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A.A.C.M. BEENACKERS, G. LAMMERS, N.J.M. KUIPERS

NOVEL CONTINUOUS REACTORS FOR CHEMICAL MODIFICATION OF STARCHES WITH IMPROVED SELECTIVITY

Abstract

Two novel continuous processes for the chemical derivatisation of starch have been developed. A gas-solid fluidized bed process for modifications with gaseous substrates and a gel process in a static mixer reactor for handling concentrated pastes. Based on results obtained with hydroxyethylation (dry-process) and hydroxypropylation (gel-process) it can be concluded that both processes are very attractive relative to the classical slurry process with respect to improved reaction selectivity, much shorter residence times and superior controlability and safety.

Introduction

Traditionally, chemical modification of starch is carned out in batch processes. However, in the past decades, the production capacity of many starch modiflcation plants has increased to such a high level that this fact alone justifies the development of continuous processes. But there is more: continuous processes often allow for a more strict process control resulting in less variation in product quality and often in safer operation. The latter is particularly important ifpoisonous or unstable reactants are used such as alkyloxides in the alkoxyethylation of starch. In addition, depending on the application, specific extra advantages may be realised in optimised continuous processes such as reduced risks of contamination of the product and the opportunity to operate with reduced fractions of water which often results in improved reaction selectivities. Because of these considerations we decided about a decade ago to develop novel continuous processes for starch modification. So far we focused on developing a continuous static mixer reactor for in situ gelatinising concentrated aqueous starch slunries followed by chemical modification in the same reactor snd on a special type of fluidized bed reactor for (semi-)dry chemical modifications with gaseous reactants. Because of the extra drive for improved safety in processes with potentially unstable

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Groningen University, Department of Chemical Engineering Nijenborgh 4, 9747 AG, Groningen, The Netherlands

reactants such as propylene oxide and ethylene oxide, we selected these reactants as the first candidates for the novel gel and gas-solid starch modifications, respectively.

The continuous static mixer reactor

With respect to continuous chemical modification of gelatinised starch, most research concentrates on the application of extruders as a reactor, particularly for cationisation [1, 2], but in our Department also in the benzylation [3] and in the acetylation and hydroxypropylation of starch [4]. Potentially, extruders can operate with slightly more concentrated pastes than static mixers, though often at the expense of starch breakdown due to high shear forces, leading to lower starch molecular weight and lower viscosity pastes [2]. Further, extruders have some major draw backs relative to static mixers. In contrast to extruders, static mixer reactors are easy to scale-up to large capacities, if necessary can be fully temperature controlled (e.g. by applying Sulzers SMR mixers), have much better plug flow characteristics (often resulting in a more homogeneous substitution), are relatively cheaper and require less maintenance. Reason enough to concentrate on the development of a static mixer reactor for chemical modification of starch.

Static mixer selection

From those static mixers presently commercially available and suitable for high viscosity applications, only KTEK's [5], Kenics and Sulzer's [6] SMX and SMXL mixers are sufficiently documented to allow for a rational relative assessment. From these, the SMX mixer has the best mixing and heat transfer characteristics (see figs. 1

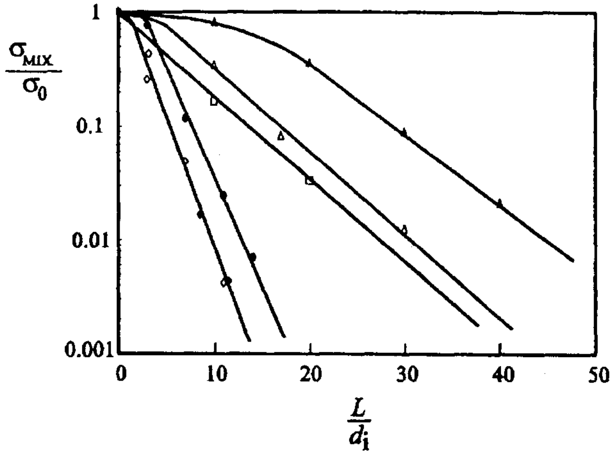


Fig. 1. Relative standard deviation in liquid composition at the mixer outlet due to incomplete mixing of two liquid flows entering the mixer, as a function of length over diameter ratio (L/d$_i$) of the mixer [7]; ◊, ♦, •: SMX; □: Kenics; △, ▲: SMXL.

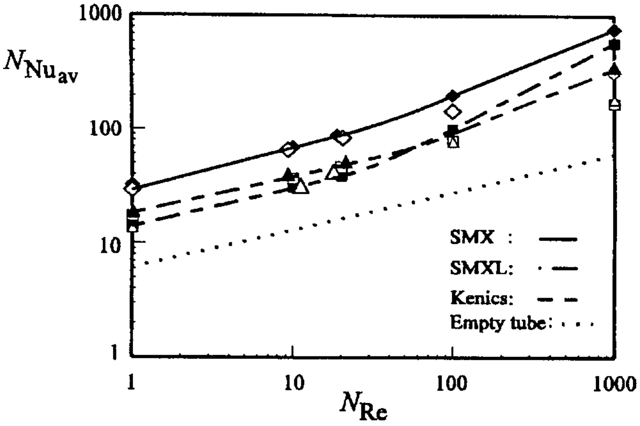


Fig. 2. Dimensionless average heat transfer coefficient to the wall as a function of the Reynolds Number; ◊, ♦: SMX; □: Kenics; △, ▲: SMXL.

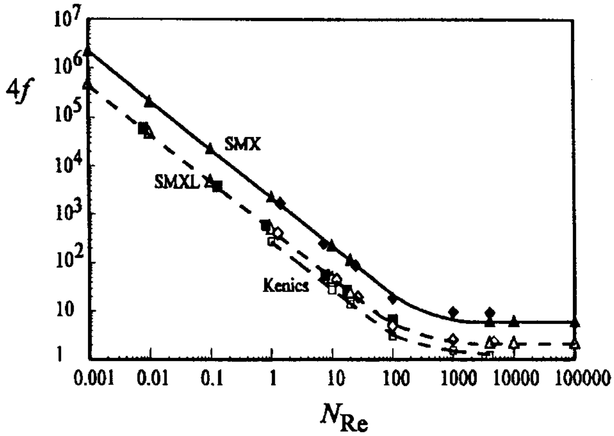


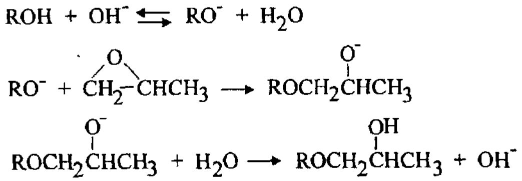
Fig. 3. Friction factor 4f as a function of N_{re} for Kenics and Sulzer SMX and SMXL static mixers [7].

and 2, respectively), though at the expense of a slightly higher pressure drop (see figure 3). Therefore, we decided to apply SMX mixers.

Chemical reactions

We applied the novel reactor for the alkali catalysed hydroxypropylation of potato starch. The following reactions occur:

Catalysed reaction with starch:



$$ROH + OH^- \rightleftarrows RO^- + H_2O$$

fast

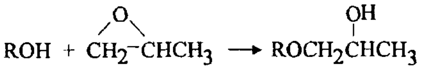
$$RO^- + CH_2\overset{O}{-}CHCