{u}''t' = w'_e t'(1 - \frac{c'}{\rho'})\, r' \qquad (6)$$

From Equation (6) the equilibrium feed rate of the granulating liquid is:

$$w'_e = \frac{F\rho''\bar{a}''c''(T''_k - T''_k)}{r'(1 - \frac{\rho''}{\rho'})} \qquad (7)$$

The practical use of this equation is facilitated by the fact that the temperature of the air at the outlet (T''_k) can be aproximated well with the help of the psychrometric diagram, in the knowledge of the characteristics of the air at the inlet, since $T''_k \approx T''_a$ (see under the heading "Experimental Results").

The applicability of Equations (3) and (7) were checked by the solution of several problems. The data needed were substituted into Equations (3) and (7) in the case of the studied model and the following values were obtained: $w'_e = 6\times10^{-5}$ kilogram per second; $w'_M = 10.5\times10^{-5}$ kilogram per second.

The feed rates obtained by the equations are quite feasible and they are compatible with the experimental observations. The calculated maximum feed rate was somewhat higher than the value of 9.2×10^{-5} kilogram per second found to be just employable. But is has to be remembered that at this feed rate an appreciable experiment was carried out so the critical liquid content of the bed was not attained. Hence the higher limit of the feasible feed rates can be well approximated by Equation (3). The equilibrium feed rate calculated by Equation (7) is a good mean value in the feasible interval. Lower rates should be applied for the granulation only if the wear strength of the granulates is to be increased or if small amounts of some additives are to be introduced and distributed in the bed (e.g. in the pharmaceutical industry). The decrease of the feed rate according to Fig. 3. and 4. increases the wear strength of the granulates and helps in the relatively homogeneous distribution of materials fed in small amounts with the granulating liquid, independently of the particle size.

SYMBOLS USED

c' concentration of the granulating liquid (kilogram per cubic metre)

c_g the binder content of the granules (weight per cent)

c''_p heat capacity of the gas (kilocalories per kilogram per Degree Centigrade)

d particle size (metre)

$\bar{d}$ average particle size (metre)

F cross section area of the apparatus (square metre)

G the mass of the bed (kilogram)

k the specific air requirement of the atomizer (kilograms per kilogram)

K_s wear strength (per cent)

r' latent heat of the solvent (kilocalories per kilogram)

Q_v heat loss (kilocalories)

T''_a air temperature at the outlet from the psychrometric diagram (Degree Centigrade)

T''_k air temperature at the outlet (Degree Centigrade)

t time (second)

t' the duration of granulation (second)

u'' gas velocity (metres per second)

$\bar{u}''$ average gas velocity (metres per second)

V the overall volume of the particles to be granulated (cubic metre)

V' the volume of the granulating liquid (cu.metre)

V'/V the relative amount of the granulating liquid (vol. per cent)

V''_p air flow of the atomizer (kilogram per second)

w' feed rate of the granulating liquid (kilogram per second)

w'_e equilibrium feed rate of the granulating liquid (kilograms per second)

w'_M maximum feed rate of the granulating liquid (kilograms per second)

x''_b absolute humidity of the air at the inlet (kilograms per kilogram)

x''_k absolute humidity of the air at the outlet (kilograms per kilogram)

x_r liquid content of the bed (kilograms per kilogram)

x_{rk} critical liquid content of the bed (kilograms per kilogram)

ρ' density of the granulating liquid (kilograms per cu.metre)

ρ'' density of the gas (kilograms per cu.metre)

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РЕЗЮМЕ

При грануляции, происходящей в псевдоожиженном слое, очень важен выбор соответствующей скорости подачи гранулирующей жидкости, поскольку этот параметр не только влияет на образование гранул, но и в значительной мере определяет производительность установки.

Авторы рассматривают влияние, оказываемое скоростью подачи гранулирующей жидкости на физические свойства (средний диаметр частиц, относительное число негранулировавшихся частиц, износостойкость, негомогенное распределение связующего вещества) образующихся гранул. На основании уравнений материального и теплового баланса была выведена зависимость для определения максимального и равновесного значения скорости подачи жидкости.

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STUDIES ON GRANULATION IN FLUIDIZED BED IV.

EFFECTS OF THE CHARACTERISTICS OF THE FLUIDIZED BED THE ATOMIZATION AND THE AIR DISTRIBUTOR UPON THE PHYSICAL PROPERTIES OF THE GRANULATES

Z. ORMÓS, K. PATAKI and B. CSUKÁS

(Research Institute for Technical Chemistry of the
Hungarian Academy of Sciences, Veszprém)

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It is important to know the influence of the characteristics of the granulator and the procedure upon the physical properties of the granulates produced, both from the point of view of the granulator design and the determination of the optimum operating parameters. However, few papers dealing with the above-mentioned questions are to be found in literature. The effect of the following factors: ratio minimum bed height to diameter of bed, degree of expansion of the fluidized bed, degree of dispersion of the granulating liquid, distance of the atomizer as measured from the air distributor and the type of the distributor upon the physical properties of the granulates produced was studied in a laboratory-size fluidized bed granulator of batch operation. In the evaluation of the experiments, the results are compared with the conclusions published in literature and the nearly optimum values for the above-mentioned variables are given.

From among the parameters having an influence upon the physical properties of granulates produced in a fluidized bed, the effect brought about by changes in the relative amount of the granulating liquid, the rate of addition of the latter, its concentration, and the total amount of binder fed in were investigated

in the previous papers of this series [1, 2]. Approximative formulae were presented on the basis of those experiments for the calculation of the mean diameter of granules and the feed rate of the granulating liquid. The present paper deals with such characteristic parameters of the procedure and the apparatus that are of importance mainly in connection with the design and operation of fluidized bed granulators. These parameters are the following:

- ratio of the minimum bed height to the diameter of the bed;
- degree of expansion of the fluidized bed;
- degree of dispersion of the granulating liquid;
- distance of the atomizer from air distributor plate;
- performance of the air distributor plate.

As an introduction, conclusions of other authors in connection with the effect of the above-mentioned variables so far published in literature are summarized. The experimental results and conclusions drawn from them are then described.

In the design of fluidized bed granulators when deciding the size of the material container, or in the case of an existing apparatus, when determining the charge weight, the question of the preferable ratio minimum bed height to bed diameter arises. Simple fluid mechanical considerations also lead to the conclusion that this geometric simplex may have an optimum value or optimum value range. It is known from literature on fluidization [3, 4] that an increased danger of channel formation, (slugging) is encountered both with too shallow and with too high beds. These irregularities have an adverse effect on the mixing, heat and mass-transfer processes and also on the granulation. In addition, the ratio bed height to bed diameter may influence the probability of collision between the atomized liquid droplets and the particles, and also the rate of agglomeration [5]. In spite of the probably considerable influence of this variable on the physical properties of the granules produced, and of its economic importance (maximum utilization of the capacity of the apparatus), no paper so far published deals with this question in the manner that it deserves.

The degree of bed expansion is a very important characteristic of fluidization and its effect must be taken into consideration in all processes carried out by fluidization. In the case of fluidized bed granulation, an appropriate choice of the degree of bed expansion is of decisive importance regarding the final size distribution particle of the product [5, 6, 7, 8]. An increase in bed expansion tends to decrease the mean granule size [5, 8] because the more vigorous motion results increased abrasion. Another factor which makes higher bed expansion undesirable is an increase in elutriation. On the other hand, too small bed expansion brings about decreased mixing, heat and mass transfer, leading to the formation of "lumps" beyond the prescribed size limit. Accordingly, the optimum value of bed expansion is always a compromise between processes which are adverse as regards granulation and which tend to act against each other.

It is very difficult to determine accurately the degree of the dispersion of the granulating liquid, i.e. the size, and size distribution of the atomized droplets. Consequently, the effect of this parameter was studied only in an indirect manner. For example, in the case of two-fluid atomizers, which are most frequently applied in the practice of fluidized bed granulators, the effect of the pressure and flow rate of the atomizing air upon the physical properties of the produced granules were studied [8, 9]. The opinion of the different authors on this question is divergent. According to the paper of SCOTT and his co-workers [5], containing mainly theoretical considerations, it is to be expected that the mean drop size of the spray influences the process of granulation. The authors ascribe this to two facts: first, increasing the degree of dispersion also increases the specific surface area of the droplets and together with it the rate of evaporation of the latter. Secondly, the size, size distribution and number of atomized droplets influence the probability of collision between the droplets and solid particles, and thus also the rate of agglomeration. However, no experiments were carried out to study the influence of the degree of atomization. According to the work of MÖBUS [8], changing the pressure of the atomizing air between certain limits

does not appreaciably influence the physical properties of the granules. Unfortunately, experimental results were not published and accordingly it is impossible to determine even the pressure range studied. Detailed experimental data have been published by DAVIES and GLOOR [9]. In contrast to the above-mentioned author, they found that upon increasing the atomizing air pressure from 0,5 to 2.0 kg/cm², the mean granule size was decreased from 438 to 292 μ.

The vertical distance of the spray nozzle from the air distributor is restricted between certain limits [5, 7]. The lower limit that can be taken into consideration is defined by the condition that the atomized liquid must not wet the distributor plate because this would lead to the formation of large lumps, clogging of the distributor and stopping of particle motion. The upper limit of the location of the atomizer is determined by the spray cone angle and the bed height, on the basis of the condition that the atomized granulating liquid should not wet the wall of the granulator. Opinions differ as to whether or not the variation of the height of the nozzle between the above-mentioned limits influences the physical properties of the granules. According to MÖBUS [8], changing the position on the nozzle does not appreciably influence the physical properties of the granules. On the other hand, various authors have observed that increasing the distance between the atomizer and the distributor brings about a decrease in the mean granule diameter [6, 9]. The change can be termed as considerable. For example, experiments carried out by RANKELL and his co-workers showed that the mean granule size was decreased from 500μ to half this value when the atomizer in a granulator, 0.3 m in diameter, was lifted from a height of 0.75 to 1.5 m [6]. The phenomenon was mainly explained by the following consideration: in the case of a highly positioned atomizer, the spray drying that is undesired from the point of view of granulation, become prevalent.

In the case of fluidized bed granulators, mainly perforated plates, sieves and porous plates are applied as distributors. A number of points simultaneously have to be taken into consideration when choosing the distributor. Economic considerations re-

quire a distributor plate that is simple, inexpensive, easy to procure, and causes a low pressure drop. Fluid mechanical considerations would require gas distributor plates made of sintered glass or metal, fireclay, or other similar porous materials, in order to obtain optimum fluidization motion and to avoid irregularities in the fluidization process [3, 4]. This question can be solved satisfactorily only if the influence of the quality of the distributor on the physical properties of the granulates produced is known. As far as the authors know, no other researchers have so far dealt with such studies.

Having reviewed the literature connected with the subject it can be stated that the parameters in question include some whose effect has yet not been studied in any way; in the case of others, mainly theoretical conclusions were drawn and the latter were checked by a few experiments only. In some cases the conclusions of various authors were contradictory to each other. To summarize it can be stated that the data in literature are insufficient to determine the approximately optimum values of the different parameters.

EXPERIMENTAL APPARATUS AND METHODS

A detailed description of the laboratory-size fluidized bed granulator used for the experiments and the experimental techniques will be dispensed with, because they are similar to those described in the second paper of this series [1]. The materials used in the experiments were a quartz sand fraction of $(0.1\text{-}0.2)\times 10^{-3}$ m particle size and a granulating liquid which was an aqueous gelatine solution of $c' = 60$ kg/m³ concentration. The relative amount of the granulating liquid as referred to the total particle volume of the starting material to be granulated ($V'/V = 20$ % by volume), the feed rate of the granulating liquid ($w' = 5.9\times 10^{-5}$ kg/sec) and the input temperature ($T_D'' = 70$ °C) were kept constant.

EXPERIMENTAL RESULTS

The results of the research work carried out in order to study the influence of the technical and apparative parameters listed at the beginning of the present paper will now be described. The influence of changes in the individual parameters upon the mean particle size of the granulated material obtained, the mean porosity of the granules and the relative amount of the "product fraction" are illustrated in the Figures. Considering the conclusions on the reproducibility of the experimental results, published in the second paper of the series [1], three parallel experiments were carried out for each experimental point. The points drawn into the Figures represent the mean value of three such parallel results. It should be noted in connection with the Figures that the only reason to connect the experimental points with straight lines was to illustrate the trends of the changes.

a) Influence of Changes in the Minimum Initial Bed Height and Bed Expansion on the Physical Properties of the Granules

In the case of a given diameter of the granulator, the minimum bed height of the material to be granulated can be altered by changing the amount of the material fed in. In the first experimental series, the initial particle volume was increased from 200×10^{-6} to 600×10^{-6} m^3, in steps of 100×10^{-6} m^3. Simultaneously, the minimum initial bed height showed an approximately threefold increase. Of course, in proportion with increasing the amount of the material, the amount of granulating liquid was also increased, so as to have a constant relative amount of granulating liquid as referred to the particle volume of the material to be granulated.

Fig. 1 shows the changes in mean granule diameter and mean porosity of granulated material plotted against the minimum initi-

al bed height. With increasing minimum initial bed height, the mean granule size shows at first an abrupt decrease and later on it converges to a limiting value. In addition, it is apparent that the change in mean granule size is strikingly large as the minimum starting bed height is increased from 6.4×10^{-2} to 8.7×10^{-2} m. The mean porosity of the granules closely follows any changes in the mean granule diameter. The relative amount of a granule fraction and any changes in this amount depending on the parameter under test are index numbers of considerable importance from the point of view of production. Fig. 2 shows the changes in the relative amount of the granules of the dimension $(0.2 \text{ to } 2.0)\times10^{-3}$ m plotted against the minimum starting bed height. The weight ratio of the granule fraction conforming to the limits $(0.2 \text{ to } 2.0)\times10^{-3}$ m is the highest (0.81 %) at a minimum starting bed height of 6.4×10^{-2} m. Further increasing the initial bed height is very disadvantageous from the point of view of this parameter.

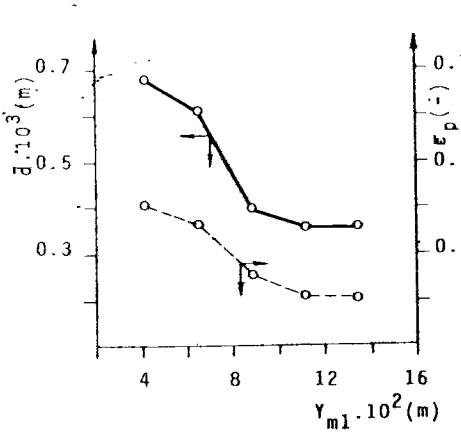

Fig. 1. $c' = 60$ kg/m³
$V'/V = 20$ vol.%
$w' = 5.9\times10^{-5}$ kg/sec

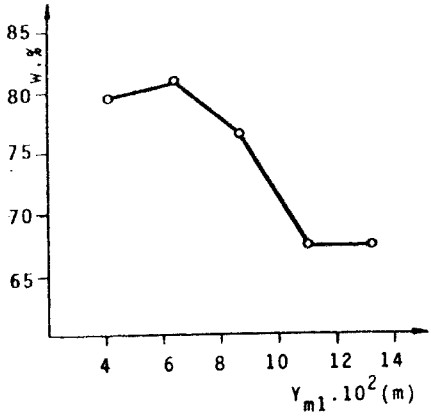

Fig. 2. d = $(0.2\text{-}2.0)\times10^{-3}$ m

The degree of expansion of the fluidized bed can be characterized in the simplest way by the ratio height of the fluidized

bed to the minimum bed height. During the granulation experiments, this ratio was approximately maintained at the predetermined value. With progressive agglomeration, the minimum bed height also changes (it generally increases). Accordingly, from time to time the air supply was stopped for a short period, the minimum bed height was determined, and the air flow rate was adjusted so as to obtain the same relative bed expansion.

In the experiments described so far, the ratio bed height to minimum bed height was the same ($Y/Y_m \approx 1.6$). In the study of the effect of bed expansion, the value Y/Y_m was increased from 1.3 to 2.5, in steps of 0.3, with the other parameters kept constant.

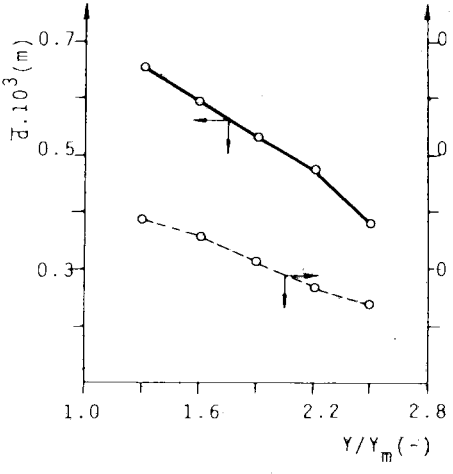

Fig. 3. c' = 60 kg/m³
V'/V = 20 vol.%
w' = 5.9x10⁻⁵ kg/sec

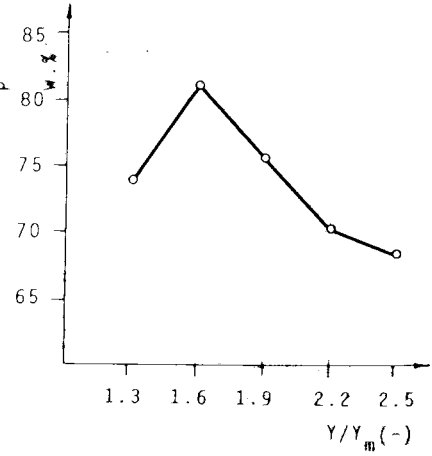

Fig. 4. d = (0.2-2.0)x10⁻³ m

Fig. 3 shows the changes in the mean granule size and the mean porosity plotted against the degree of bed expansion. While increasing the ratio height of the fluidized bed to the minimum bed height from 1.3 to 2.5, the mean granule size showed a - near-

ly linear - decrease. Upon increasing the bed expansion, the mean porosity of the granulates also decrease nearly linearly in the range studied. It is apparent from Fig. 4 that the weight fraction of the granules of the $(0.2 \text{ to } 2.0)_{\times}10^{-3}$ m size range first increases and thereupon it gradually decreases with increasing bed expansion. The maximum value is at - or near to - a bed expansion of 1.6.

b) Influence of Liquid Dispersion and Location of the Atomizer on the Physical Properties of the Granules

In the case of the two-fluid atomizer used in these experiments, the degree of liquid dispersion can be influenced by adjusting the pressure of the atomizing air. With constant feed rate of the liquid to be atomized, the degree of liquid dispersion is increased by increasing the air pressure. In order to determine the connection between the two variables, it would have been necessary to measure the drop size distribution in the atomized stream, and the variations of the latter as a function of the air stream. However, such a detailed study of atomization was beyond the scope of the present experiments and it was considered sufficient, in order to be able to draw conclusions of a qualitative nature, to study the effect of the degree of liquid dispersion in an indirect manner, through the influence of the changes in the atomizing air stream.

In the next series of experiments, the only changed parameter was the air mass flow of the atomizer. The atomizing air flow in these experiments was increased from $(6.7 \text{ to } 30.5)_{\times}10^{-5}$kg/sec in four steps. It is apparent from Fig. 5 that the mean particle size of the granulated material is not influenced to an appreciable degree even if the atomizing air flow is changed considerably. The mean granule diameter changes in the $(0.57 \text{ to } 0.66)_{\times}10^{-3}$ m range: at first it increases and thereupon it slightly decreases. The mean porosity of granules shows an abrupt increase and afterwards

its value remains constant. The relative amount of the granulated fraction corresponding to the size range $(0.2 \text{ to } 2.0)\times10^{-3}$ m changes according to a curve passing a flat maximum when plotted against increasing air atream - as shown in Fig. 6. However, it should be noted that when further increasing the atomizing air flow, at a value of 43.3×10^{-5} kg/sec, the experiment could no longer be evaluated. Accordingly, the changes in the physical properties of the granules brought about by the atomizing air stream are not as slow and gradual as could be judged on the basis of Figs. 5 and 6, but abrupt changes can be observed under a lower and over an upper limiting value. The explanation for this fact is that adequate dispersion of the liquid stops under a certain given air stream, whereas too fast an atomizing air stream virtually "shoots" the liquid into the layer and the material to be granulated clots unto the air distributor plate.

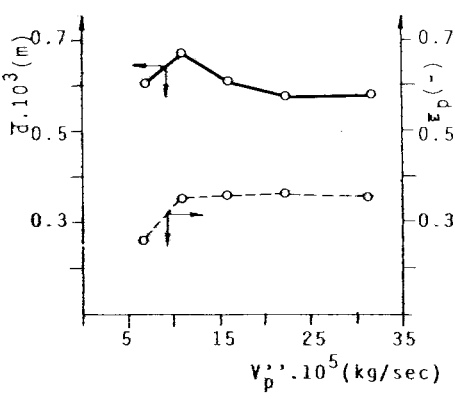

Fig. 5. c' = 60 kg/m³
V'/V = 20 vol.%
w' = 5.9×10^{-5} kg/sec

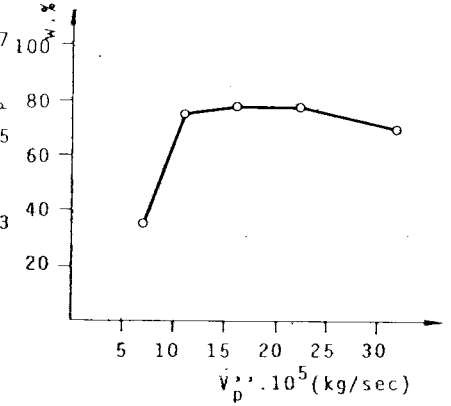

Fig. 6. d = $(0.2\text{-}2.0)\times10^{-3}$ m

The task of the next experimental series was to determine the effect of changes in the height of the atomizer on the physi-

cal properties of the granules produced. In these experiments, the vertical distance of the atomizer, as measured from the air distributor plate, was changed from 9.10^{-2} to 24.10^{-2} m in steps of 3.10^{-2} m.

At the same time, all other variables were maintained at a constant value. The mean particle size and mean porosity of the obtained granules plotted against the distance of the atomizer as measured from the air distributor is shown in Fig. 7, determined

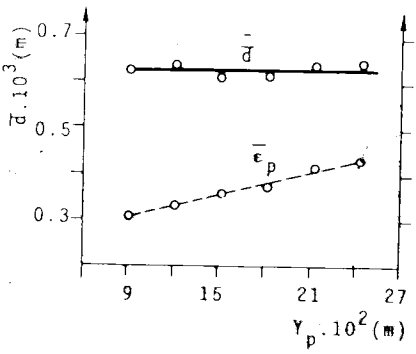

Fig. 7. c' = 60 kg/m³
V'/V = 20 vol.%
w' = 5.9×10^{-5} kg/sec

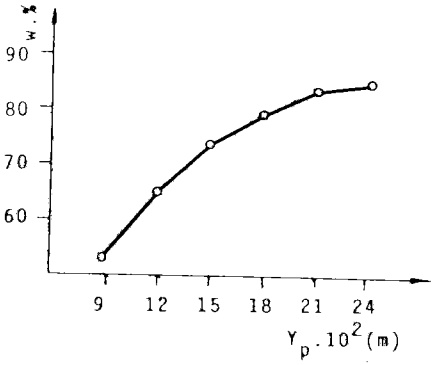

Fig. 8. d = $(0.2-2.0)\times10^{-3}$ m

in these experiments. It is apparent from the Figure that the height of the location of the atomizer does not influence the mean granule diameter to a considerable degree within the studied range. The mean granule size value fluctuates between about 0.60×10^{-3} and 0.65×10^{-3} m. In this case, the mean porosity does not follow the changes in mean diameter, but it gradually increases with the increasing distance between the air distributor plate and the atom-

izer. Location of the atomizer has a most marked influence on the granule size distribution of the product. This is illustrated by Fig. 8 which shows changes in the relative amount of the granule fraction corresponding to the predetermined size range - $(0.2\text{-}2.0)\times 10^{-3}$ m - plotted against the distance between the atomizer and the distributor. By lifting the atomizer from a height of 9.10^{-2} to 24.10^{-2} m, the amount of granules of product fraction was increased, according to the trend apparent from the Figure, from ∿ 53 % to ∿ 86 % by weight.

c) Influence of the Quality of the Air Distributor on the Physical Properties of the Granules

The influence of the quality of the distributor on the physical properties of the granules was studied with the application of four different distributors, under otherwise identical conditions. The distributor plates studied were the following: porous glass plates, sieves of 25×10^{-6} and 90×10^{-6} m openings, and a perforated plate of 12 mm perforations with a free surface ratio of 0.45; in order to prevent the escape of the granules, a sieve of 25×10^{-6} m openings was placed under the latter.

These experiments revealed the result that the mean granule size, mean porosity and particle size distribution of the granulated material obtained are practically independent on the quality of the air distributor.

EVALUATION OF THE EXPERIMENTAL RESULTS

According to the results of the present experiments, increasing the minimum starting bed height of the starting material decreases the mean granule size, and together with it, the mean

porosity of the final product. An explanation for this phenomenon can be given - as has already been pointed out in the introduction - by two reasons. Increasing the starting bed height over a certain limit, this results in decreased uniformity of the fluidization, slugging and strong bubble formation being produced. The latter brings about an increase in the degree of regranulation. The second important effect of increasing the initial bed height in fluidized bed granulation is that - as far as the ratio of the wetted surface area of the bed to the total surface area is unchanged - increasing the bed height decreases the probability of the solid particles meeting a liquid droplet. In granulation tasks, it is generally required that as much of the product as possible should conform to the size limits defined by the purpose of application.

With this in mind, and on the basis of Fig. 2 and other experimental findings, it can be stated that in fluidized bed granulators it is preferable to choose an initial bed height that corresponds to 1/2 to 2/3 of the bed diameter (i.e. the inner diameter of the granulator). In the case of initial bed higher than that, the amount of particles left ungranulated will increase and the amount of the granules of product fraction will decrease.

In the case of a given starting material and a given binder, the degree of regranulation primarily depends on the intensity of the motion of the particles and on the degree of bed expansion. The decisive importance of this parameter regarding final granule composition was confirmed by the present experiments and is also in agreement with the findings of other authors [5, 6, 7, 8]. According to Fig. 3, the mean granule diameter and porosity show an abrupt decrease with increasing bed expansion, due to the increased abrasion of the granules. It can be concluded on the basis of Fig. 4 that the approximately optimum value is a relative bed expansion to about 1.6 times the initial value.

The experimental results illustrated in Figs. 5 and 6 justify the conclusion that the degree of liquid dispersion has, within certain limits, no appreciable influence upon the physical proper-

ties of the granules produced in the process. Increasing the atomizing air flow, primarily influences the particle size distribution however, as it is apparent from Fig. 6, in the middle part of the studied range, over a rather wide interval, even this influence is negligible. The amount of the "product fraction" is practically unchanged when the specific amount of atomizing air is increased to double its value, from 1.8 to 3.6 kg air/kg liquid.

The conclusions of the authors as to the influence of the degree of atomization agree with the opinion of MÖBUS [8] and disagree with the experimental results of DAVIES and GLOOR [9]. In addition to the different experimental conditions and techniques, this discrepancy can be explained by the fact that the drop size distribution of the atomized liquid, or any changes in it, were unknown in both cases and consequently the experimental results cannot be compared.

Some authors [6, 9] observed a decrease in mean granule size if the distance of the atomizer, as measured from the air distributor plate, was increased. In their opinion this is caused by the fact that the drops must travel a longer way to reach the bed if the position of the atomizer is higher. In this case, the smaller droplets may dry and lose their adhesive property. In the opinion of the authors of the present paper, whether the above-mentioned process - undesired with regard to granulation - does or does not occur, is determined not only, and not primarily by the position of the atomizer. Factors such as, e.g. the temperature of air leaving the bed, the concentration of the granulating liquid, and the fineness of the spray, etc., are responsible in this respect. The above process did not occur in the range studied in the present experiments and it can be stated on the basis of Fig. 7 that when changing the distance of the atomizer, as measured from the distributor, within the practically feasible range, the mean granule size remains unchanged. However, an interesting phenomenon can be observed on Fig. 7. This is the following: the higher position of the atomizer leads (even in the case of decreasing mean particle size) to the production of granules of higher porosity. This observation can be explained by the fact that increasing the

distance of the nozzle from the air distributor plate, granule production can also occur in a bed of lower density, where the abrasive and compacting effects are less pronounced than in a fluidized bed of higher density. In the case of an unchanged cone angle of spray, the higher position of the atomizer increases the wetted surface area of the bed, i.e. the wetting is more uniform; and consequently the amount of granules of "product fraction" is increased (cf. Fig. 8). Of course, this can be true only up to a certain limit, since in the case of a too highly positioned nozzle, part of the granulating liquid wets the wall of the granulator instead of the bed as was pointed (out in the introduction), this is disadvantageous from several points of view.

On the basis of the results of these experiments and the experience on granulation acquired over several years, the following formula is proposed for the determination of the approximately optimum distance of the atomizer as measured from the air distributor plate:

$$Y_a = Y_{m1} + 0.8 \frac{D_b}{2 \operatorname{tg} \frac{\alpha}{2}} \qquad (1)$$

Equation (1) expresses that the granulating liquid is to be atomized on top of the dense layer ($Y_d \approx Y_m$) in such a way - in order to prevent "carry up to the wall" - that the diameter of the circular wetted patch on top of the dense layer is 0.8 times the diameter of the apparatus.

The result obtained in connection with the influence of the type of distributor is of major importance. It can be concluded that it is unnecessary to apply distributors made of a porous plate, whose production on an industrial scale is difficult and expensive, and whose resistance against flow is high. The particle size distribution and other physical properties of the granulated material by the granulation process remain unchanged, if instead of a porous plate, a sieve of adequate mesh is used as a support. A perforated plate of large free cross sectional area is placed under the sieve to supply mechanical strength.

The results reported in the present paper were applied in the design of the pilot-plant and the industrial-scale fluidized bed granulator. The correctness of the design principles is confirmed by the fact that the physical properties of the granules produced by the equipment, correspond in every way to the predetermined standard.

SYMBOLS USED

c'	concentration of the granulating liquid (kg/m³)
D_b	diameter of the apparatus (m)
$\bar{d}$	mean granule diameter (m)
d	particle size or sieve pore size (m)
T_b''	temperature of input air (°C)
V	total particle volume of material to be granulated (m³)
V'	volume of granulating liquid (m³)
V_p''	atomizing air stream (kg/sec)
V'/V	relative amount of granulating liquid (vol.%)
w'	feed rate of granulating liquid (kg/sec)
Y	height of the fluidized bed (m)
Y_m	minimum bed height (m)
Y_{m1}	minimum starting bed height (m)
Y/Y_m	degree of bed expansion (dimensionless)
Y_d	height of the dense layer (m)
Y_a	distance of the spray nozzle, as measured from the air distributor (m)
α	angle of spray (degree)
$\bar{\varepsilon}_p$	average porosity of granules (dimensionless)

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РЕЗЮМЕ

В целях проектирования установок, гранулирующих посредством псевдоожиженного слоя, и определения оптимальных условий их работы важно знать каков действие оказывают технологические и аппаратурные характеристики на физические свойства образующихся гранул. В литературе встречается лишь незначительное число работ, подробно занимающихся этим вопросом. Авторы данной статьи на основании экспериментов, проведенных в условиях лабораторного реактора периодического действия с псевдоожиженным слоем, определили отношение минимальной высоты слоя/к диаметру слоя, зависимость размера слоя от скорости газа, а также то, в какой степени влияет на физические свойства гранул вид воздухораспределительной пластины и расстояние распылительной головки от этой пластины. Кроме того, авторы сравнили свои экспериментальные результаты с соответствующими литературными данными, и далее представили оптимальные значения вышеупомянутых переменных.

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STUDIES ON THE HYDRODYNAMICS OF FLUIDIZED LAYERS III. CALCULATION OF LAYER EXPANSION IN SYSTEMS FLUIDIZED WITH A LIQUID

Z. ORMÓS and T. BLICKLE

(Research Institute for Technical Chemistry of the Hungarian Academy of Sciences, Veszprém)

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The equations for the calculation of the void fraction of layers fluidized with a liquid, most widely known from literature, and those derived from the first paper of the series are briefly described. The equations are transformed to a form which can readily be applied in practice even in the case of porous particles. The mean values of the "constant coefficients" of the equations, and the dependence or independence of the different "constants" on the various parameters was studied. The calculation methods are evaluated by the comparison of void fraction values determined experimentally and calculated by the proposed equations.

The expansion of fluidized layers can - among others - be characterized by the void fraction [1]. A number of calculation methods are known for the determination of the void fraction of layers fluidized with a liquid on the basis of the flow rate of the liquid, the diameter of the particles and other parameters. In the previous paper of the present series, an equation was derived in a theoretical manner which enables the void fraction of layers fluidized with a liquid to be calculated [2].

The present paper briefly summarizes the most important equations for the calculation of void fractions known from litera-

ture. Equations taken both from literature and proposed by the authors are evaluated critically. In the course of the latter, the dependence or independence of the "constant coefficients" of the equations on the parameters of the liquid and of the particles was studied, and the applicability of the equations was put to a trial by the comparison of results obtained, on the one hand, by calculation with the equations, and, on the other, by experimental measurements.

METHODS FOR THE CALCULATION OF THE VOID FRACTION OF LAYERS FLUIDIZED WITH A LIQUID

When deriving equations for the calculation of the void fraction of fluidized systems and studying the laws of such systems, a number of researchers have come to the conclusion that the void fraction is proportional to the flow rate of the fluid and the falling rate of the individual particles.

To a considerable degree, RICHARDSON and ZAKI [3] promoted the theories related to the expansion of fluidized layers known up to now. The equations they proposed describe the dynamic equilibrium of the individual particles as a function of the particulars of the layer and of the apparatus. The following groups were determined by analysis:

$$\frac{U'}{u_e} = f\left(Re, \frac{d}{D}, \bar{\varepsilon}'\right) \tag{1}$$

The data relating to layer expansion were given in the following form:

$$\frac{U'}{u_e} = \bar{\varepsilon}_c'^{\,a_1} \tag{2}$$

According to the above equation, the function flow rate of the liquid vs. void fraction, when drawn in a lg-lg co-ordinate system, gives a straight line whose slope is a_1. The experimental data were examined by this method and the following equations were presented for the calculation of a_1:

$$a_1 = (4.35 + 17.5 \frac{d}{D}) Re^{-0.03}, \quad \text{if } 0.2 < Re < 1 \tag{3}$$

$$a_1 = (4.45 + 18.0 \frac{d}{D}) Re^{-0.1}, \quad \text{if } 1 < Re < 200 \tag{4}$$

$$a_1 = 4.45 \cdot Re^{-0.1}, \quad \text{if } 200 < Re < 500 \tag{5}$$

$$a_1 = 2.39, \quad \text{if } 500 < Re < 500 \tag{6}$$

The Reynolds-number contained in these expressions is the following:

$$Re = \frac{U' \, d \, \rho'}{\mu'} \tag{7}$$

JOTTRAND [4] proposed two equations for the calculation of the void fraction of fluidized layers. One of these is essentially identical to Equation (2) described in the foregoing, whereas the other is the following:

$$\lg \frac{u_e}{U'} = a_2 (1 - \bar{\epsilon}_c') \tag{8}$$

Equation (8) represents, according to the author, a good approximation if the void fraction is within the range of 0.7 to 1 and the value of a_2 is 2.63.

In his book on fluidization, BLICKLE [5] proposed - among others - the following expression for the calculation of the void fraction:

$$\bar{\epsilon}_c' - \epsilon_m' = \frac{U' - U_m'}{u_e} \tag{9}$$

It has already been pointed out in connection with the examination of the above Equation that a better agreement with expe-

rimental data can be obtained by application of the following supplemented formula [6]:

$$\bar{\varepsilon}_c'^2 - \varepsilon_m'^2 = a_3 \frac{U' - U_m'}{u_e} \tag{10}$$

SAXTON and his co-workers [7] proposed an equation for the calculation of the void fraction of layers fluidized with a liquid based upon the cell-model theory of homogeneous fluidization:

$$(1 - \bar{\varepsilon}_c')^{-1/3} - (1 - \varepsilon_m')^{-1/3} = 18.8\ Re\ Ar^{-0.86} \tag{11}$$

where the Reynolds-number is equal to Equation (7) and the Archimedes number is the following:

$$Ar = \frac{(\rho - \rho')\rho' d\ g}{\mu'^2} \tag{12}$$

Connections describing the streaming of the fluid, the motion of the particles and the layer expansion in systems fluidized with a liquid were derived, starting from the physical model; these were described in the first paper of the present series [2]. The following equation was obtained for the expansion of layers fluidized with a liquid [2]:

$$\bar{\varepsilon}_c' = 1 - 0.75\ (1 - \frac{U'}{u_e})^{3/2} \tag{13}$$

In the practical application of the above equation it was found that the value of the constant differs in practice from the theoretically derived value of 0.75 to a considerable degree, and consequently the equation can be written in the following form [6, 8]:

$$\bar{\varepsilon}_c' = 1 - a\ (1 - \frac{U'}{u_e})^{3/2} \tag{14}$$

Considering that Equation (14) is valid even at the minimum fluidization rate, the following equation can be given for the calculation of the void fraction [2]:

$$\bar{\varepsilon}'_c = 1 - \frac{1 - \varepsilon'_m}{(1 - \frac{U'_m}{u_e})^{3/2}} (1 - \frac{U'}{u_e})^{3/2} \qquad (15)$$

In the following, the applicability of Equations (2), (8), (10), (11), (14) and (15) is examined according to the two points of view mentioned in the introduction of the present paper. Naturally, in addition to these equations, a large number of calculation methods have been described in literature [5, 6, 9, 10, 11, 12, 13, etc.]. However, the description and evaluation of these is outside of the scope of the present paper whose intention is only to illustrate the applicability of a few of the more widely known calculation methods and to compare them with the Equations (14) and (15) derived by the authors.

EXPERIMENTAL AND MEASUREMENT TECHNIQUES

The technique based on the determination of layer height was applied for the determination of the mean void fraction in the experimental studies on the expansion of layers fluidized with a liquid. The experiments were carried out in a cylindrical glass apparatus with a diameter D = 0.04 m which contained a fritted glass disk of the porosity of G2 in order to sustain the fluidized layer. The height of the latter was measured, to an accuracy of a few millimetres, by means of a scale secured to the wall of the apparatus and the mean void fraction was calculated with the following formula:

$$\bar{\varepsilon}'_Y = \frac{Y - \frac{G}{\rho F}}{Y} \qquad (16)$$

The quantity of the streaming liquid (water) was measured with a rotameter. The linear flow rate was calculated from the volumetric flow rate and the cross sectional area of the apparatus.

The minimum void fraction values were calculated from the minimum fluidization layer height by means of Equation (16). The minimum layer height was determined by measuring the layer height produced upon slow reduction of the liquid flow rate.

The minimum fluidization rate was obtained from the measured mean void fraction-flow rate values by extrapolation of the flow rate to the minimum void fraction.

The mean falling rate of the tested particle fractions was determined, having plotted the liquid flow rate against the measured mean void fraction values in a lg-lg plot, by graphical extrapolation of the liquid flow rate to the value of $\bar{\varepsilon}' \to 1$.

The mean porosity of the particles was determined by application of a technique, based on the identical space filling properties of particles of similar shape, proposed by the authors of this paper [14].

EXPERIMENTAL RESULTS

The experiments on layer expansion were carried out with a total of 29 particle fractions prepared of 5 different materials. The streaming liquid in the experiments was tap water of 12 - 14 ^{o}C temperature. The extent of layer expansion was determined with each particle fraction at 13 to 15 different flow rates. The dependence of the void fraction of the layer on the flow rate of the liquid is not presented in detail, merely the most important data are summarized in tabular form.

The most important physical properties of the examined granular materials (such as density, and porosity), the mass of the material weighed in for the experiment, the mean size and the size limits of the tested grain fractions, as well as the experimental data pertaining to the minimum void fraction, minimum fluidization rate and the mean falling rate of the particles are summarized in Tables 1. to 5. shown in the following.

Table 1. System glass beads—water

ρ = 2960 kg/m^3, ε_p = 0, G = 0.08 kg

	$\bar{d} \cdot 10^3$ (m)	ε'_{mt}	$U'_m \cdot 10^2$ (m/sec)	$\bar{u}_e \cdot 10^2$ (m/sec)
1	0.15	0.44	0.06	2.0
2	0.18	0.44	0.12	2.5
3	0.25	0.44	0.20	3.2
4	0.42	0.44	0.30	4.2

Table 2. System sand—water

ρ = 2635 kg/m^3, $\bar{\varepsilon}_p$ = 0, G = 0.05 kg

	$d \cdot 10^3$ (m)	ε'_{mt}	$U_m \cdot 10^2$ (m/sec)	$\bar{u}_e \cdot 10^2$ (m/sec)
1	0.10 - 0.20	0.51	0.08	1.2
2	0.20 - 0.32	0.51	0.13	2.5
3	0.32 - 0.40	0.51	0.19	3.9
4	0.40 - 0.50	0.51	0.26	5.0
5	0.50 - 0.63	0.51	0.39	5.9
6	0.63 - 0.80	0.51	0.64	7.0
7	0.80 - 1.00	0.51	1.10	9.0

Table 3. System hematite—water

$\rho = 4150\ kg/m^3$, $\bar{\varepsilon}_p = 0.12$, $G = 0.09\ kg$

	$d \cdot 10^3$ (m)	ε'_{mt}	$U'_m \cdot 10^2$ (m/sec)	$\bar{u}_e \cdot 10^2$ (m/sec)
1	0.10 - 0.20	0.56	0.10	1.5
2	0.20 - 0.32	0.56	0.30	4.0
3	0.32 - 0.40	0.55	0.60	6.0
4	0.40 - 0.50	0.55	0.95	7.5
5	0.50 - 0.63	0.56	1.30	9.5
6	0.63 - 0.80	0.57	1.70	12.0
7	0.80 - 1.00	0.57	2.20	15.0

Table 4. System porous nickel spheres—water

$\rho = 7450\ kg/m^3$, $\bar{\varepsilon}_p = 0.32$, $G = 0.13\ kg$

	$d \cdot 10^3$ (m)	ε'_{mt}	$U'_m \cdot 10^2$ (m/sec)	$\bar{u}_e \cdot 10^2$ (m/sec)
1	0.20 - 0.32	0.60	0.5	7.0
2	0.32 - 0.40	0.59	0.8	12.0
3	0.40 - 0.50	0.59	1.1	18.0
4	0.50 - 0.63	0.59	1.4	25.0
5	0.63 - 0.80	0.58	1.8	33.0

Table 5. System burnt clay—water

ρ = 2420 kg/m^3, $\bar{\varepsilon}_p$ = 0.50, G = 0.03 kg

	$d \cdot 10^3$ (m)	ε'_{mt}	$U'_m \cdot 10^2$ (m/sec)	$\bar{u}_e \cdot 10^2$ (m/sec)
1	0.20 - 0.25	0.75	0.12	1.4
2	0.25 - 0.32	0.75	0.18	1.8
3	0.32 - 0.40	0.76	0.25	2.4
4	0.40 - 0.50	0.76	0.36	3.2
5	0.50 - 0.63	0.76	0.45	3.8
6	0.63 - 0.80	0.76	0.55	4.6

APPLICATION AND EVALUATION OF THE CALCULATION METHODS

The starting point in the examination of the formulas proposed for the calculation of the void fraction is that these enable determination of the free volume or liquid-filled volume fraction. There is no problem in the case of materials consisting of compact granular materials; however in the case of porous particles the void fraction values determined in practice experimentally refer not only to the free space between the particles, but also include the pore space of the particles filled with the liquid. This is brought about by the fact that the density of the particles is determined in most cases with the pycnometer technique with the application of a liquid which has good wetting properties and in which the material of the particles is insoluble. This means that by this technique practically the density of the solid forming the material of the particles is determined and only the closed pores and channels, or those of such small dimensions as to be impermeable for the liquid may cause some deviation. Moreover, it often

occurs that the density values are simply taken from literature or from handbooks; however, such data most frequently refer to the compact material. Whether it is a density value determined by a pycnometer, or one taken from literature that is substituted into Equation (16), the obtained (experimentally determined) void fraction values include the total volume permeable by the liquid. The aforesaid should be taken into consideration in the evaluation of the calculation methods, because in the case of heap of porous particles this is the only reliable method of evaluation.

Starting from the definition of the void fraction and based on geometric considerations, the following connection between the two kinds of void fraction values may be written:

$$\bar{\varepsilon}'_t = \varepsilon_p + (1 - \varepsilon_p)\,\bar{\varepsilon}'_c \tag{17}$$

Accordingly, in order to be able to carry out the calculation, the mean porosity of the heap of particles has to be known. A simple measuring technique, which can be utilized in an easy way, has been developed by the authors [14].

In the application of Equation (2) described by RICHARDSON and ZAKI [3] the first question is the following: which is the equation that is to be used for the calculation of the "constant" a_1. Calculations were carried out in this respect and it was concluded that in the case of the models encountered in practice it is Equation (4) that is most frequently applicable. Accordingly, on the basis of Equations (2), (4) and (7) the following can be written:

$$\bar{\varepsilon}'_t = \varepsilon_p + (1 - \varepsilon_p)\left(\frac{U'}{u_e}\right) \frac{Re^{0.1}}{4.45 + 18\,\frac{d}{D}} \tag{18}$$

The next question which is encountered is whether the Reynolds number is to be calculated for each separate liquid flow rate. The above problem is unequivocally settled by the data presented in Table 6.

Table 6. System sand—water

$d \cdot 10^3$ (m)	a_1 calculated $\bar{\varepsilon}' = 0.6$	a_1 calculated $\bar{\varepsilon}' = 0.8$	a_1 calculated $\bar{\varepsilon}' = 1$	a_1 measured (mean)
0.10 - 0.20	5.1	4.5	4.3	4.1
0.20 - 0.32	4.4	4.0	3.8	3.7
0.32 - 0.40	4.1	3.8	3.6	3.4
0.40 - 0.50	3.9	3.6	3.5	3.2
0.50 - 0.63	3.8	3.5	3.4	3.0
0.63 - 0.80	3.6	3.4	3.3	2.9
0.80 - 1.00	3.5	3.3	3.2	2.8

As it is apparent from Table 6, the agreement between the a_1 values determined experimentally on the one hand, and calculated with Equation (4) on the other, is best if $\bar{\varepsilon}' = 1$, i.e. if the mean falling velocity of the particles is substituted into the equation.

Considering this fact, Equation (18) can be written in the following form:

$$\bar{\varepsilon}_t' = \varepsilon_p + (1 - \varepsilon_p)\left(\frac{U'}{u_e}\right)\frac{(u_e \, d \, \rho')^{0.1}}{\mu'^{0.1}(4.45 + 18 \frac{d}{D})} \qquad (19)$$

Fig. 1 shows the difference between the void fraction values determined experimentally and calculated by Equation (19), plotted against the experimentally determined value. It can be concluded from the Figure that the relative deviation is in all cases lower than ± 10 %, and in the overwhelming majority of the cases it is lower than + 5 %. Computer evaluation led to the conclusion that the mean relative deviation is ± 2 %.

Equation (8), described by JOTTRAND [4], can - considering Equation (17) - be written in the following form:

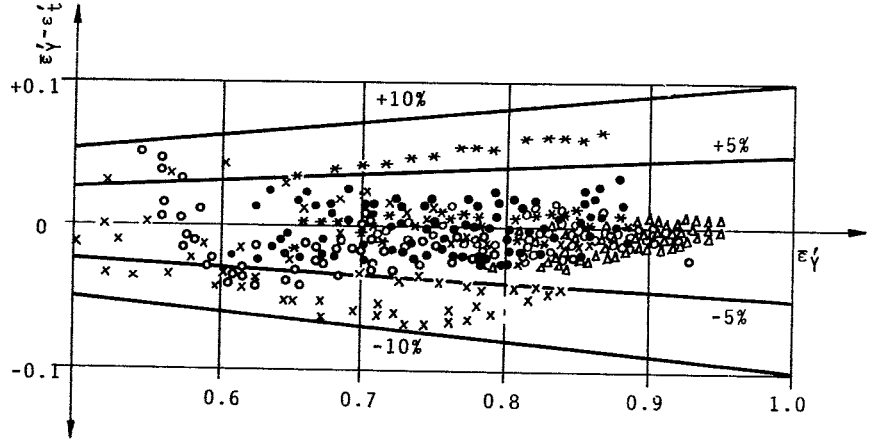

Fig.1. x - glass beads; o - sand; • - hematite; * - porous nickel spheres; Δ - porous burnt clay

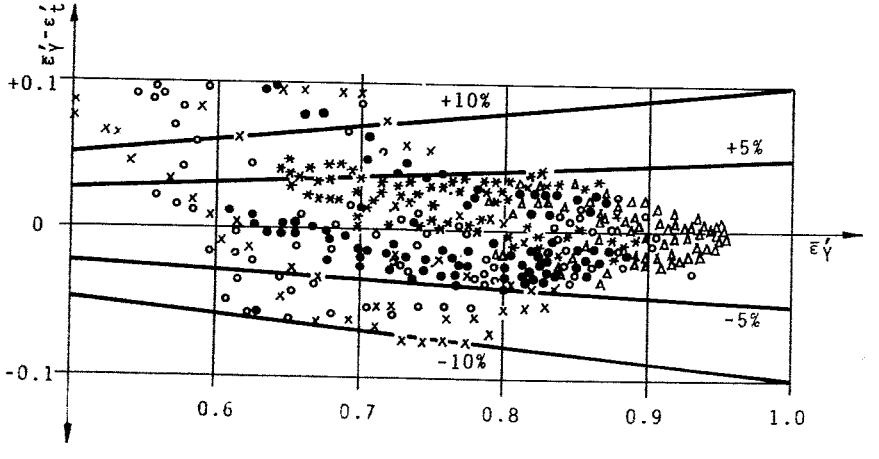

Fig.2. x - glass beads; o - sand; • - hematite; * - porous nickel spheres; Δ - porous burnt clay

$$\bar{\varepsilon}'_t = 1 - \frac{1 - \varepsilon_p}{a_2} \lg \frac{u_e}{U'} \qquad (20)$$

The value of the "constant" a_2 of the equation was determined for the model substances used in the experiments in about 400 cases and $a_2 = 1.75$ was obtained as a mean value. The mean scattering of the "constant" a_2, as a function of flow rate, was found to be $\sigma = \pm 9$ %, whereas the scattering depending on a particle size was $\sigma = \pm 13$ %.

The difference in void fraction values determined experimentally and calculated by Equation (20) ($a_2 = 1.75$), plotted against the experimentally determined value is shown in Fig. 2. It is apparent from the Figure that the relative deviation is, in most cases, lower than ± 10 % and the average relative deviation is +5 and -3 %.

On the basis of Equation (10) [5] and taking Equation (17) into consideration, the following equation can be written:

$$\bar{\varepsilon}'_t = \varepsilon_p + (1 - \varepsilon_p) \left(\frac{\varepsilon'_{mt} - \varepsilon_p}{1 - \varepsilon_p}\right)^2 + a_3 \frac{U' - U'_m}{u_e}^{1/2} \qquad (21)$$

The mean value of the "constant" is $\bar{a}_3 = 1.15$, its mean scattering depending on the flow rate of the liquid is $\sigma = \pm 18$ %, its mean scattering depending on the particle size is $\sigma = \pm 16$ %.

The difference in void fraction values determined experimentally and calculated by Equation (21) ($a_3 = 1.15$), plotted against the experimentally determined value is shown in Fig. 3. It can be concluded from the Figure that except for a few cases the relative deviation is lower than ± 10 %. The mean relative deviation was found to be ± 4 %.

In the examination of Equation (11) derived by SAXTON and his co-workers [7] it was found possible to bring it to a simpler form by substitution of Equations (7) and (12):

$$(1 - \bar{\varepsilon}')^{-1/3} - (1 - \varepsilon'_m)^{-1/3} = \frac{U'}{u_e} \qquad (22)$$

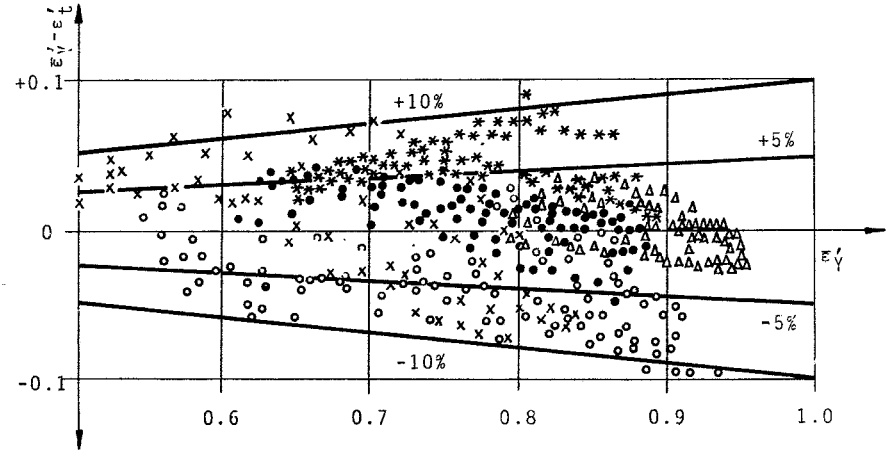

Fig.3. x - glass beads; o - sand; • - hematite; * - porous nickel spheres; Δ - porous burnt clay

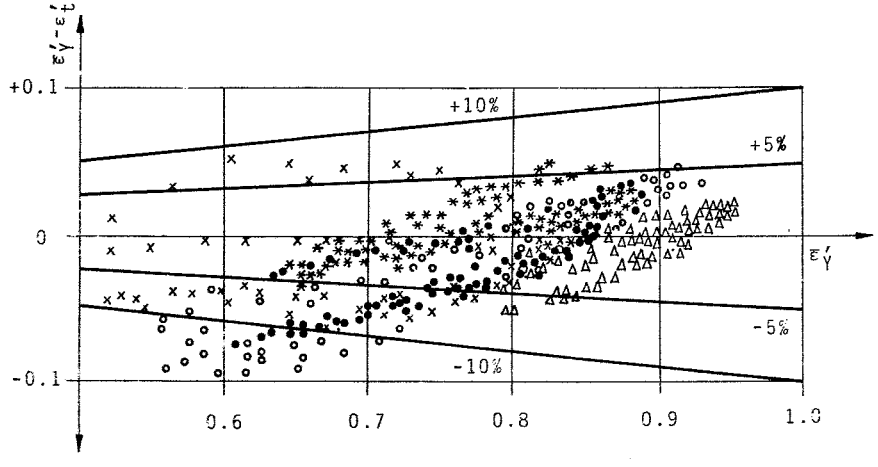

Fig.4. x - glass beads; o - sand; • - hematite; * - porous nickel spheres; Δ - porous burnt clay

On the basis of Equations (22) and (17), the following formula can be written for the calculation of the void fraction:

$$\bar{\varepsilon}'_t = 1 - \frac{(1 - \varepsilon'_{mt})(1 - \varepsilon_p)}{[(1 - \varepsilon_p)^{1/3} + (1 - \varepsilon'_m)^{1/3} \frac{U'}{u_e}]^3} \tag{23}$$

The difference in void fraction values determined experimentally and calculated by Equation (23), plotted against the experimentally determined values, is shown in Fig. 4. It is apparent from the Figure that in the overwhelming majority of the cases the relative deviation is lower than +5 and -10 %. The mean relative deviation is +2 and -5 %.

Taking Equations (14) [2] and (17) into consideration the Equation derived by the authors is the following:

$$\bar{\varepsilon}'_t = 1 - a_4 (1 - \varepsilon_p)(1 - \frac{U'}{u_e})^{3/2} \tag{24}$$

It was found in the experiments that the mean value of the "constant" $\bar{a}_4 = 0.55$, its average scattering depending on the flow rate is $\sigma = \pm 6$ % and its average scattering depending on the particle size is $\sigma = \pm 10$ %. Accordingly, Equation (24) can be written in the following form:

$$\bar{\varepsilon}'_t = 1 - 0.55 (1 - \varepsilon_p)(1 - \frac{U'}{u_e})^{3/2} \tag{25}$$

The difference in mean void fraction values determined experimentally and calculated by Equation (25) plotted against the experimentally determined value is shown in Fig. 5. It is apparent from the Figure that the relative deviation is in all cases lower than ± 10 % and in the overwhelming majority of the cases lower than ± 5 %. The average mean deviation is +3 and -2 %.

Equation (15) [2], as written on the basis of Equation (14) derived by the authors can be brought to a simpler form:

$$\bar{\varepsilon}'_t = 1 - (1 - \varepsilon'_{mt})(\frac{u_e - U'}{u_e - u'_m})^{3/2} \tag{26}$$

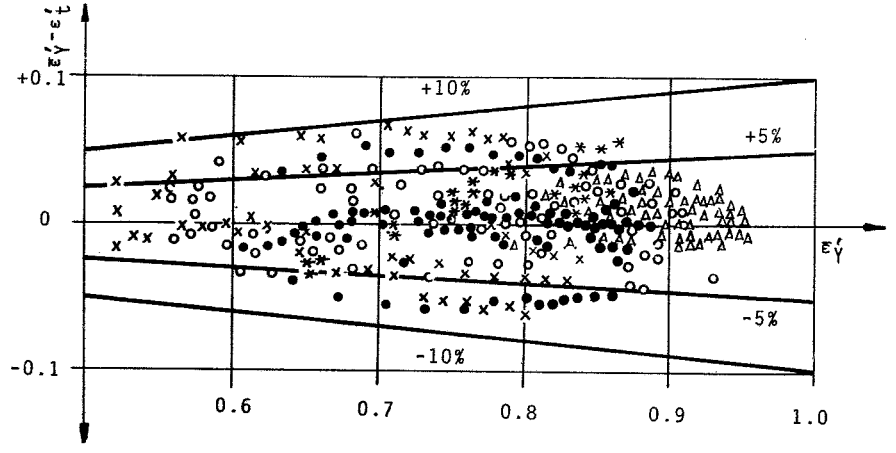

Fig.5. x - glass beads; o - sand; • - hematite; * - porous nickel spheres; Δ - porous burnt clay

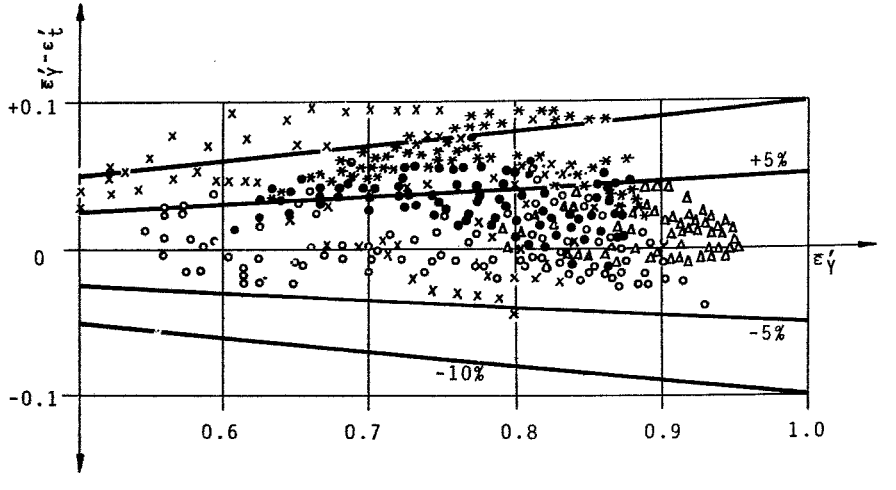

Fig.6. x - glass beads; o - sand; • - hematite; * - porous nickel spheres; Δ - porous burnt clay

The difference in the void fraction values determined experimentally and calculated by Equation (26), plotted against the experimentally determined values, is illustrated in Fig. 6. It can be concluded from the Figure that the relative deviation of the measured and calculated values is in the overwhelming majority of the cases lower than +10 and -5 %. The mean relative deviation is +4 and -2 %.

Summarizing the aforesaid it can be concluded that from among the formulas used for the calculation of the void fraction of layers fluidized with a liquid, Equation (19) derived from the Equation (4) of RICHARDSON and ZAKI [3], and Equation (25) derived from the Equation (14) by the authors of the present paper [2] are those yielding results which best approximate the values determined experimentally.

The agreement was also fairly good in the case of the other examined formulas; however, in case of these the mean relative deviation was on the one hand higher, e.g. Equations (20) and (21), and on the other the higher deviation is asymmetrical, e.g. with Equations (23) and (26). It is to be noted that from among the above Equations (20) and (23) yield values which at higher layer expansions show a good agreement with the experimental data. Equations (19) and (25) describe the layer expansion correctly in the whole range and consequently the application of these is recommended for the calculation of the expansion of fluidized layers.

SYMBOLS USED

a_1, a_2, a_3, a_4 constans

Ar Archimedes-number [cf. Equation (12)]

d diameter of the particles (metre)

$\bar{d}$ mean diameter of the particles (metre)

D diameter of the apparatus (metre)

F cross sectional area of the apparatus (m^2)

g gravitational acceleration (m/sec^2)

G mass of the particles present in the layer (kg)

Re Reynolds-number [cf. Equation (7)]

u_e falling rate of the particles (m/sec)

$\bar{u}_e$ mean falling rate of the particles (m/sec)

U' linear flow rate of the liquid as referred to the total cross sectional area of the apparatus (m/sec)

U'_m minimum fluidization liquid flow rate (m/sec)

Y height of the layer (m)

Y_m minimum layer height (m)

$\bar{\varepsilon}'$ mean void fraction of the layer

$\bar{\varepsilon}'_c$ calculated mean void fraction of the layer

ε'_m minimum void fraction of the layer

ε'_{mt} minimum total void fraction or liquid volume fraction of the layer

ε_p pore volume fraction of the particles

$\bar{\varepsilon}_p$ mean pore volume fraction of the particles

$\bar{\varepsilon}'_t$ calculated mean total void fraction or liquid volume fraction of the layer

$\bar{\varepsilon}'_Y$ mean total void fraction or liquid volume fraction, determined on the basis of layer height measurement

μ' dynamic viscosity of the liquid (kg/sec·m)

ρ density of the particles (kg/m^3)

ρ' density of the liquid (kg/m^3)

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РЕЗЮМЕ

В данной статье авторы кратко ознакомливают с имеющимися в литературе наиболее распространенными уравнениями, а также с выведенными ими в предыдущей статье данного цикла зависимостями, для вычисления доли свободного объема псевдоожиженных посредством жидкости слоев. Указанные зависимости приводятся к виду, практически непосредственно применимому, распространяющемуся даже на случай пористых частиц. Авторами определены средние значения имеющихся в уравнениях "постоянных сомножителей", кроме того, "постоянные" были проверены на зависимость от различных параметров. Была проведена проверка расчетных методов посредством сравнения полученных экспериментально и рассчитанных по уравнениям значений доли свободного объема.

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VERFAHREN ZUR HERSTELLUNG VON FETTSÄUERZUCKERESTERN

A. UJHIDY, J. SZÉPVÖLGYI und Z. SZABÓ*

(Forschungsinstitut für Technische Chemie der Ungarischen
Akademie der Wissenschaften, Veszprém und
*Zentralforschungsinstitut für die Lebensmittelindustrie, Budapest)

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Die Darstellung einer Gruppe der oberflächenaktiven Stoffe, der Fettsäurezuckerester Saccharosepalmitat und Saccharosestearat wurde untersucht, mit besonderer Rücksicht auf die Erhöhung des Monoestergehaltes im Produkt. Die optimalen Parameter der chargenweisen Darstellung des an Monoester reichen Fettsäurezuckeresters im Laboratoriummaßstab werden auf Grund der Versuchsergebnisse angegeben. Versuche zur halbkontinuierlichen Darstellung von Fettsäurezuckerestern im Dünnschichtreaktor wurden ebenfalls durchgeführt.

EINLEITUNG

Die Zuckerester der Fettsäuren werden im allgemeinen durch die Umesterung von C_{15}-C_{20} Fettsäurealkylestern mit einem Zucker in Lösung, in Anwesenheit eines geeigneten Katalysators hergestellt.

Die ersten Versuche zur Darstellung von Zuckerester wurden Mitte des vorigen Jahrhunderts durchgeführt, als BERTHELOT [1] einen Zuckerester durch Erhitzen von Saccharose mit Stearinsäure herzustellen versuchte. LORAND [2] gewann den Zuckerester der Palmitinsäure in der Reaktion von Zucker mit Palmitinsäureanhydrid in Monochloressigsäure als Lösungsmittel, in Anwesenheit eines Magnesiumperchlorat-Katalysators.

Die Umesterung des Methylstearats mit Zucker wurde von OSIPOW und Mitarb. [3] eingehend untersucht in Dimethyl-formamid und Dimethylsulfoxyd als Lösungsmittel.

Die Umesterung ist eine Gleichgewichtsreaktion, und das Gleichgewicht soll durch die rasche Entfernung des in der Reaktion gebildeten Methanols in Richtung der Bildung des Saccharoseesters verschoben werden. Dies kann durch die Erhöhung der Temperatur erreicht werden. Diese Möglichkeit ist aber wegen der Karamelbildung des Zuckers und der Nebenreaktionen begrenzt. Es ist nicht zweckmässig, die Temperatur über 130-135 ^{o}C zu steigern.

Zur Erhöhung der Wirksamkeit der Entfernung des Methanols, und dadurch zur Verschiebung des Gleichgewichtes haben OSIPOW und Mitarb. [4] das Reaktionsgemisch durch einen Dünnschichtverdampfer, worin die Flüssigkeit einen turbulenten Film bildete, umlaufen lassen.

In der Umesterungsreaktion bilden sich der Mono-, und der Diester der Saccharose und unter Umständen höher veresterte Derivate. Vom Gesichtspunkt der praktischen Verwendung aus ist der Saccharosemonoester günstiger als der Diester. Der Monoester löst sich nämlich in Wasser unter Bildung einer kolloidalen Lösung,während der Diester mit Wasser eine schleimige Dispersion gibt. Deswegen ist es zweckmäßig, die Umesterungsreaktion so zu führen, daß der Anteil des Monoesters in dem Produkt maximal sei. OSIPOW [4] erreichte diesen Ziel durch dem Reaktionsgemisch zugesetzte Wasserspuren. Unter dem Einfluß des Wassers reagierten die Polyester mit der freien Saccharose zum Monoester.

Die von OSIPOW [5] im Laboratorium ausgearbeitete Mikroemulsionsmethode bedeutet eine neue Art für die Herstellung von Fettsäurezuckerester. Das Prinzip der Methode liegt darin, daß die ineinander nicht löslichen und daher nur in Anwesenheit eines Lösungsmittels reagierenden Zucker und Methylester in einer sehr feinen Dispersion (Tropfengröße 0,01-0,06 μ) miteinander direkt reagieren können.

Der Gehalt an Monoester in dem Produkt wurde von ZAJIC und BARES [6] dadurch erhöht, daß die Umesterungsreaktion in einem ge-

eigneten Zeitpunkt durch Blockierung des Katalysators, durch Zugabe einer sauren Verbindung eingefroren wurde.

Das Patent [7] verwendete für die Umesterung - von den bisher geschilderten Methoden abweichend - ein Anionenaustauscher--Harz als Katalysator. Das Harz hat den Vorteil, daß es von dem Produkt leicht zu trennen ist. Über die Regenerierung, bzw. wiederholte Verwendung des Harzes wurden aber bisher keine Einzelheiten angegeben.

Die bei der Umesterung verwendeten Lösungsmittel riechen unangenehm und sind toxisch, deswegen soll das Produkt von diesen mit besonderer Sorgfalt befreit werden. Die Lösungsmittelspuren können aber wegen der guten Adsorptionseigenschaften der Fettsäureester nur mühsam entfernt werden. Ein weiteres Problem stellt die Gewinnung des Produktes in relativ reinem Zustand dar.

Die verschiedenen Mitteilungen geben für die Entfernung der letzten Lösungsmittelspuren ferner für die Reinigung des Produktes meistens komplizierte Extraktionsverfahren an [3, 4, 8, 9, 10].

Das Ziel unserer Arbeit war, die Umesterungsreaktion - zur Vermeidung der ziemlich mühsamen Trennung der Mono- und Diester - zweckmäßig so zu führen, daß die Konversion des Zuckers und der Anteil des Monoesters in dem Produkt maximal wird.

Beschreibung der Versuche

Fettsäurezuckerester wurden aus Fettsäuremethylestern durch Umesterung nach drei verschiedenen Methoden hergestellt. Die verwendeten Methoden sind die folgenden:

a) Umesterung nach der Mikroemulsionsmethode,

b) Herstellung von Fettsäurezuckerestern diskontinuierlich,

c) Herstellung von Fettsäurezuckerestern im Dünnschichtreaktor halbkontinuierlich.

Vor der ausführlichen Beschreibung der Versuchsergebnisse werden die zur Analyse des umgeesterten Produktes ausgearbeiteten Verfahren zusammengefasst.

Das in der Umesterungsreaktion erhaltene Produkt wurde von dem Lösungsmittel durch Destillation befreit, die letzten Lösungsmittelspuren wurden danach durch zweistündige Behandlung des Produktes in der Trockenpistole - bei 1-2 Torr und 100 °C - entfernt. Das zur Analyse auf diese Weise vorbereitete Produkt enthielt unreagierten Methylester, Zucker, Seife, Katalysator, ferner Saccharoseester.

Der Methylestergehalt des Produktes wurde nach alkalischer Verseifung durch Messung des entstehenden Methanols bestimmt [11]. Die Methode ist auch zur Bestimmung sehr geringer Mengen von Methanol geeignet, und die Messungen sind gut reproduzierbar.

Der Zucker- und Zuckerestergehalt des Produktes wurde nach Extraktion mit n-Butanol-Wasser Gemisch durch Messung der optischen Drehung der Wasser- bzw. der Butanolphase bestimmt. Bei Kenntnis der Drehung der Butanolphase, des Gewichtes des in der Phase aufgelösten festen Stoffes, ferner der spezifischen Drehung des Saccharosemonostearates bzw. des Distearates kann der Anteil des Mono- und des Diesters in der Probe bestimmt werden. Der Seifengehalt der Probe (K-Stearat, bzw. K-Palmitat) wurde auf folgende Weise bestimmt: zu ein aliquotes Volumen der Butanolphase wurde das gleiche Volumen kohlendioxidfreien destillierten Wassers zugefügt, und mit 0,1 N Salzsäure in Anwesenheit von Methylorange Indikator titriert.

Das durch Destillation von dem Lösungsmittel befreite Rohprodukt enthielt - wegen seiner oberflächenaktiven Eigenschaft - noch etwa 0,2 % Dimethylformamid. Wegen des toxischen Charakters dieser Verbindung soll die Menge des in dem Produkt vorhandenen Dimethylformamids bekannt sein. Der Gehalt an Dimethylformamid des Produktes wurde laut Mitteilung [12] bestimmt. Das Prinzip der Methode ist, daß das Dimethylformamid beim Kochen mit Lauge verseift wird, und sich das entstandene Dimethylamin photometrisch quantitativ bestimmen läßt.

Die Werte der Konversion, der Ausbeute und der Selektivität wurden zur Auswertung der Ergebnisse der Umesterungsversuche aus den Analysenergebnissen auf folgende Weise Bestimmt:

K = [(eingewogenes MSt-unreagiertes MSt)·100]/eingewogenes MSt

A = [SME·100]/eingewogenes MSt

S = [SME·100]/[eingewogenes MSt-unreagiertes MSt]

wobei

K die Konversion (%)
A die Ausbaute (%)
S die Selektivität (%)
MSt Menge des Methylesters (Mol)
SME Menge des Saccharosemonoesters (Mol)

Umesterung nach der Mikroemulsionsmethode

Einerseits um das in Mitteilung [5] beschriebene Mikroemulsions-Laboratoriumsverfahren zu reproduzieren, andererseits zur Ausarbeitung einer eventuellen neuen Darstellungsmethode wurden Versuche zur Synthese von Fettsäurezuckerester nach der Mikroemulsionsmethode in Propylenglykol als Lösungsmittel durchgeführt. Zu einem in Propylenglykol aufgelösten Gemisch von Zucker, Methylstearat und Kaliumkarbonat wurde unter intensivem Rühren Natriumstearat zugefügt. Das Propylenglykol wurde in einem Volumen verwendet, in dem das Gemisch leicht gerührt werden konnte.

Mehrere parallele Versuche wurden mit Reaktionsdauern von 2, 4 und 6 Stunden bei 105 °C durchgeführt. Es wurde festgestellt, daß, obwohl die Konversion mit der Zeit zunahm, die Menge des Saccharoseesters auch nach einer 6-stündigen Reaktionszeit nicht mehr betrug als einige Prozente. Gleichzeitig nahm die Seifenbildung als unerwünschte Nebenreaktion zu.

Weitere Nachteile dieser Methode sind die Folgenden: es ist schwierig, die Emulsion zu erhalten, die Wahrscheinlichkeit der Karamelbildung ist hoch, ferner kann eine Umesterung mit dem als

Lösungsmittel verwendeten Propylenglykol eintreten. Auf Grund dessen ist die Mikroemulsionsmethode laut unserer Erfahrungen zur Erzeugung einer größeren Menge einheitlichen Produktes nicht geeignet.

Diskontinuierliche Umesterung

Unsere Versuche wurden in einem mit Rückflußkühler, Tropftrichter und Thermometer versehenen Dreihalskolben durchgeführt, welcher von außen mit einem Ölbad geheizt wurde. Während der Umesterungsreaktion betrug der Druck im Reaktionsraum 100-150 Torr. Die durch die Siedekapillare eingesaugte Luft rührte das Reaktionsgemisch befriedigend um.

Wurde die Umesterung in Dimethylsulfoxyd bei 90 °C, mit einem 3:1 Molverhältnis von raffiniertem Zucker und Methylester, mit einer Katalysatormenge von 0,049 g K_2CO_3/g Methylester durchgeführt, so betrug die Konversion des Methylesters etwa 80 %, und die Ausbeute 30 %. Mit der Erhöhung der Katalysatormenge nahm die Konversion und die Ausbeute in geringem Maße zu, die Seifenbildung verstärkte sich aber ebenfalls beträchtlich. Unter ähnlichen Reaktionsbedingungen wurde die Umesterung in Dimethylformamid als Lösungsmittel ebenfalls durchgeführt, wo bei einer Konversion von 80-90 % eine Ausbeute von 70-75 % erreicht werden konnte.

Gemäß unseren Versuchen konnte das Dimethylsulfoxyd mit einem Verlust von 20-30 %, und das Dimethylformamid mit einem von 2-5 % regeneriert werden. Im weiteren wurde daher Dimethylformamid als Lösungsmittel verwendet.

Zwei Forderungen müssen bei der Durchführung der Umesterungsreaktion erfüllt werden: neben einer möglichst hohen Konversion soll auch der Monoestergehalt so hoch wie möglich gehalten werden. Durch die richtige Auswahl der Versuchsparameter kann die Konversion bis auf 98-100 % gesteigert werden, wobei es zwecks Erhöhung des Monoestergehaltes wünschenwert ist, laut der Literatur 0,1 % Wasser dem Reaktionsgemisch zuzufügen.

Laut unserer Vorversuchen nimmt aber sowohl die Geschwindigkeit der Umesterungsreaktion, wie auch die Konversion ab, wenn 0,1 % Wasser zu Beginn der Reaktion zum Reaktionsgemisch zugefügt wird.

Als erstes Problem wurde daher untersucht, wie ein Produkt von entsprechender Reinheit mit guter Konversion ohne Zugabe von Wasser erzeugt werden könnte. In jedem Fall wurde Kaliumkarbonat als Katalysator verwendet. Die Versuchsangaben sind in der Tabelle 1. aufgeführt.

Die Versuche No. 1. und 2. zeigten, daß die Zusammensetzung des Produktes mit der Erhöhung der Temperatur günstiger wird, da auch die Geschwindigkeit der Reaktion zwischen dem Diester und Zucker neben der Geschwindigkeit der Entstehung des Diesters bei höherer Temperatur höher wird. Der Grund für die bei 95°C erreichte höhere Konversion liegt darin, daß das Verhältnis Katalysator/ /Methylester in dem Versuch No. 1. größer war.

Diese beiden Versuche waren eigentlich auf die Kontrolle der in der Literatur angegebenen Daten ausgerichtet und zeigten, daß bei diesen Versuchsbedingungen entweder die Konversion, oder die Zusammensetzung des Produktes ungünstig war.

Laut der Literatur kann der Gehalt an Monoester des Produktes auch so gesteigert werden, daß die Aktivität des als Katalysator verwendeten Kaliumkarbonats in einer gewissen Phase der Umesterungsreaktion (wo die Menge des Monoesters erwartungsgemäß die größte ist) blockiert wird, wodurch die unerwünschten Nebenreaktionen beseitigt werden können. Daher wurde der Katalysator in den Versuchen No. 3. und 4. nach einer Reaktionsdauer von 6 Stunden durch Zugabe von beinahe äquivalenten Mengen CH_3COOH bzw. H_3PO_4 blockiert. Diese Methode führt mit der angewandten Reaktionsdauer nicht zum erwünschten Ziel, da am Anfang der Reaktion hauptsächlich Diester entsteht.

Eine andere Möglichkeit zu der Erhöhung des Monoesteranteiles besteht darin, daß die notwendige Menge des Methylesters in Dimethylformamid aufgelöst und in mehreren Portionen dem Gemisch zugeführt wird. Auf diese Weise wurde der Methylester in den Versu-

Tabelle 1. Diskontinuierliche Umesterungsversuche ohne Zugabe von Wasser

No	Reaktions-	Temp.	K_2CO_3/MSt	Zusammensetzung des Produktes (%)					K	A	S	Bemer-
	dauer (St)	(°C)	(g/g)	Zucker	MSt	Seife	SME	SDE	(%)	(%)	(%)	kung
1	12	95	0,107	59,80	0,00	2,75	20,30	14,40	100,0	43,6	43,6	x
2	12	105	0,081	61,50	0,43	1,62	21,60	13,20	82,6	46,2	55,9	x
3	6	120	0,054	59,30	5,64	0,51	16,03	12,80	75,6	34,1	45,0	xx
4	6	120	0,054	57,30	2,58	0,20	15,10	26,70	88,4	32,1	36,3	xx
5	6	120	0,054	64,10	10,77	0,37	9,90	10,00	51,5	21,0	40,7	xxx
6	7	120	0,054	63,30	10,58	0,14	12,40	6,60	52,5	26,5	50,4	xxx
7	7	120	0,054	59,00	5,60	0,50	23,50	10,50	74,8	50,0	66,9	xxxx

Molverhältnis Zucker/Methylester: 2,90
Verhältnis Dimethylformamid/Zucker: 3,3 ml/g

x Zugabe des Katalysators in zwei Portionen, nach Ablauf von 0 und 2 Stunden
xx Blockierung des Katalysators bei dem Versuch No. 86. mit Essigsäure, bei 4. mit Phosphorsäure
xxx MSt in DMF aufgelöst in drei gleichen Portionen nach Ablauf von 0, 1,5 und 3 Stunden zugegeben
xxxx Zugabe von MSt wie bei No. 5. und 6., Zugabe des Katalysators in zwei Portionen nach Ablauf von 0 und 2 Stunden.

chen No. 5., 6. und 7. in drei gleich großen Mengen zu Beginn der Reaktion, nach 1,5 und nach 3 Stunden dem Gemisch zugegeben.

Da das Zucker:Methylester Molverhältnis in dem Reaktionsgemisch in jedem beliebigen Zeitpunkt größer war als 2,9, war es zu erwarten, daß sich hauptsächlich Monoester bildet, und gleichzeitig die Menge des Katalysators und die Reaktionszeit vermindert werden können.

Es wurde aber festgestellt, daß weder die Konversion, noch die Ausbaute die erwünschte Erhöhung aufwiesen, im Gegenteil, die Ergebnisse waren weniger günstig, weil der nach Ablauf von 1,5 Stunden zugefügte Methylester nur 4,5, bzw. 5,5 Stunden lang, während der nach 3 Stunden zugefügte Ester nur 3, bzw. 4 Stunden lang reagieren konnte. Diese Beobachtung unterstützte wiederholt, daß zur Vollendung der Umesterung eine längere Zeit notwendig ist.

Auf Grund der Versuche No. 6. und 7. konnte festgestellt werden, daß es am günstigsten ist, wenn der Katalysator portionsweise dem System zugefügt wird. Sowohl die Konversion, als auch die Zusammensetzung des Produktes ist nähmlich im letzten Fall (No. 7.) günstiger. Der Grund dafür besteht darin, daß auf diese Weise eine beinahe konstante Katalysatorkonzentration in dem System gewährleistet werden kann.

Durch die vorher erwähnte Änderung der Versuchsparameter kann die erwünschte Verbesserung der Zusammensetzung des Produktes laut Angaben der Tabelle 1.nicht erreicht werden. Zur Darstellung eines Produktes mit höherem Monoestergehalt schien es zweckmäßig, Wasser zum Reaktionsgemisch derart zuzuführen, daß die Umesterungsreaktion nicht langsamer bzw. die Konversion des Methylesters nicht niedriger wird.

Den ungünstigen Einfluß des Wassers auf die Reaktion wollten wir so vermeiden, daß das Wasser nicht im Laufe der Umesterungsreaktion zu dem Reaktionsgemisch zugefügt wurde, sondern nach Ablauf der Reaktion. Das wasserhaltige Gemisch wurde nachher 1 Stunde bei einer Temperatur gerührt, welche niedriger war, als die Reaktionstemperatur. Die optimale Zeitdauer dieser Behandlung betrug 1 Stunde, weil sich das Monoester/Diester-Verhältnis nach einer Stunde nicht mehr änderte.

Tabelle 2. Diskontinuierliche Umesterungsversuche und zusätzliches Ausrühren mit Wasser

No	Reaktionsdauer (St)	Temperatur (°C)	Kat/MSt (g/g)	Zusammensetzung des Produktes (%)					K (%)	A (%)	S (%)	Bemerkung
				Zucker	MSt	Seife	SME	SDE				
8	1,5 1	120[x] 95[xx]	0,054	61,30	5,65	1,25	14,20	16,80	74,5	30,1	40,4	
9	3 1	120[x] 95[xx]	0,054	60,10	3,76	0,95	17,30	13,20	83,0	36,7	44,2	
10	4 1	120[x] 95[xx]	0,054	58,10	2,91	0,70	22,30	9,40	87,0	47,3	54,4	
11	6	120[x] 95[x]	0,054	57,60	3,10	0,38	28,30	8,80	86,1	59,8	69,4	
12	1,5 1	120[x] 95[xx]	0,054	39,10	9,15	3,10	37,50	9,33	75,0	48,0	64,1	
13	3 1	120[x] 95[xx]	0,054	37,60	8,66	3,00	41,50	4,06	76,8	53,2	67,1	
14	11 1	95[x] 90[xx]	0,107	56,02	0,14	1,95	31,00	8,50	99,5	66,7	68,0	xxx

15	11 1	105^{x} 95^{xx}	0,081	55,00	0,00	1,50	32,40	8,60	100,0	67,5	67,5	xxx
16	11 1	105^{x} 95^{xx}	0,081	45,80	6,51	1,50	32,90	0,10	77,0	70,0	90,5	xxx
17	11 1	105^{x} 95^{xx}	0,081	33,81	2,98	3,33	32,90	18,20	91,7	42,6	46,4	xxx
18	11 1	105^{x} 95^{xx}	0,081	56,30	0,17	1,26	38,80	0,59	99,4	82,7	83,3	xxx Na_2CO_3
19	11 1	105^{x} 95^{xx}	0,081	43,85	1,40	1,92	26,90	16,90	95,3	42,7	45,0	xxx Na_2CO_3

x während der Reaktion

xx während des Ausrührens mit Wasser

xxx Zugabe des Katalysators in zwei Portionen nach Ablauf von 0 und 4 Stunden

Molverhältnis Zucker/Methylester: 2,88 (No. 8, 9, 10, 11, 14, 15, 18)
2,00 (No. 16, 19)
1,39 (No. 12, 13, 17)

Zum Ausrühren zugegebene Menge von Wassers: 0,10 % (No. 14)
0,13 % (No. 8, 9, 10, 11, 12, 13,
1,20 % (No. 15, 16, 17, 18, 19)

Das Ergebnis der mit Wasserzugabe durchgeführten Versuche ist in der Tabelle 2. ersichtlich.

Die Reaktionstemperatur und die Reaktionsdauer stellen miteinander eng verbundene Parameter dar, deswegen wurde der Einfluß dieser beiden untersucht. Die Erhöhung der Reaktionszeit bei 120°C ergab eindeutig die Zunahme der Konversion und der Ausbeute (Versuche No. 8., 9., 10. und 11). Die Zunahme des Verhältnisses Monoester:Diester mit der Erhöhung der Reaktionsdauer weist ebenfalls darauf hin, daß der Diester in der Anfangsperiode der Reaktion das Hauptprodukt ist.

Aus dem Vergleich des Versuchs No. 11. mit den Versuchen No. 5., oder 3. und 4. (Tabelle 1.) ist es ersichtlich, daß durch ein Ausrühren mit Wasser günstigere Ergebnisse erreicht werden können, als durch Zugabe des Methylesters in drei Portionen, oder durch Blockierung des Katalysators mit Säuren. (Der Katalysator wurde in allen diesen vier Fällen auf einmal, am Anfang der Reaktion dem Reaktiongemisch zugegeben.)

Die Ergebnisse der mit einem Molverhältnis von 1,39 zwischen dem Zucker und Methylester durchgeführten Versuche No. 12. und 13. stimmen mit unseren früheren Feststellungen über den Effekt der Reaktionsdauer überein.

Unsere weiteren Versuche wurden zwecks Vermeidung der Karamelbildung bei niedrigerer Temperatur und mit einer längeren Reaktionszeit durchgeführt. Wegen der längeren Reaktionsdauer wurde der Katalysator zweckmäßigerweise in 2 Portionen zum Gemisch gegeben: 2/3 der gesamten Menge wurde am Anfang der Reaktion, das übrige 1/3 nach Ablauf von 4 Stunden zugefügt.

Weitere Umesterungsversuche wurden bei 95 °C und bei 105 °C, mit der Reaktionsdauer von 11 Stunden, und nachfolgendem einstündigem Ausrühren mit Wasser durchgeführt (Versuche No. 14. und 15.). In beiden Fällen wurde ein Produkt mit höhem Monoestergehalt mit guter Konversion erhalten. Die Seifenbildung wurde in diesen Versuchen durch die herabgesetzte Katalysatormenge geringer, während die Erhöhung der Wassermenge das Verhältnis Monoester/Diester verbesserte.

Auf Grund der durchgeführten Versuche schienen die bei dem Versuch No. 15. angewandten Parameter optimal zu sein. Das Monoester:Diester-Molverhältnis betrug in diesem Fall 5,5:1.

Zwecks Senkung der Selbstkosten des Produktes wurde die Möglichkeit einer Verminderung des Molverhältnisses Zucker:Methylester unter Beibehaltung der optimalen Werte der übrigen Parameter untersucht (Versuche No. 15., 16. und 17.). Es konnte aber festgestellt werden, daß die Verminderung des Molverhältnisses bei der angewandten Temperatur nicht zweckmässig ist.

Neben Kaliumkarbonat wurde auch die katalytische Wirkung des Natriumkarbonats untersucht. Das Natriumkarbonat könnte sich günstiger erweisen, als das Kaliumkarbonat, da es nicht toxisch ist, und dadurch die praktische Verwendung des Produktes nicht stört.

Natriumkarbonat erwies sich sowohl bei einem Molverhältnis von 2,88 zwischen dem Zucker und Methylester, als auch bei dem Molverhältnis von 2,00 (Versuch No. 18. und 19.) als ein günstigerer Umesterungskatalysator und erhöhte in erster Linie die Ausbeute beträchtlich.

So beträgt z.B. das Verhältnis Monoester:Diester bei den in Anwesenheit von Kaliumkarbonat oder Natriumkarbonat durchgeführten Versuchen 5,5 bzw. 93,9 gemäß der Angaben der Versuche No. 15. bzw. 18. Der zweite Wert ist günstiger, als die bisher beschriebenen. Auf Grund dessen sind die optimalen Werte der Parameter hinsichtlich der Konversion und der Bildung des Monoesters die folgenden:

Reaktionstemperatur	105 °C
Reaktionszeit	11 Stunden
Dauer der Behandlung mit Wasser	1 Stunde
Menge des zugefügten Wassers	1,2 % der Gesamtmenge des Reaktionsgemisches
Katalysator	Na_2CO_3
Zugabe des Katalysators	2/3 am Anfang der Reaktion 1/3 nach 4 Stunden
Lösungsmittel	Dimethylformamid
Verhältnis Dimethylformamid/Zucker	3,3 ml/g
Molverhältnis Zucker/Methylester	2,88.

Halbkontinuierliche Umesterung im Dünnschichtreaktor

Wie oben beschrieben, nimmt die Umesterung ziemlich viel Zeit in Anspruch. Um die Reaktionszeit der Umesterung zu vermindern, wurde auf Grund der in der diskontinuierlichen Einrichtung gewonnenen Versuchsergebnisse eine halbkontinuierliche bzw. Rezirkulationseinrichtung im Laboratoriummaßstab entworfen, gebaut und betrieben.

Der Hauptteil der Einrichtung besteht aus einem Rotationsdünnschichtreaktor aus rostfreien Stahl mit einem inneren Durchmesser von 53,3 mm und einer aktiven Oberfläche von 0,057 m^2, mit geteiltem Heizmantel und mit Wischern versehenem Rotor (Typ. Sambay). Die Rohrachse des Rotors wurde in Längsrichtung mehrfach perforiert, um das Absaugen der in der Reaktion entstandenen Methanoldämpfen auch auf diese Weise zu sichern.

Die Einrichtung wurde durch das in dem Heizmantel strömende Glyzerin geheizt, während das Reaktionsgemisch in dem System durch eine Pumpe umgewälzt wurde. Der Druck in Dünnschichtreaktor betrug 100-150 Torr.

Der Vorteil des Dünnschichtreaktors besteht darin, daß das in der Reaktion entstehende Methanol infolge der günstigen Stoffübergangsverhältnisse schon in dem Moment seiner Entstehung entfernt werden kann, so daß die Gleichgewichtsreaktion in Richtung der Bildung der Saccharoseester verschoben werden kann. Der andere Grund, weshalb die Anwendung einer Dünnschichtreaktors zweckmäßig ist, besteht darin, daß voraussichtlich keine Karamelbildung bei der verhältnismäßig hohen Temperatur infolge des kurzen Aufenthaltes der Reaktanten in dem Reaktor eintritt, weil der Temperaturkoeffizient der Reaktion der Karamelbildung kleiner ist, als die der Umesterung.

Da die Umesterung ein langsamer Vorgang ist, wurde das Reaktionsgemisch wegen des kurzen Aufenthaltes im Reaktor zur Erreichung einer guten Konversion in der Abbildung 1. dargestellten Versuchseinrichtung rezirkuliert. Auf diese Weise stand das Reaktions-

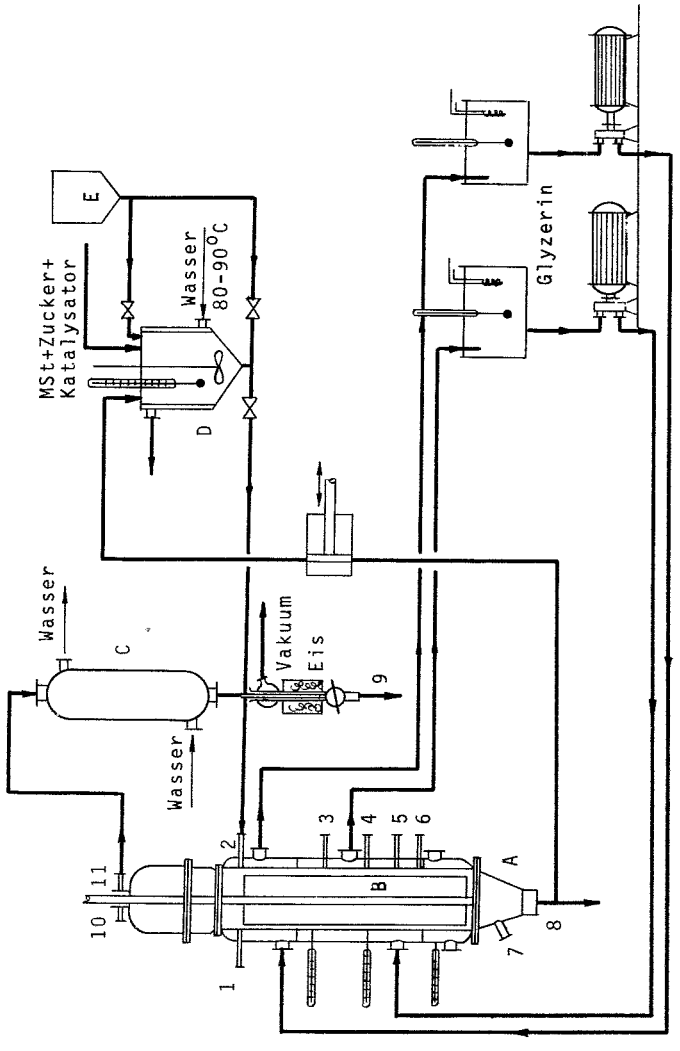

Abb. 1. Die halbkontinuierliche Versuchseinrichtung. 1-6 – Zufuhrstutzen; 7-8 – Produktabnahme; 9 – Methanolabnahme; 10-11 – Methanoldämpfe; A – Dünnschichtreaktor; B – Rotor; C – Kühler; D – Vermischer und Zufuhrbehälter; E – Behälter für Dimethylformamid

gemisch einerseits mit der wärmeren Wand des Filmreaktors in Kontakt, und hielt sich andererseits verhältnismäßig lang in dem Zufuhrbehälter D auf, welcher bei einer Temperatur von 95 °C gehalten wurde.Die durchschnittliche Verweilzeit des Reaktionsgemisches wurde durch Änderung der Geschwindigkeit der Umwälzung reguliert. Diese Geschwindigkeit betrug 22 ml/Min und 100 ml/Min.

Die Erzeugungs- und Betriebskosten der halbkontinuierlichen Versuchseinrichtung liegen höher, als die der diskontinuierlichen Einrichtung. Die Durchführung der Umesterung in einem Dünnschichtreaktor kann also nur in dem Fall als begründet betrachtet werden, wenn die Reaktionszeit der Umesterung bei unveränderter Konversion und Zusammensetzung des Produktes mindestens auf 20 % der in den diskontinuierlichen Versuchen notwendigen Reaktionszeit herabgesetzt werden kann.

Gemäß der durchgeführten Versuche war die optimale Zeitdauer der diskontinuierlichen Umesterung 11 Stunden.

In den halbkontinuierlichen Versuchen wurde das Molverhältnis Zucker:Methylester auf den bei den diskontinuierlichen Versuchen als optimal gefundene Wert 2,9:1 eingestellt.

In unseren Versuchen konnte festgestellt werden, daß das Verhältnis Monoester:Diester durch eine Behandlung des Reaktionsgemisches nach der Beendigung der Reaktion in die Richtung der Bildung des Monoesters verschoben werden kann. Mit diesem Ziel wurden die in der Tabelle 3. zusammengefassten Versuche in der halbkontinuierlichen Einrichtung vorgenommen. Das Reaktionsgemisch wurde 1,5 Stunden lang mit einer Rezirkulationsgeschwindigkeit von 100 ml/Min in der Versuchseinrichtung rezirkuliert, das bei dem gegebenen Volumen einem Rezirkulationsverhältnis von 22,5 entsprach. (Das Rezirkulationsverhältnis gibt an, wievielmal die Pumpe das gesamte Volumen des Reaktionsgemisches innerhalb der gegebenen Reaktionszeit umgewälzt hat.)

Nachher wurde das Reaktionsgemisch nach Zugabe von Wasser (2,1 % auf die Gesamtmenge berechnet) in einem mit Rückflußkühler und Rührer versehenen Rundkolben 1 Stunde bei 95 °C gerührt. Parallel zu diesem Versuch wurde ein analoger Versuch ohne Zugabe von Wasser durchgeführt.

Tabelle 3: Umesterungsversuche im Dünnschichtreaktor und zusätzliches Ausrühren mit Wasser

No	Reaktionsdauer (St)	Temperatur (°C)	Wasser	Zusammensetzung des Produktes (%) Zucker	MSt	Seife	SME	SDE	K (%)	A (%)	S (%)
20	1,5[x]	120	-	57,60	7,70	1,50	19,90	16,10	64,0	28,2	44,1
	1,0[xx]	95	+								
21	1,5[x]	120	-	61,70	6,65	1,30	31,10	0,00	69,0	67,0	97,0
	1,0[xx]	95	+								
22	1,5[x]	130	-	61,20	8,96	0,95	25,50	0,00	58,3	56,0	96,1
	1,0[xx]	95	+								
23	1,5[x]	130	-	63,05	10,10	0,70	23,50	0,00	53,2	51,5	96,7
	1,0[xx]	95	+								

x im Dünnschichtreaktor

xx während des Ausrührens mit Wasser

Molverhältnis Zucker/Methylester: 2,900

Verhältnis K_2CO_3/MSt: 0,087 g/g

Verhältnis Dimethylformamid/Zucker: 3,3 ml/g

Geschwindigkeit der Rezirkulierung 100 ml/Min

Die Durchführung der Umesterung in dem Dünnschichtreaktor bei 120 °C (Versuche No. 20. und 21.) führte zu der Feststellung, daß die Konversion trotz dem hohen Rezirkulationsverhältniss infolge der kurzen durchschnittlichen Verweilzeit gering ist. Eine Behandlung mit Wasser (Versuche No. 21.) verbesserte aber die Zusammensetzung des Produktes wesentlich.

In der bei 130 °C durchgeführten Umesterung nimmt die Konversion mit der Erhöhung der Temperatur nicht zu,sondern ab. Diese Erscheinung kann dadurch erklärt werden, daß die Berührung der Reaktanten infolge des größeren Rezirkulationsverhältnisses intensiver ist, und sich neben der Reaktion des Zuckers mit dem Methylester auch die konkurrierende Reaktion des Zuckers mit dem Diester abspielt. Die Erhöhung der Reaktion zwischen dem Zucker und Diester wird auch durch die Tatsache unterstüzt, daß bei 130 °C, auch ohne Behandlung mit Wasser, ein diesterfreies Produkt erhalten wurde (No. 22.).

In dem mit Wasser behandelten Reaktionsgemisch No. 23. war die Konversion geringer als in dem parallelen mit Wasser nicht behandelten Versuch No. 22. Der Grund dafür ist, daß die Reaktion auch während der einstündigen bei 95 °C durchgeführten Behandlung weiterläuft, die Zugabe von Wasser vermindert aber die Geschwindigkeit der Umesterung.

In der halbkontinuierlichen Einrichtung wurde also nur bei einer Reaktionszeit von 6 Stunden, bei einem Rezirkulationsverhältnis von 15-20 eine genügend hohe Konversion erreicht, wobei die optimale Temperatur des Dünnschichtreaktors 120-125 °C betrug. Zur Erzeugung eines Produktes mit günstiger Zusammensetzung war aber auch bei den optimalen Werten der Parameter ein Ausrühren mit Wasser notwendig.

Wegen des hohen Kostenbedarfs der halbkontinuierlichen Einrichtung, der Verkürzung der Reaktionszeit um nicht mehr als 40-50 %, und wegen der Notwendigkeit des Ausrührens mit Wasser, welche die ganze Technologie in eine diskontinuierliche Technologie umwandelt, ist es deshalb zweckmäßiger, die Umesterungsreaktion diskontinuierlich zu verwirklichen.

Die Verarbeitung des nach dem Ausrühren mit Wasser erhaltenen Reaktionsgemisches

Nach dem Ausrühren mit Wasser wurden die Lösungsmittel in einem Vakuum von 2-5 Torr abdestilliert. Nach dieser Methode destillierte das im Laufe des Ausrührens zugefügte Wasser schon in der Anfangsperiode der Destillation aus.

Da die Destillation bei einer Temperatur von 84-85°C erfolgt, und die Gesamtmenge der Lösungsmittel innerhalb von 2,5-3 Stunden aus dem Gemisch entfernt wird, kann die Konzentration des Mono- und Diesters nach den Gleichgewichtswerten verschoben werden, was eine Zunahme des Gehaltes des Produktes an Diester mit sich bringt. Um das zu vermeiden, wird 0,1-2% Wasser, auf das Anfangsgewicht des destillierten Gemisches berechnet, 30 Minuten nach dem Beginn der Destillation hinzugegeben (ungefähr von dieser Zeit an destilliert das bei dem Ausrühren zugegebene Wasser aus). Das im Laufe der Destillation zugegebene Wasser ändert die Konversion gemäß den Versuchsangaben kaum, die Umesterung kann also am Ende des einstündigen Ausrührens mit Wasser als beendet betrachtet werden, die Zusammensetzung des Produktes ändert sich aber abhängig von der Menge des Wassers wesentlich.

Das günstigste war dasjenige Verfahren, wo Wasser in einer Menge von 0,2-1 % des destillierten Gemisches nach Ablauf einer halben Stunde dem Reaktionsgemisch zugefügt wurde.

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РЕЗЮМЕ

Авторы изучают метод получения одной из групп поверхностно-активных веществ - сахарных эфиров жирных кислот: пальмитата сахарозы и стеарата сахарозы, причем особое внимание уделяется повышению содержания сложного моноэфира в конечном продукте. На основании экспериментальных данных авторы указывают оптимальные параметры получения сахарных эфиров жирных кислот, при которых в условиях периодически действующей лабораторной установки, они добились высокого содержания сложного моноэфира. Эксперименты проводились в ротационном пленочном реакторе полунепрерывного действия.

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ALGEBRAIC DESCRIPTION OF TECHNICAL CHEMICAL SYSTEMS III.

TRANSFORMATIONS OF MATERIAL SYSTEMS

T. BLICKLE and T. BENCZE

(Research Institute for Technical Chemistry of the Hungarian Academy of Sciences, Veszprém and Institute of System Engineering)

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Material systems and the changes occurring in them were described with algebraic methods in the previous paper [1]. However, there is a basic connection between the two subjects: the changes occur on the material systems, and produce new ones from them. This may be termed transformation and is described in the following manner;

$$v : \binom{a_o}{a_v} \qquad (1)$$

This expression means that the material system a_o is, as a consequence of the change v_1, transformed to material system a_v. In the following the changes will be discussed and the relations between the mentioned changes and other material systems will be examined.

In technical chemical processes, the changes occur in operational units [2]. The material system of the operational unit is a composition of the starting material system with that of being produced. In the following this will be termed a quasi union of the two material systems and is designated by:

$$\hat{a} = a_o \cup a_v$$

The material system of the operational unit and the change occurring in it is also a description of the technical chemical process. This is termed a change-material composition and is designated by:

$$v_1 \Diamond \hat{a} \tag{3}$$

The content of Equations (1) and (3) being identical:

$$v_1 \left(\begin{matrix} a_e \\ a_v \end{matrix} c\right) \triangleq v_1 \Diamond \hat{a} \tag{4}$$

may be written, provided that:

$$\hat{a} = a_e \cup a_v$$

Expression (4) is called a Z technical chemical transformation, or - briefly - a Z transformation, and its designation is:

$$Z = [v : \left(\begin{matrix} a_e \\ a_v \end{matrix} c\right) \triangleq v_1 \Diamond \hat{a}] \tag{5}$$

An explanation of the concepts so far presented and a few new concepts are given in the following.

Starting and Resultant Material System

Let $A \supset a_i$ be a set of material systems. Four relations are interpreted in connection with this set according to the following:

Elements a_i and a_j are in relation φ_1 if - and only if - they are material streams continuously enterning into an operational unit. Relation φ_1 defines a partial set A_o of the set A:

$$a_i, a_j \in A$$

if

$$a_i \varphi_1 a_j \tag{6}$$

we may write

$$a_i, a_j \in A_o$$

However, instead of designation $A_o = \{a_{o,1}; a_{o,2}; \ldots a_{o,n}\}$ the following can be introduced:

$$A_o = a_{o,1} \circ a_{o,2} \circ \ldots \ldots \circ a_{o,n} \qquad (7)$$

Elements a_i and a_j are in relation φ_2 if - and only if - they are material streams continuously discharging from an operational unit. In a manner totally similar to the previous case we can write:

$$A_v = a_{v,1} \circ a_{v,2} \circ \ldots \ldots \circ a_{v,n} \qquad (8)$$

Elements a_i and a_j are in relation φ_3 if - and only if - they represent the material system of a given operational unit at the beginning of the process:

$$A_o^x = a_{o,1}^x \circ a_{o,2}^x \circ \ldots \ldots \circ a_{o,n}^x \qquad (9)$$

Elements a_i and a_j are in relation φ_4 if - and only if - they represent the material system of a given operational unit at the end of the process:

$$A_v^x = a_{v,1}^x \circ a_{v,2}^x \circ \ldots \ldots \circ a_{v,n}^x \qquad (10)$$

In the following, A_o and A_o^x will be termed starting material systems, A_v and A_v^x resultant material systems.

Change

The definition of ZADEK [3] can be applied to material systems. According to this, the system is the totality of objects which are connected by interactions and mutual connections. The following items of information will be considered as the objects of the material system: crystal structure, chemical structure, biological structure, state, dimensions, distribution, form, temperature, pressure, homogeneous connection and heterogenous con-

nection. The material system is the structure of these, the structure being defined by the mutual connections. It is the objects that alter during a change. The set of objects which form the material system a_i will be denoted by $\eta(a_i)$. In accordance with this, the connection between the change and the material systems will be described by the following equation:

$$v = [\eta(A_o) \cup \eta(A_o^x)] \setminus [\eta(A_v) \cup \eta(A_v^x)] \tag{11}$$

(The symbols that are usual in the theory of sets are used: $A \cap B$ is the common part of sets A and B; $A \cup B$ is the combination of sets A and B; $A \setminus B$ is the difference of sets A and B.)

The change:

$$v = \eta(A_o) \setminus \eta(A_v) \tag{12}$$

will in the following be termed stationary, whereas the change:

$$v^x = \eta(A_o^x) \setminus \eta(A_v^x) \tag{13}$$

will be termed intermitted and the change:

$$v^\circ = [\eta(A_o) \cup \eta(A_o^x)] \setminus [\eta(A_v) \cup \eta(A_v^x)] \tag{14}$$

unstationary.

The changes pertaining to the object difference of the material system were given in the previous paper [1]. The change is termed elementary if the sum of the difference set is one. In this case, the resultant material system produced by the change differs from the starting material system in one object only.

Transformation

On the basis of the aforesaid, the transformation according to Equation (1) can in general be given in the following form: the expression

$$v_1 : \begin{pmatrix} A_o + A_o^x \\ A_v + A_o^x \end{pmatrix} \qquad (15)$$

is termed transformation if the condition:

$$v_1 = [\eta(A_o) \cup \eta(A_o^x)] \setminus [\eta(A_v) \cup \eta(A_v^x)]$$

is fulfilled.

A transformation transforming a set A_o to A_v is termed stationary (v); that transformating A_o^x to A_v^x is termed intermittent (v^x); that transforming $(A_o + A_o^x)$ to $(A_v + A_v^x)$ is termed unstationary (v^o). The transformation can be regarded as the internal transformation of set A, since:

$$A_o, A_o^x, A_v, A_v^x, A_v^x \leq A \qquad (16)$$

If the objects of the starting and resultant material systems are identical, the transformation is, in the algebraic sense of the word, a permutation. For example, the transformation:

$$v_9 \wedge \delta_4 : \begin{pmatrix} K_1 \Rightarrow K_2 \rightarrow K_3 \\ K_1 \Rightarrow K_3 \rightarrow K_2 \end{pmatrix}$$

is a permutation.

The transformation is termed a multiple one, if more than one of the objects of the starting system are changed. A multiple transformation may be homogeneous, when the same change occurs more than once, for example:

$$(v_9 \wedge \delta_2)^2 : \begin{pmatrix} K_1 \rightarrow K_2 \rightarrow K_3 \\ K_1 \Rightarrow K_2 \Rightarrow K_3 \end{pmatrix}$$

As can be seen, the homogeneous transformation is designated by v^m. Here the exponent shows how many times the change occurs. If the starting material system is such that one given change may occur m_t times, but $m < m_t$, the transformation is selective with respect to the material system. For example:

$$v_9 \wedge \delta_2 : \begin{pmatrix} K_1 \rightarrow K_2 \rightarrow K_3 \\ K_1 \Longrightarrow K_2 \rightarrow K_3 \end{pmatrix}$$

It is apparent from the above that the starting and resultant material systems define the change in an unequivocal way, whereas the reverse is not true.

The multiple transformation may be heterogenous, when more than one change occurs. For example:

$$(v_5 \wedge \delta_1) \wedge (v_9 \wedge \delta_2) : \begin{pmatrix} K_1 \rightarrow K_2 \rightarrow K_3, & T_1 \\ K_1 \Longrightarrow K_2 \rightarrow K_3, & T_2 \end{pmatrix}$$

(T_1 and T_2 represent temperatures.)

The transformation is of identical order if the number of the materials of the starting and the resultant material system is the same; if the number of the starting materials is higher, the transformation is of the combining, if lower, it is of the decomposing type:

$$v : \begin{pmatrix} a_{0,1} \circ a_{0,2} \\ a_{v,1} \circ a_{v,2} \end{pmatrix}; \quad v : \begin{pmatrix} a_{0,1} \circ a_{0,2} \\ a_{v,1} \end{pmatrix}; \quad v : \begin{pmatrix} a_{0,1} \\ a_{v,1} \circ a_{v,2} \end{pmatrix} \qquad (16)$$

If it is continuous and not discrete objects that are altered during the change, the degree of change can be given by designating it by s and writing it in the exponent. Two such continuous transformations can be:

$$v_1^{s1} : \begin{pmatrix} a_o \\ a_{v,1} \end{pmatrix} \quad \text{and} \quad v_1^{s2} : \begin{pmatrix} a_o \\ a_{v,2} \end{pmatrix} \qquad (17)$$

and then we set the following postulations:

$$o < s_1 < 1 : \quad o < s_2 < 1$$

if $s_1 = 0$, $a_o = a_{v,1}$

if $s_1 > s_2$, the deviation of $a_{v,1}$ from a_o is greater than that of $a_{v,2}$; i.e. if the changing object is x, we may write

$$|x_{v,1} - x_o| > |x_{v,2} - x_o|$$

The transformation v^s: $(\overset{a_2}{a_1})$ is termed the inverse transformation of v^{-s}: $(\overset{a_1}{a_2})$. In the case of discrete changes, s is an integral number.

The transformation v_1 : $(\overset{A_{0,1}}{A_{v,1}})$ and v_2 : $(\overset{A_{0,2}}{A_{v,2}})$ are termed similar if:

$$v_1 = v_2 \tag{18}$$

The two transformations mentioned in the above are equal if:

$$\begin{aligned} A_{0,1} &= A_{0,2} \\ A_{v,1} &= A_{v,2} \end{aligned} \tag{19}$$

Quasi Union

The quasi union of two material systems is not defined unequivocally; it depends on the properties of the material systems.

The steps of the definition of quasi union are the following:

The Concept of Mean Material Systems

A mean temperature and pressure are supposed for the material systems present in the operational unit; only one state pertains to a given chemical structure and the information as to distribution is disregarded. Accordingly a material system $\bar{a}$ is obtained, whose information content is the following: crystal structure, chemical structure, biological structure, dimensions, form, homogeneous and heterogeneous connection.

The Combination (Union) of Material Systems

The following two rules are valid:

$$a_1 \cup a_1 = a_1 \tag{20}$$

$$a_1 \cup a_2 = \begin{cases} a_1 \Longrightarrow a_2 \\ a_2 \Longrightarrow a_1 \\ a_1 \rightarrow a_2 \\ a_2 \rightarrow a_1 \end{cases} \tag{21}$$

knowing the material systems it is possible to decide which equality is the appropriate one.

Accordingly, the quasi union of the operational unit can be defined, taking the aforesaid into consideration, in the following manner:

$$\hat{a} = A_o \cup A_o^x \cup A_v \cup A_v^x \tag{22}$$

The particular components of the material system $\hat{a}$ present in the operational unit are the auxiliary materials. A filling auxiliary material ($\hat{a}$") is termed that is added to the system at the beginning of the process and can be removed in an unchanged state at the end of the process:

$$\hat{a}" = A_o^x \cap A_v^x \tag{23}$$

A material system introduced continuously into the operational unit and leaving it in an unchanged state is termed recirculating auxiliary material ($\hat{a}$):

$$\hat{a} = A_o \cap A_v \tag{24}$$

The material system changing during the process can be described by:

$$\hat{a}' = A_o \setminus A_v \cup A_v \setminus A_o \cup A_o^x \setminus A_v^x \cup A_v^x \setminus A_o^x \tag{25}$$

On the basis of Equations (22) to (25) we can write:

$$\hat{a} = \hat{a}' \cup \hat{a}" \cup \hat{a}" \tag{26}$$

Permutations

According to the algebraic interpretation, the following transformations can be regarded as permutations:

$(v_5 \Lambda \delta_1) \Lambda (v_5 \Lambda \delta_1)^{-1}$ heat exchange

$(v_7 \Lambda \delta_1) \Lambda (v_7 \Lambda \delta_1)^{-1}$ e.g. rectification

$v_9 \Lambda \delta_4$ e.g. hypersorption

None of the other transformations is a permutation.

Connection Between the Starting Material Systems and the Change

Certain starting material systems postulate the occurrence of a given change.

Such are the following:

A_o postulates v_1. If there are two entering material streams $(A_{0,1} \circ A_{0,2})$ they postulate $v_8 \Lambda \delta_2$ in order to reach the state $A(K_1 \leftrightarrow K_2)$. The reverse of the above is that two leaving material streams postulate $v_8 \Lambda \delta_3$.

If the temperature of the entering material streams is different, the v_5 temperature change will occur, whereas in the case of a difference in pressure the result will be the v_6 change in pressure.

A homogeneous system may be formed, i.e. the change $v_9 \Lambda \delta_2$ may occur if the entering material system or that present in the operational unit is heterogeneous. If both material systems are gases, the change $v_9 \Lambda \delta_2$ always occurs; if they are liquids, the change occurs in most of the cases; if they are solids, the change does not occur.

Connection Between the Material System and the Change

The starting and the resultant material systems and the change are in such a connection as to determine the third one, if the other two are given. However, this system cannot in all cases be totally free, there are some restrictions. These are summarized in the following.

A considerable part of the change may act on any type of material system, there being no restrictions. Such changes are: transportation ($v_1 \Lambda \delta_1$), change in scattering ($v_2 \Lambda \delta_1$), increasing or decreasing the dimensions ($v_3 \Lambda \delta_1$), any type of change in temperature or pressure [$v_5 \Lambda (\delta_1 V \delta_2 V \delta_3)$, $v_6 \Lambda (\delta_1 V \delta_2 V \delta_3)$].

The combination of material streams is possible only in the case of two input material streams, the separation only in the case of two output material streams. The same holds for transformations $v_8 \Lambda \delta_2$ and $v_8 \Lambda \delta_3$; however, there are further restrictions. The heterogeneous system resulting from the change $v_8 \Lambda \delta_2$ may be $\delta_a \rightarrow \delta_b$, $\delta_a \leftrightarrow \delta_b$ or $\delta_b \rightarrow \delta_a$, depending on material properties and the quantitative relations. In the case of solid-liquid systems, the heterogeneous system may be changed on addition or on removal of one of the materials; this holds both for $v_8 \Lambda \delta_2$ and $v_8 \Lambda \delta_3$.

A change in the form is possible only in the case of a solid system, production of form in the case of a "fictive solid material", the demolition of form in the case of a "fictive liquid or gas".

It is self-evident that the change which transforms heterogeneous ones: $v_8 \Lambda \delta_2$ postulates a heterogeneous input system which - except for the case of a solid-solid heterogeneous system - may be changed to a homogeneous one. The case is just the opposite with the change of the $v_8 \Lambda \delta_2$ type, with the difference that this change can separate neither a solid-solid nor a gas-gas homogeneous system.

The change $v_8 \Lambda \delta_2$ transposes a heterogeneous connection, and accordingly the starting material consists of at least two mate-

rial streams, at least one of them being a heterogeneous system. The same holds true of the resultant material system. Consequently, a minimum of three components must be present, from which two or less may be solid, because such a type of change is not possible between exclusively solid materials. Furthermore, not more than one of the components may be a gas, since a heterogeneous gas-gas system cannot exist. The change $v_9 \wedge \delta_4$ transposes a homogeneous connection in the following general system:

$$A_o\{[K_1(\beta_a) \Longrightarrow K_2(\beta_b)] \rightarrow K_3(\beta_c)\} + v_9 \wedge \delta_4 =$$

$$= A_v\{K_1(\beta_a) \rightarrow [K_2(\beta_b) \Longrightarrow K_3(\beta_c)]\} \qquad (27)$$

where a, b and c may be 1, 2 and 3.

The following abbreviations were applied in the description of the combinations, for example:

$$A\{[K_1(\beta_2) \Longrightarrow K_2(\beta_1)] \rightarrow K_3(\beta_3)\} = (2,1,3) \qquad (28)$$

Accordingly, the possible triple combinations are the following:

(1,1,1) (2,2,2) (3,3,3) (28.a)

(1,1,2) (1,1,3) (2,2,1) (2,2,3) (3,3,1) (3,3,2) (28.b)

(1,2,3) (28.c)

The laws decreasing the number of the possible combinations are the following:

a) No change in state occurs, and consequently the starting and the resultant materials are of the same combination;

b) A gas-gas heterogeneous system cannot exist;

c) A solid-solid homogeneous system cannot be decomposed by a solid;

d) In the case of the homogeneous connection of materials od the same state, the direction $\Longrightarrow$ is optional, $\beta_a \Longrightarrow \beta_b = \beta_b \Longrightarrow \beta_a$, whereas in the case of materials of different states, the direction is determined by the form of appearance;

e) A solid material may enter from a solid homogeneous system only into another homogeneous system;

f) A solid material present in a gas may not be exchanged for another solid;

g) A solid-solid system may be formed only from a homogeneous system;

h) Only one change may take place;

i) A change must take place;

j) A solid present in a gas may not be exchanged by a liquid, neither can a liquid be exchanged by a gas.

The combination remains unaltered by the change, only the system goes over from one permutation into another; taking the prohibitive laws into consideration, the remaining changes are the following:

From the line (28.a) there remains only the combination (2,2,2):

$$[\beta_2 \Longrightarrow \beta_2'] \rightarrow \beta_2'' \quad = \quad [\beta_2 \Longrightarrow \beta_2''] \rightarrow \beta_2'$$

The permutations of the second combination of line (28.b) are the following:*

	(1,1,2)	(1,2,1)	(2,1,1)
(1,1,2)	d	e	+
(1,2,1)	e	+	d
(2,1,1)	+	d	+

The permutations of the second combination of line (28.b) are the following:

	(1,1,3)	(1,3,1)	(3,1,1)
(1,1,3)	d	e	+
(1,3,1)	g	+	d
(3,1,1)	+	e	f

*The cases which do occur in reality are designated by + in the Table, whereas those prohibited are indicated by the code letter of the prohibiting law.

The permutations of the third combination of line (28.b) are the following:

	(2,2,1)	(2,1,2)	(1,2,2)
(2,2,1)	d	+	+
(2,1,2)	+	+	d
(1,2,2)	+	d	+

The permutations of the fourth combination of line (28.b) are the following:

	(2,2,3)	(2,3,2)	(3,2,2)
(2,2,3)	d	+	+
(2,3,2)	+	+	d
(3,2,2)	+	d	+

The permutations of the fifth combination of (28.b) are:

	(3,3,1)	(3,1,3)	(1,3,3)
(3,3,1)	d	b	+
(3,1,3)	b	b	b
(1,3,3)	+	b	+

The permutations of the sixth combination of (28.b) are:

	(3,3,2)	(3,2,3)	(2,3,3)
(3,3,2)	d	b	+
(3,2,3)	b	b	b
(2,3,3)	+	b	+

The permutations of the combinations of line (28.c) are:

	(1,2,3)	(1,3,2)	(2,1,3)	(2,3,1)	(3,1,2)	(3,2,1)
(1,2,3)	i	+	d	h	h	+
(1,3,2)	+	i	h	+	d	h
(2,1,3)	d	h	i	+	+	h
(2,3,1)	h	+	+	i	h	d
(3,1,2)	h	d	+	h	i	j
(3,2,1)	+	h	h	d	j	i

Starting material	Change	
A_o	$v_1\wedge\delta_1 \vee v_2\wedge\delta_1 \vee v_3\wedge(\delta_2\vee\delta_3)\vee(v_6\vee v_5)\wedge(\delta_1\vee\delta_2\vee\delta_3)$	1
$A_{0,1} \circ A_{y0,2}$	$v_1\wedge\delta_2$	2
A_{y0}	$v_1\wedge\delta_3$	3
$A\{\beta_a\}\circ A\{\beta_b\}$	$v_8\wedge\delta_2$	4
$A\{\beta_a \leftrightarrow \beta_b\}\circ A\{\beta_b\}$	$v_8\wedge\delta_2$	5
$A\{\beta_a \rightarrow \beta_b\}\circ A\{\beta_b\}$	$v_8\wedge\delta_2$	6
$A\{\beta_a \leftrightarrow \beta_b\}$	$v_8\wedge\delta_3$	7
$A\{\beta_a \leftrightarrow \beta_b\}$	$v_8\wedge\delta_3$	8
$A\{\beta_2 \rightarrow \beta_1\}$	$v_8\wedge\delta_3$	9
$A\{K[\beta_1,(\alpha_5)_1]\}$	$v_4\wedge\delta_1$	10
$A\{K^+[\beta_1,\alpha_4,o]\}$	$v_4\wedge\delta_2$	11
$A\{K^+[\beta_a,o,\alpha_5]\}$	$v_4\wedge\delta_3$	12
$A\{\beta_a\}$	$v_7\wedge\delta_1$	13
$A\{\beta_a\}$	$v_7^{-1}\wedge\delta_1$	14
$A\{\beta_1\}$	$(v_7\wedge\delta_1)^2$	15
$A\{\beta_3\}$	$(v_7\wedge\delta_1)^{-2}$	16
$A\{\beta_a \rightarrow \beta_b\}$	$v_9\wedge\delta_2$	17
$A\{\beta_a \Longrightarrow \beta_b\}$	$v_9\wedge\delta_3$	18
$A\{\beta_a \rightarrow \beta_b\}\circ A\{\beta_c\}$	$v_8\wedge\delta_4$	19
$A\{\beta_a \Longrightarrow \beta_a' \rightarrow \beta_b\}$	$v_9\wedge\delta_4$	20
$A\{\beta_a \Longrightarrow \beta_a' \rightarrow \beta_b\}$	$v_9\wedge\delta_4$	21
$A\{\beta_a \Longrightarrow \beta_b \rightarrow \beta_b'\}$	$v_9\wedge\delta_4$	22
$A\{\beta_a \Longrightarrow \beta_b \rightarrow \beta_c\}$	$v_9\wedge\delta_4$	23
$A\{\beta_a \Longrightarrow \beta_b \rightarrow \beta_c\}$	$v_9\wedge\delta_4$	24
$A\{K[(\alpha_{14})_1,\beta_1]\}$	$v_{10}\wedge\delta_1$	25
$A\{K[(\alpha_{15})_1]\}$	$v_{11}\wedge\delta_1$	26
$A\{K[(\alpha_{15})_1] \rightarrow K[(\alpha_{15})_2]\}$	$v_{11}\wedge\delta_2$	27
$A\{K[(\alpha_{15})_1]\}$	$v_{11}\wedge\delta_3$	28
$A\{K[(\alpha_{15})_1] \rightarrow K[(\alpha_{15})_2]\}$	$v_{11}\wedge\delta_4$	29
$A\{K[(\alpha_{16})_1,\beta_1]\}$	$v_{12}\wedge\delta_1$	30
$A\{K[(\alpha_{16})_1,\alpha_{16},\beta_1]\}$	$v_{12}\wedge\delta_2$	31
$A\{K[(\alpha_{16})_1,\alpha_{16},\beta_1]\}$	$v_{12}\wedge\delta_3$	32
$A\{K[(\alpha_{16})_1,\beta_1]\}$	$v_{12}\wedge\delta_4$	33

	Product	Remark
1	A_v	any material
2	A_v	any material
3	$A_{v,1} \circ A_{v,2}$	any material
4	$A\{\beta_a \rightleftarrows \beta_b\}$	a = 1,2,3 b = 1,2,3
5	$A\{\beta_b \rightarrow \beta_a\}$	a = 1,2 b = 1,2
6	$A\{\beta_a \leftrightarrow \beta_b\}$	a = 1,2 b = 1,2
7	$A\{\beta_a\} \cdot A\{\beta_b\}$	a = 1,2,3 b = 1,2,3
8	$A\{\beta_a \rightarrow \beta_b\} \cdot A\{\beta_b \rightarrow \beta_a\}$	a = 1,2 b = 1,2
9	$A\{\beta_1 \leftrightarrow \beta_2\} \circ A\{\beta_2\}$	
10	$A\{K[\beta_1,(\alpha_5)_2]\}$	
11	$A\{K[\beta_1,\alpha_4,\alpha_5]\}$	
12	$A\{K[\beta_a,o,o]\}$	a = 2,3
13	$A\{\beta_{a+1}\}$	a = 1,2
14	$A\{\beta_{a-1}\}$	a = 2,3
15	$A\{\beta_2\}$	
16	$A\{\beta_1\}$	
17	$A\{\beta_a \Rightarrow \beta_b\}$	a = 1,2,3 b = 1,2,3 a ≠ b ≠ 1
18	$A\{\beta_c \rightarrow \beta_b\}$	a = 1,2,3 b = 1,2,3 a = b ≠ 3
19	$A\{\beta_a\} \cdot A\{\beta_c \rightarrow \beta_e\}$	a,c,e=1,2,3 (one only twice, 3 only once)
20	$A\{\beta_a \Rightarrow \beta_a' = \beta_b \rightarrow (\beta_a' \cdot \beta_b)\}$	a = 2, b = 1,2,3
21	$A\{\beta_b \Rightarrow \beta_a' \rightarrow \beta_a\}$	a, b = 1,2,3 a ≠ b
22	$A\{\beta_a \Rightarrow \beta_b' \rightarrow \beta_{b'}\}$	a=1,3; b=1,2,3: a ≠ b; a = 3; b = 2
23	$A\{\beta_a \Rightarrow \beta_c \rightarrow \beta_b\}$	a = 1,2; b,c = 1,2,3; a ≠ b ≠ c
24	$A\{\beta_c \Rightarrow \beta_c \rightarrow \beta_a\}$	a,b,c = 1,2,3 a ≠ b ≠ c
25	$A\{K[(\alpha_{14})_2,\beta_1]\}$	
26	$A\{K[(\alpha_{15})_2]\}$	
27	$A\{K[(\alpha_{15})_3]\}$	
28	$A\{K[(\alpha_{15})_2] \Rightarrow K[(\alpha_{12})_2]\}$	
29	$A\{K[(\alpha_{15})_2] \Rightarrow K[(\alpha_{13})_2]\}$	
30	$A\{K[(\alpha_{15})_2,\beta_1]\}$	
31	$A\{K[(\alpha_{15})_2,\alpha_{12},\beta_1]\}$	
32	$A\{K[(\alpha_{14})_2,\alpha_{12},\beta_1]\}$	
33	$A\{K[\alpha_{14},\alpha_{15}]\}$	

The chamical change v_{11} postulates a homogeneous material system, $v_{11}\Lambda\delta_2$ acts in the case of at least two input, and $v_{11}\Lambda\delta_3$ at least two output components. $v_{11}\Lambda\delta_4$ acts in the case of two input and two output components.

Micro-biological changes (v_{12}) postulate a solid material.

The connections between the changes and the material systems are summarized in the Table.

Total Changes

Let the sum of elementary changes, consisting of such a minimum number of terms as not to permit the occurrence of a fictive material system among the products, be termed a total change. The following principles may be defined for the production of total changes on the basis of the elementary changes:

a) The starting material and the product of the elementary chemical changes may be homogeneous only, and the chemical change is to be complemented to a total change in accordance with this.

b) If the product of the chemical reaction is a solid, β_1^+ and it is complemented by supplying a crystal structure.

c) If a solid, is produced in the change, β_1^{+++}, i.e. it is complemented by supplying a crystal structure, shape and dimensions; the reverse is true in the case of a disappearance.

d) If the product of the change is a liquid, β_2^+, it is complemented by supplying dimensions.

e) In the line $0 \rightarrow \Longrightarrow$only one step is possible in the course of the elementary change.

For the sake of brevity, only those signs were given which are of some importance in the examination.

The chamical changes are always written as quasi-homogeneous ones and they are complemented with elementary changes, depending on the phases, so as to obtain total changes.

For example:

$$Na_2CO_3 + H_2O + CO_2 = 2\ NaHCO_3$$

The description of a chemical reaction as a quasi-homogeneous change:

$$A\{K[H_2O,\beta_2] \Longrightarrow K[Na_2CO_3,\beta_1] \Longrightarrow K[CO_2,\beta_3]\} + \nu_{11}\Lambda\delta_2 =$$

$$= A\{K[H_2O,\beta_2] \Longrightarrow K[NaHCO_3,\beta_1]\}$$

The supplementary elementary changes are the following:

$$A\{K[H_2O,\beta_2]\} \circ A\{K[\alpha_{14},Na_2CO_3,\beta_1,\alpha_4,\alpha_5]\} + \nu_2\Lambda\delta_2 =$$

$$= A\{K[H_2O,\beta_2] \rightarrow K[\alpha_{14},Na_2CO_3,\beta_1,\alpha_4,\alpha_5]\}$$

$$A\{K[H_2O,\beta_2] \rightarrow K[\alpha_{14},Na_2CO_3,\beta_1,\alpha_4,\alpha_5]\} + \nu_8\Lambda\delta_2 =$$

$$= A\{K[H_2O,\beta_2] \Longrightarrow K^{+++}[\alpha_{14},Na_2CO_3,\beta_1,\alpha_4,\alpha_5]\}$$

$$A\{K[H_2O,\beta_2] \Longrightarrow K^{+++}[\alpha_{14},Na_2CO_3,\beta_1,\alpha_4,\alpha_5]\} + \nu_{11}\Lambda\delta_1 =$$

$$= A\{K[H_2O,\beta_2] \Longrightarrow K^{++}[O,Na_2CO_3,\beta_1,\alpha_4,\alpha_5]\}$$

$$A\{K[H_2O,\beta_2] \Longrightarrow K^{++}[O,Na_2CO_3,\beta_1,\alpha_4,\alpha_5]\} + \nu_4\Lambda\delta_3 =$$

$$= A\{K[H_2O,\beta_2] \Longrightarrow K^{+}[O,Na_2CO_3,\beta_1,\alpha_4,O]\}$$

$$A\{K[H_2O,\beta_2] \Longrightarrow K^{+}[O,Na_2CO_3,\beta_1,\alpha_4,O]\} + \nu_3\Lambda\delta_3 =$$

$$= A\{K[H_2O,\beta_2] \Longrightarrow K[O,Na_2CO_3,\beta_1,O,O]\}$$

$$A\{K[H_2O,\beta_2] \Longrightarrow K[O,Na_2CO_3,\beta_1,O,O]\} \circ A\{K[CO_2,\beta_3]\} + \nu_9\Lambda\delta_2 =$$

$$= A\{K[H_2O,\beta_2] \Longrightarrow K[O,Na_2CO_3,\beta_1,O,O] \rightarrow K[CO_2,\beta_3]\}$$

$$A\{K[H_2O,\delta_2] \Longrightarrow K[O,Na_2CO_3,\delta_1,O,O] \rightarrow K[CO_2,\delta_2]\} + \nu_9\Lambda\delta_2 =$$

$$= A\{K[H_2O,\delta_2] \Longrightarrow K[O,Na_2CO_3,\delta_1,O,O] \Longrightarrow K[CO_2,\delta_3]\}$$

$$A\{K[H_2O,\delta_2] \Longrightarrow K[O,NaHCO_3,\delta_1,O,O]\} + \nu_3\Lambda\delta_3 =$$

$$= A\{K[H_2O,\delta_2] \rightarrow K^{+++}[O,NaHCO_3,\delta_1,O,O]\}$$

$$A\{K[H_2O,\delta_2] \rightarrow K^{+++}[O,NaHCO_3,\delta_1,O,O]\} + \nu_{10}\Lambda\delta_2 =$$

$$= A\{K[H_2O,\delta_2] \rightarrow K^{++}[\alpha_{14},NaHCO_3,\delta_1,O,O]\}$$

$$A\{K[H_2O,\delta_2] \rightarrow K^{++}[\alpha_{14},NaHCO_3,\delta_1,O,O]\} + \nu_4\Lambda\delta_2 =$$

$$= A\{K[H_2O,\delta_2] \rightarrow K^{+}[\alpha_{14},NaHCO_3,\delta_1,O,\alpha_5]\}$$

$$A\{K[H_2O,\delta_2] \rightarrow K^{+}[\alpha_{14},NaHCO_3,\delta_1,O,\alpha_5]\} + \nu_3\Lambda\delta_2 =$$

$$= A\{K[H_2O,\delta_2] \rightarrow K[\alpha_{14},NaHCO_3,\delta_1,\alpha_4,\alpha_5]\}$$

$$A\{K[H_2O,\delta_2] \rightarrow K[\alpha_{14},NaHCO_3,\delta_1,\alpha_4,\alpha_5]\} + \nu_4\Lambda\delta_3 =$$

$$= A\{K[H_2O,\delta_2]\} \rightarrow A\{K[\alpha_{14},NaHCO_3,\delta_1,\alpha_4,\alpha_5]\}$$

$$A\{K[H_2O,\delta_2]\} \rightarrow A\{K[\alpha_{14},Na_2CO_3,\delta_1,\alpha_4,\alpha_5]\} + \nu_{11} =$$

$$= A\{K[\alpha_{14},NaHCO_3,\delta_1,\alpha_4,\alpha_5]\} \rightarrow A\{K[H_2O,\delta_2]\}$$

Partial Transformations

In the overwhelming majority of cases, the total transformations do not go on to completion, but only partially. For example, the symbol of the transformation corresponding to crystallization:

$$\nu_{10} \wedge \delta_3 \quad : \begin{pmatrix} \beta_2 \Longrightarrow \beta_1 \\ \beta_2 \rightarrow \beta_1 \end{pmatrix}$$

expresses that according to the "picture" there is no solid (β_1) dissolved ($\Longrightarrow$) in the liquid (δ_2). If the transformation occurs only partially, crystallization can be expressed by the following symbol:

$$\nu_{10} \wedge \delta_3 \quad : \begin{pmatrix} \beta_2 \Longrightarrow \beta_1 \\ \beta_2 \Longrightarrow \beta_1 \rightarrow \beta_1 \end{pmatrix}$$

If the crystallization is continued on the produced material system $\beta_2 \Longrightarrow \beta_1 \rightarrow \beta_1$, a material system $\beta_2 \Longrightarrow \beta_1 \rightarrow \beta_1$ is obtained again, despite the fact that the two systems differ from each other. This difference is a quantitative one; however, up to now, quantitative discriminations were not made. Neither will the definition of the concrete quantity of the materials be needed in the following algebraic description; it is only necessary that a system of definitions be applied which enables the materials of different quantities to be discriminated. This was already carried out in transformations where the change is continuous by the introduction of the degree of change. Such transformations are the following:

$$(\nu_1 \vee \nu_2 \vee \nu_3 \vee \nu_4 \vee \nu_{10} \vee \nu_{11} \vee \nu_{12}) \wedge \delta_1$$

$$(\nu_5 \vee \nu_6 \vee \nu_{12}) \wedge \delta_2$$

There is no need for a separate discrimination of quantity in the case of these transformations. Similarly, it is not necessary to introduce such a designation in the transformations which do not occur individually.

$$(\nu_7 \vee \nu_8 \vee \nu_{11}) \wedge (\beta_2 \vee \beta_1)$$

The other transformations are dealt with in more detail.

In the formation and dissolution of a heterogeneous connection, the output material system is equal to the unified material

system in such a way that the quantity of one of the phases is changed. The quantitative parameter is designated by p and q and the only reservations are that $0 < p, q < 1$ and that $\beta_a^{p_1}$; $\beta_a^{p_2}$ if $p_1 > p_2$ and $\beta_a^{p_1}$ means in this case a larger quantity of material than $\beta_a^{p_2}$.

Accordingly:

$$v_8\Lambda\delta_i:\begin{pmatrix}\beta_a\rightarrow\beta_b^{p_1}\circ\beta^{q_1} & p_1>p_2 & i=3 \text{ and } p_2=0 & \text{corresponds to a perfect decomposition}\\ \beta\rightarrow\beta^{p_2}\circ\beta^{q_2} & p_1<p_2 & i=2 \text{ and } p_2=1 & \text{corresponds to a perfect combination}\end{pmatrix}$$

The following equationa are valid:

$$p_1 + q_1 = 1$$

$$p_2 + q_2 = 1$$

$$p_1 + p_2 = 1$$

In cases where the above Equations hold, q_1 and q_2 will not be written in the following.

In the case of the formation and dissolution of the homogeneous connection, in a way similar to the above, we may write:

$$v_9\Lambda\delta_i:\begin{pmatrix}\beta_a\rightarrow\beta_b^{p_1}\rightarrow\beta_b & p_1>p_2 & i=3 & p_2=0 & \text{perfect decomposition}\\ \beta_a\rightarrow\beta_b^{p_2}\rightarrow\beta_b & p_1<p_2 & i=2 & p_2=1 & \text{perfect combination}\end{pmatrix}$$

In the case of chemical combination and decomposition:

$$v_{11}\Lambda\delta_i:\begin{pmatrix}[\beta_a\rightarrow\beta_b]^{p_1}\rightarrow\beta_c & p_1>p_2 & i=2 & p_1=1 & \text{total combination}\\ [\beta_a\rightarrow\beta_b]^{p_2}\rightarrow\beta & p_1<p_2 & i=3 & p_1=0 & \text{total decomposition}\end{pmatrix}$$

In changes of state, materials of both the states are present in the starting and resultant material systems:

$$(v_7 \wedge \delta_1)^i: \begin{pmatrix} \beta_1^{p_1} \Longrightarrow \beta_2 & p_1 > p_2 & i=1 & p_2=0 & \text{total change} \\ \beta_1^{p_2} \Longrightarrow \beta_2 & p_1 < p_2 & i=-1 & p_2=1 & \text{total change} \end{pmatrix}$$

In the translocation of a heterogeneous connection:

$$v_8 \wedge \delta_4: \begin{pmatrix} \beta_a \rightarrow \beta_b^{p_1} \circ \beta_c \rightarrow \beta_b \\ \beta_a \rightarrow \beta_b^{p_2} \circ \beta_c \rightarrow \beta_b \end{pmatrix} \quad \text{if} \quad p_2 = \begin{cases} 0 \\ 1 \end{cases} \quad \text{total change}$$

In the translocation of a homogeneous connection:

$$v_9 \wedge \delta_4: \begin{pmatrix} \beta_a \Longrightarrow \beta_b^{p_1} \rightarrow \beta_b \Longrightarrow \beta_c^{q_1} \rightarrow \beta_c & p_2 = 1 & q_2 = 0 \\ \beta_a \Longrightarrow \beta_b^{p_2} \rightarrow \beta_b \Longrightarrow \beta_c^{q_2} \ \beta_c & p_2 = 0 & q_2 = 1 \end{pmatrix} \quad \text{total change}$$

In chamical exchange:

$$v_{11} \wedge \delta_4: \begin{pmatrix} [\beta_a \Longrightarrow \beta_b]^{1-p_1} \Longrightarrow [\beta_c \Longrightarrow \beta_d]^{p_1} \\ [\beta_a \Longrightarrow \beta_b]^{1-p_2} \Longrightarrow [\beta_c \Longrightarrow \beta_d]^{p_2} \end{pmatrix} p_2 = \begin{cases} 0 \\ 1 \end{cases} \quad \text{total change}$$

Finally, in changes of the type $v_1 \wedge (\delta_2 \vee \delta_3)$ the quantitative parameter relates to the ratio of the split material stream, i.e.:

$$v_1 \wedge \delta_i: \begin{pmatrix} a_1^{p_1} \circ a_1^{1-p_1} & p_2 = 1 & i = 2 \\ a_1^{p_2} \circ a_1^{1-p_2} & p_1 = 1 & i = 3 \end{pmatrix}$$

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РЕЗЮМЕ

В предыдущей сообщеении этой темы (1) алгебраическими методами описывались материальные системы и происходящие в них изменения. Основная зависимость образуется между происходящими в материальной системе изменениями и получающимися вследствие их новыми системами. Это называют преобразованием и обозначают следующим образом:

$$v_1 : \begin{matrix} a_o \\ a_v \end{matrix} \qquad 1.$$

Вышеуказанное выражение означает, что под действием изменения v_1 материальная система a_0 преобразуется в систему a_v. Далее авторы рассматривают различные изменения и исследуют зависимости, которые имеют место между указанными изменениями и остальными материальными системами.

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THERMAL STABILITY OF CHEMICAL REACTORS

A. LÁSZLÓ and Mrs.J. DENCS

(Department of Chemical Process Engineering,
Veszprém University of Chemical Engineering)

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The occurrence of thermal instability of large chemical reactors is a well known fact. Experience has shown that during the start and shut down periods, the instability can be considerable and even dangerous. On more than one occasion it was observed that a relatively small change of the feed rate (B), the concentration (c_0) or the temperature of the feed (T_0) caused a rapid drop of the temperature and conversion of a working reactor, characterized by high temperature and high degree of conversion. There are apparent contradictions in the observations of reactors running at low temperature and with a small degree of conversion, that an insignificant alteration of the previously mentioned parameters resulted in a sudden increase of temperature and conversion. In practice, this latter phenomenon was called "ignition", independently from the fact whether burning or an increase of the catalyst temperature only took place. A different type of instability could be observed and also reproduced at certain critical parameter values, when the working condition of a reactor changed suddenly between the mentioned limits, and regarding the thermal phenomena, an oscillation came into existence.

Summing up the experiences, it can be stated that there are narrow unstable domains in the working conditions of a reactor which cannot be described merely by the heat balance of the system.

WAGNER [1] first elucidated the causes of this phenomenon in his theoretically well grounded work. Due to the Second World War his article was not widely available, and van HEERDEN [2] again

elaborated the conditions of the stability in 1953. BILOUS and AMUNDSON's article [3] published in 1955, examined this thermal stability, and for this the linearisation of their mathematical model was used. As a result, numerous researchers have dealt with the problem. VOLTER and SALNIKOV summarized the published statements in their book [4].

In the present work it will be shown that in the thermal sense both the extreme types of reactors, i.e. the adiabatic and isotherm reactors can be discussed, utilizing the same theory. The following discussion is based on the well mixed reactors.

Starting with the well known equation (e.g. [5]),which describes the rate of heat generation:

$$\dot{Q}_R = \nu_i \; r \; \Delta H \; V_R \tag{1}$$

It is known that the expression of the reaction rate ($\nu_i \; r$) can be divided into the product of two functions, one of these depends on temperature, the other one is only the function of the concentration:

$$(\nu_i \; r) = k(T) \; f(c)$$

In the following, the thermal stability will be examined only, so the substitution of $f(c) \equiv c$ is introduced, i.e. the derived equations refer to the reactions of first order, but the thermal considerations are also valid for reactions of any kind of order.

The ARRHENIUS' equation is commonly accepted and valid for the description of the k(T) function:

$$k(T) = A \; e^{-\frac{E}{RT}} \tag{2}$$

In the case of tank reactors it is known [6] that the actual concentration c or the degree of conversion x , is the function of the initial concentration (c_o) and the mean residence time ($\bar{t}$); substituting Eq. (2) into this relation:

$$c = c_o(1 - x) = c_o \frac{1}{1 + k\bar{t}} = c_o \frac{1}{1 + Ae^{-\frac{E}{RT}}\bar{t}} \qquad (3)$$

i.e. the generated heat given by Eq. (1) is as follows:

$$\Delta Q_R = \nu_i \Delta H \, V_R \, c_o \frac{A e^{-\frac{E}{RT}}}{1 + Ae^{-\frac{E}{RT}}\bar{t}} \bar{t} .$$

Using simple transformations, the following equation of suitable form can be written:

$$\Delta \dot{Q}_R = \nu_i \Delta H \, V_R \, c_o \frac{1}{\bar{t}} \frac{A \bar{t} e^{-\frac{E}{RT}}}{1 + A \bar{t} e^{-\frac{E}{RT}}} \qquad (5)$$

If in Equation (5) all the quantities - with the exception of the temperature - are constants, then the heat generated in an adiabatic reactor will be proportional with the following function:

$$Y = \frac{e^{-\frac{1}{T}}}{1 + e^{-\frac{1}{T}}} \qquad (6)$$

For isotherm reactors, this seems to be less of a problem because the substitution T = constant theoretically holds. However, this is valid only in principle, chemical engineers are aware that isotherm reactors work in a similar manner to heat exchangers, and there exists a certain inner temperature (T) which differs from the temperature of the wall (T_1); this forms the boundaries of their working conditions and determines their dimensions. Therefore, in the practice either the amounts of heat generated at the mentioned temperatures or the quotient of these heat quantities have to be taken into account. Regarding Equation (4) at temperatures (T) and (T_1), and taking their quotient:

$$\Delta\dot{Q}_R^* = \frac{\Delta\dot{Q}_R}{\Delta\dot{Q}_{Rf}} = \frac{1 + \frac{1}{A\,\bar{t}}\, e^{\frac{E}{RT_1}}}{1 + \frac{1}{A\,\bar{t}}\, e^{\frac{E}{RT}}} \tag{7}$$

If in this case A, $\bar{t}$, E and R are constants, then a relation can be obtained which is similar to Equation (6):

$$Y^* = \frac{1 + e^{\frac{1}{T_1}}}{1 + e^{\frac{1}{T}}} \tag{8}$$

Plotting $\Delta\dot{Q}_R$ or $\Delta\dot{Q}_R^*$ vs. T, the result is a sigmoid heat generation curve, known from literature. As an example, HODOSSY's work [7] can be mentioned. Here the author examined the hydrogenation of furfural to furfuryl alcohol and plotted the measured values. The results were the mentioned sigmoid curves.

In addition, for setting up a relation with Equation (6) valid for adiabatic reactors, the numerator and denominator of Equation (8) is multiplied by [exp(- 1/T)] and transforming the result we obtain:

$$Y^* = \frac{e^{-\frac{1}{T}}}{1 + e^{-\frac{1}{T}}} + \frac{e^{\frac{1}{T_1} - \frac{1}{T}}}{1 + e^{-\frac{1}{T}}} \tag{9}$$

It is now evident that although the conditions are equal, why the degree of conversion in isotherm reactors is higher compared to the same one of adiabatic reactors. The first term of Equation (9) is identical with Equation (6) valid for adiabatic reactors, and to this a second term is added. If the latter is marked with Y_1, thus:

$$Y^* = Y + Y_1 \tag{10}$$

The above relation is shown in Fig. 1. Introducing the designation

$$e^{\frac{1}{T_1}} \equiv D$$

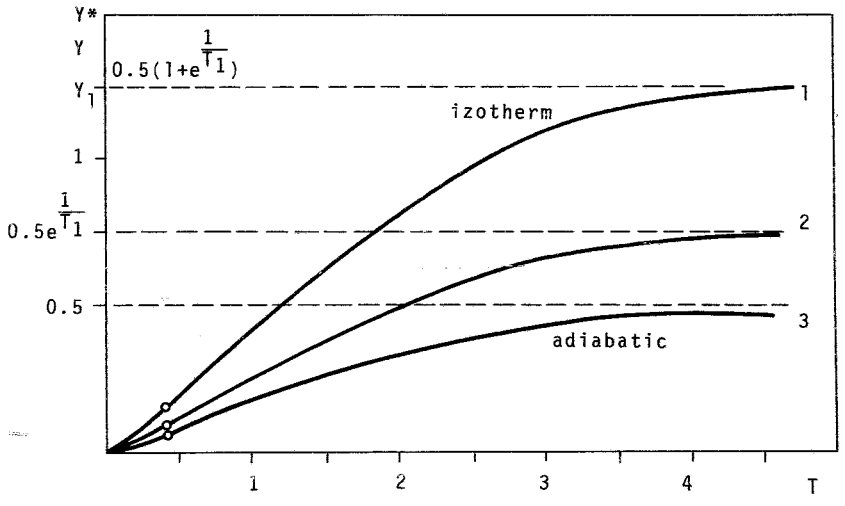

Fig. 1. 1 - $Y^* = Y + Y_1 = (1 + e^{1/T_1}) \frac{e^{-1/T}}{1 + e^{-1/T}}$

2 - $Y_1 = e^{1/T} \frac{e^{-1/T}}{1 + e^{-1/T}}$ $(T = 2.5)$; 3 - $Y = \frac{e^{-1/T}}{1 + e^{-1/T}}$

so the result is basically the same, but it is expressed differently as it is shown below:

$$Y^* = Y + \frac{D\, e^{-1/T}}{1 + e^{-1/T}} \tag{11}$$

or

$$Y^* = (1 + D) \frac{e^{-1/T}}{1 + e^{-1/T}} = (1 + D)\, Y \tag{12}$$

Although there are significant differences between the working conditions and characteristics of adiabatic and isotherm reactors, the conclusion can be drawn that they can be treated theoretically on the basis of the same principle.

This result provided encouragement to proceed further, transgressing the theory and methods usually applied in chemical engineering science, and to introduce the methods used in process control for the examination of the thermal stability of chemical reactors.

At first it was assumed that a chemical reactor as a whole is a dynamic system which can exist in different steady states. The response of the system was examined: if it is disturbed whether it returns to the previous steady state or does not. LJAPUNOV's first method was used in the examination of small disturbances, but if the disturbances were major, the non-linear model was solved and the plotted phase-plane provided the answer to the question.

The steady states of the system can be determined by the help of the

1. main isoclinics,
2. heat generation and removal curves,
3. bifurcating diagrams.

The last two methods can be applied well in practice and with their assistance the optimum working parameters of a reactor can be determined. The methods used and the experiments will be discussed in the following paper.

Acknowledgement

The authors are indebted to Mrs. M. Varga for her assistance in the mathematical analysis.

SYMBOLS

A pre-exponential factor (1/sec)

B feed rate (cu. metre/second)

c concentration (kg moles/cu. metre)

c_o concentration of the feed (kg moles/cu. metre)

E activation energy (kilocalories/kg mol)

ΔH heat of reaction (kilocalories/kg mol)

k reaction rate constant (1/second)

$\Delta\dot{Q}_R$ heat generation rate (kilocalories/second)

$\Delta\dot{Q}_{Rf}$ heat generation rate at the temperature of the wall (kilocalories/second)

$\Delta\dot{Q}_R^* = \Delta\dot{Q}_R/\Delta\dot{Q}_{Rf}$ (dimensionless)

r reaction rate (kg moles/cu. metre)

R gas constant (kilocalories/kg mol ^oK)

$\bar{t}$ mean residence time (second)

T temperature (^oK)

T_o feed temperature (^oK)

T_1 wall temperature (^oK)

V_R reactor volume (cu. metre)

x degree of conversion (dimensionless)

ν_i stoichiometric coefficient of the i-th component (dimensionless)

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РЕЗЮМЕ

Неустойчивое поведение непостоянного типа больших химических реакторов является хорошо известным явлением. Как показывает практика, неустойчивость может быть довольно значительной и даже опасной, особенно в случае пуска или останова реактора. Часто замечали что у реакторов, работающих в режимах с высокой температурой и высокой степенью превращения, изменение скорости подачи вещества (B) концентрации (c_0) или температуры (T_0) приводило к неожиданному снижению температуры и конверсии. Кажется противоречивым тот факт, что незначительное изменение указанных параметров приводит к скачкообразному увеличению температуры и степени превращения. В практике об этом последнем явлении говорят, что реактор "загорелся", независимо от того действительно ли происходит горение или только неожиданный разогрев катализатора. В отличие от вышеописанного, авторы наблюдали и неоднократно воспроизвели при определенных критических параметрах такую неустойчивость, когда поведение реактора в определенных границах неожиданно изменялось, реактор осциллировал.

Обобщив результаты можно сказать, что существуют такие узкие неустойчивые условия работы реактора, которые нельзя описать уравнением теплового баланса системы.

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DETERMINATION OF THE ASH AND MOISTURE CONTENT OF MINERAL COALS BY NEUTRON SLOW-DOWN

G. FALUDI, E. HÁZI and Z. CSAPÓ

(Department of Radiochemistry, Veszprém University of Chemical Engineering)

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The intensity of thermal neutrons in the vicinity of a neutron source emitting fast neutrons, depends on the concentration of the elements capable of slowing down the neutrons in the medium surrounding the source.

The possibilities for the determination of the ash and moisture content of mineral coals, were studied on the basis of this fact by the application of two sorts of geometrical arrangements. Factors interfering with the determinations were also studied. According to these investigations, the technique can be applied with coal of low ash content (up to 20 %) mainly for the purpose of ash content determination, with an error of ± 0.3 % ash content, whereas in the case of coal of high ash content (higher than 50 %) it can be used for humidity content determination, with an error of ± 0.2 % humidity.

INTRODUCTION

In the case of elements of low atomic number, from among the interactions between fast neutrons and matter - i.e. elastic scattering, inelastic scattering and nuclear reactions - it is first of all elastic scattering that occurs with a very high probability. The loss in energy brought about by the elastic scattering - to a very good approximation - is equal to the value

calculated on the basis of the equations of classical physics on elastic impact. Accordingly, the difference between the energy of the neutron before and after collision can be expressed by the following formula:

$$E_2 = E_1 \frac{A^2 + 2A\cos\vartheta + 1}{(A+1)^2} \tag{1}$$

where E_1 is the energy of the neutron before the collision,
E_2 is the energy of the neutron after the collision,
A is the mass number of the atom taking part in the collision,
ϑ is the angle of scattering

By introduction of the symbol

$$\left(\frac{A-1}{A+1}\right)^2 = \alpha$$

Equation (1) may be written in the following form:

$$\frac{E_2}{E_1} = \frac{1}{2}[(1+\alpha) + (1-\alpha)\cos\vartheta] \tag{2}$$

In the case of frontal collision, when $\vartheta = \pi$, the maximum decrease in energy brought about by one collision, i.e. the maximum relative decrease in energy can be deduced from Equation (2):

$$E_1 - E_{2_{min}} = (1-\alpha)E_1 \quad \text{and} \quad \frac{E_1 - E_{2_{min}}}{E_1} = 1 - \alpha \tag{3}$$

The higher the relative change in energy brought about by one collision, on the one hand, the number of collisions necessary for slowing down to a given final energy level is lower, and on the other hand, the path necessary for slowing down is shorter.

It is apparent from Equations (1), (2) and (3) that the loss in energy brought about by elastic collision is inversely proportional to the atomic number of the nucleus taking part in the collision. Nuclei of lower atomic number possess a stronger slowing down capability.

The aforesaid present a possibility for the determination of components which are of outstanding neutron moderating capability. If the mixture or solution to be studied is exposed to a fast neutron radiation of constant flux, the number (or intensity) of low-energy (thermal) neutrons will change in accordance with the concentration of the component of high neutron slowing down capability.

On the basis of the neutron slowing down capability of the hydrogen and carbon atoms, it is possible to determine the ash and moisture content of mineral coal; this problem is of a very high practical importance.

According to the papers published in literature, the principle of measurement based on the slowing down of neutrons has primarily been utilized in the development of techniques and apparatus serving the determination of the moisture content. For example,the moisture content of soil, concrete, wood, paper, sugar and ore mixtures, etc., has been measured in this way [1, 2, 3, 7, 9, 10, 12].

A number of authors have dealt with the application of this technique for the determination of the moisture content of mineral coal [1, 13], whereas its application for the purpose of ash content determination was so far rather limited [4].

DESCRIPTION OF THE MEASURING TECHNIQUE

It follows from the considerations on the slowing down path length - described in the preceding section - that the establishment of an optimal geometry is a very important condition of the applicability of the technique [6, 8]. Two - according to a number of point of view, basically different - geometric arrangements can be realized; these are schematically shown in Fig. 1. In the case of geometry realizing a "scattering of large space angle", the radio-isotipic neutron source, emitting fast neutrons, and the

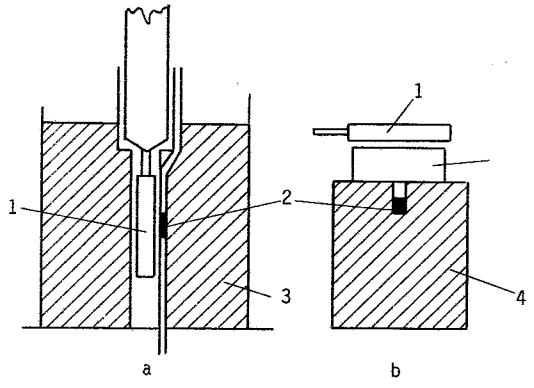

Fig. 1. The different arrangements of neutron source and detector a - "scattering of large space angle" geometry; b - "absorption-type" geometry; 1 - detector; 2 - neutron source; 3 - coal; 4 - paraffin

detector sensitive to slow neutrons, are placed in the immediate vicinity of each other. The measuring head containing the neutron source and the detector are immersed into the relatively large sample.

Taking the conclusion of KÜHN [1] - referring to the absolute value of the slowing down path lengths in hydrogen and carbon - into consideration and using a BF_3 counted tube as a detector (300 mm length and 38 mm diameter), a coal column of 600 mm height and 600 mm in diameter can be considered as an "infinite volume". The detector should be located in the middle of the coal column, in its longitudinal axis, whereas the optimum position for the neutron source is in the immediate vicinity of the detector, at a height of the middle part of the latter.

The change in the relative intensity of the slow neutrons, plotted against the diameter of the coal column for the case of a coal sample of 10 % ash and 3 % humidity content, of a maximum grain size of 6 mm and with application of a 9 mg Ra/Be neutron source is shown in Fig. 2 (the height of the coal column is 600 mm).

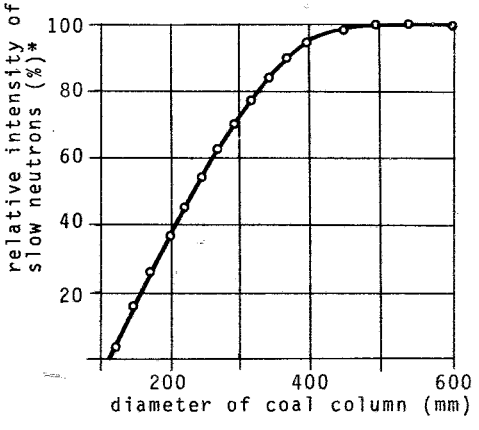

Fig. 2. The relation between the relative intensity of neutrons and geometry of coal column

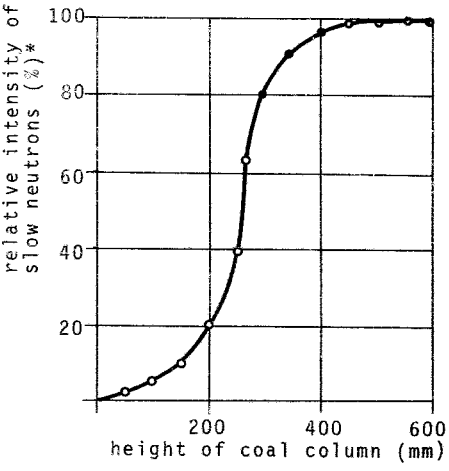

Fig. 3. How the relative neutron intensity depends on the geometry of the coal column

*Basis of reference: the intensity pertaining to "infinitely large volume".

The relative change in the intensity of the slow neutrons as plotted against the height of the coal column, in the case of the same coal sample, is shown in Fig. 3. (The diameter of the coal column was 600 mm and the distance between the bottom of the coal column and that of the detector was in all cases 100 mm.)

On the basis of Figs. 2 and 3, the minimum dimensions - "optimum dimensions" - pertaining to the maximum slow neutron intensity are the following: height 480 mm and diameter 400 mm of the coal column.

The calibration curve shown in Fig.4 is obtained if the optimal geometry is ensured and the measurement is carried out with identical space filling and the sample is of constant grain size and moisture content; the curve shows the relative change in the

intensity of slow neutrons, plotted against the ash content. On the basis of this calibration curve, and considering the scattering (σ) value calculated from the results of a large number of determinations (50), the error of the ash content determination changes in the case of different ash content ranges as illustrated by Table 1.

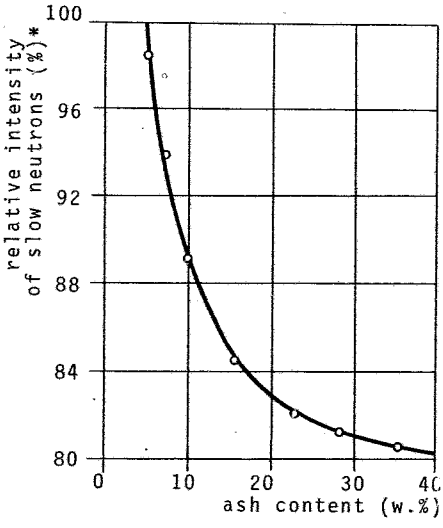

Fig. 4. Calibration curve ("scattering of large space angle" geometry

*Basis of reference: the intensity pertaining to the sample of 5 % ash content (particle size: 0 to 6 mm, moisture content: 10.6 %)

In practical application, in certain cases, the unchanged particle size distribution and constant level of moisture content is ab ovo assured on account of the coal processing technology applied, e.g. in the case of coal refuse utilization, where after desintegration, the ore and the refuse rock are separated in a hydrocyclone, or for example, in the utilization of ahidrated lignites in power stations.

Table 1

Ash content range	Absolute error	Relative error
6 - 15 %	± 0.29 % ash	± 2.9 %
15 - 30 %	± 0.45 % ash	± 1.5 %
above 30 %	± 0.6 % ash	± 1.2 %

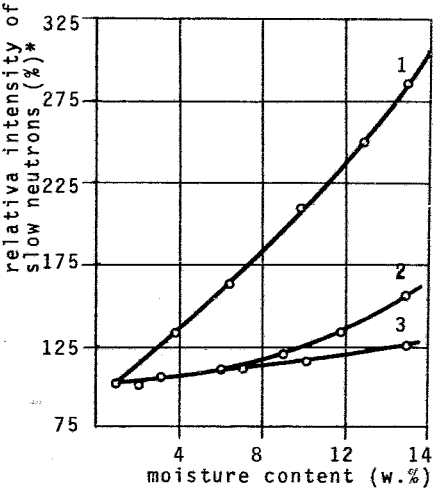

Fig. 5. The effect of moisture content of coal on the relative intensity of slow neutrons. Ash content (w.%): 1 - 78; 2 - 28; 3 - 10

*Basis of reference: the intensity measured on samples of the various coals containing 1 % moisture

If the measurement described in the foregoing is carried out with coal samples of constant ash, but variable moisture content, a calibration curve enabling moisture content determination is obtained; such a curve, established for three different sorts of coal containing different amounts of ash content, is shown in Fig. 5.

It is apparent from the curves shown in Fig. 5 that the sensitivity of the moisture content determination depends on the ash content of the coal: the technique is less sensitive in the case of coals of lower ash content. This effect can be explained by the high carbon content pertaining to a low ash content and the high neutron slow-down capability of carbon. Considering the statistical nature of radiometric measurements, the absolute error of the moisture determination can - for the coal samples of different ash content illustrated in Fig.5 - be compared on the basis of the data summarized in Table 2.

Table 2

Ash content	Absolute error of moisture content determination
10 %	± 0.54 % moisture content
28 %	± 0.36 % moisture content
78 %	± 0.22 % moisture content

If the constancy of moisture content and particle size distribution cannot be ensured in the ash content determination, random fluctuations in the moisture content may cause considerable errors in the ash determination. (A 1 % change in the moisture content corresponds, in the case of 10 % ash content, to a deviation of 2.1 % in ash content.)

In certain cases - especially when considering the unique requirements of industrial application - it may be justified to use "absorption-type" geometry, for example in the case of a continuous measurement carried out on material moved on a conveyor belt. In such an arrangement, a layer of well-defined thickness of the sample is placed between the fast neutron source and the slow neutron detector. The optimum layer thickness of the sample, dependent on a number of parameters, varies generally between 80 and 150 mm. This same geometry can also be applied for experimental laboratory measurements, because it is easy to handle on account of the relatively small amount of sample. For example, the application of various types of neutron detectors and factors interfering with the measurement can advantageously be studied with this geometry. The small amount of the needed sample also enables artificial coal "samples" to be synthetized in a wide ash content range. A calibration curve, plotted for the 5 to 100 % ash content range is ahown in Fig. 6. The layer thickness of the sample in this experiment was 100 mm, the particle size and moisture content of the sample was the same as of that used in the studies carried out with "high space angle" scattering. By comparing Figs. 4 and 6 (calibration curves), the drawback of the "absorption" geometry, i.e. its low sensitivity, becomes apparent.

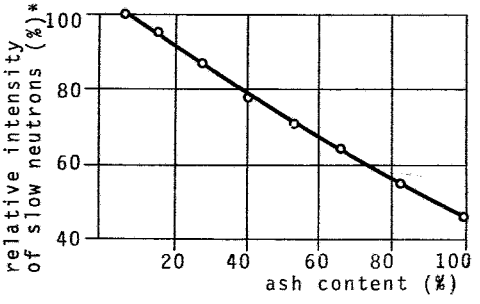

Fig. 6. Calibration curve ("absorption-type" geometry)

*Basis of reference: the intensity pertaining to a sample of 5 % ash content

INTERFERING FACTORS

If the volume weight or particle size of the samples or the chemical composition of the ash components in the samples used for ash - or moisture - content determination are different, it is to expected that interferences will occur.

As opposed to other radiometric ash or moisture determination techniques, changes in the chemical composition of the components of the ash do not interfere with the determination in the measuring technique based on the slowing-down of neutrons. This is explained by the fact that the elements which substitute each other are likewise of poor neutron slowing-down capability, as compared to the carbon or hydrogen atom.

Changes in the particle size distribution of the sample act through changes in the volume weight.

Changes in the volume weight act as an interfering factor since the number (concentration, [atom/cm^3]) of the atoms capable of slowing down neutrons (carbon and hydrogen) change even in the case of an identical ash and moisture content.

Figs. 7, 8 and 9 show the changes in the intensity of slow neutrons, plotted against the volume weight, for coal samples of a given ash content at different moisture content values. The limits of the volume weight intervals shown in the Figures correspond to the loosest and most compact space fillings possible, i.e. they are extreme values. With adequate particle size distribution ensured, it can be assumed that any spontaneous changes in space in filling do not surpass $\pm$ 0.01 g/cm^3 even in the case of industrial processes. Changes of this magnitude in volume weight - as can be judged from the calibration curves presented in Figs. 4 and 6 - cause an error of the magnitude shown in Table III. The data refer to coals of various ash contents and to both of the geometries.

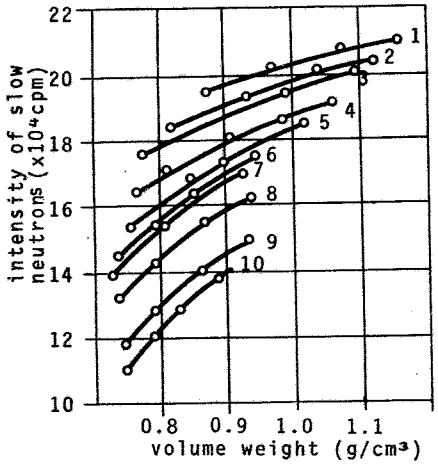

Fig. 7. The effect of volume weight of moist coal having 10 w.% ash content on the intensity of slow neutrons. Moisture content (w.%): 1 - 24.66; 2 - 21.68; 3 - 19.70; 4 - 16.76; 5 - 14.32; 6 - 11.80; 7 - 10.00; 8 - 6.39; 9 - 3.00; 10 - 0.50

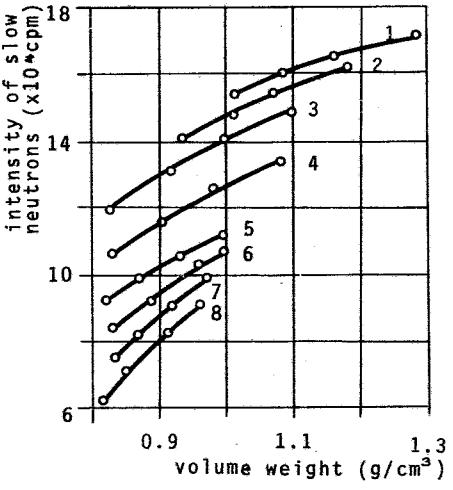

Fig. 8. The effect of volume weight of moist coal having 28 w.% ash content on the intensity of slow neutrons. Moisture content (w.%): 1 - 23.70; 2 - 20.74; 3 - 17.79; 4 - 14.86; 5 - 11.90; 6 - 8.98; 7 - 5.10; 8 - 2.00

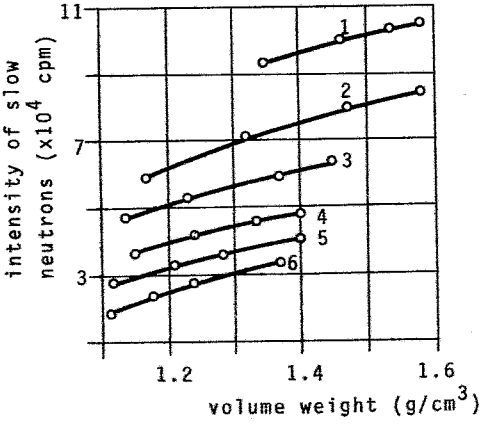

Fig. 9. The effect of volume weight of moist coal having 78 w.% ash content on the intensity of slow neutrons. Moisture content (w.%): 1 - 15.36; 2 - 12.48; 3 - 9.56; 4 - 6.60; 5 - 3.66; 6 - 0.66

Table 3

Ash content (%)	Absolute error in the ash content determination (%)
10	± 0.3
28	± 0.5
78	± 1.1

The interfering action of changes in the volume weight can be eliminated by a combination of the ash - or moisture - content determination, based on neutron slowing-down, with volume weight determination by gamma ray absorption. This is an already solved problem in the case of the determination of the humidity content of soils [5, 11].

DISCUSSION OF THE RESULTS

The method proposed in the foregoing enables the determination of two parameters that are of importance in connection with the production and processing of mineral coals, these parameters being ash content and moisture content. With coal samples of low ash content, the technique is mainly applicable for ash content determination, whereas in the case of coal samples of high ash content it is preferably used for the determination of the moisture content. In the case of coal of a high ash content (such as e.g. refuse) the determination of the moisture content - or its adjustment to a predetermined value - is important with a view to further processing (e.g. sintering in order to produce an additive to concrete, concrete production, and filling, etc.).

It is an advantage of the technique that the size of the material involved in the determination, i.e. the "sample size" is

very large, especially if the "large space angle scattering" geometry is applied. For example, practically all the material is measured, in case of a measuring sonde placed into a coal storage bunker, while it passes the sensor. Thus the information obtained can be regarded a very good average value. Further advantages are continuous operation and immediate availability of the results; the latter enables application for process control purposes as well.

Considering the advantages enumerated in the foregoing, the technique duly deserves intensive ineterst, when compared with the usual procedure involving sampling, drying for moisture determination and incineration for ash content determination, despite the fact that care must be exercised to overcome some interfering factors.

It is justified to combine the technique with other radiometric methods (e.g. gamma absorption, or reflexion) for the determination of the ash content in order to eliminate the interferences.

For practical application, considering industrial conditions, in the case of geometry producing "large space angle scattering" it is preferable to apply a Ra-226/Be or Am-241/Be neutron source, together with a BF_3-type counter tube.

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РЕЗЮМЕ

Плотность термических нейтронов вблизи испускающего быстрые нейтроны источника зависит от концентрации элементов, тормозящих нейтроны.

Изучалось определение содержания пепла и влажности в каменных углях на основании вышеуказанного явления для случая двух экспериментальных установок. Авторы изучали влияющие на проведение эксперимента факторы. Данные экспериментов показали, что упомянутый метод применим для определения влажности с точностью до ±0,3% в случае углей с малым (до 20 весовых %) содержанием пепла, и с точностью до ±0,2% в случае углей с высоким содержанием пепла (более 50 весовых %).

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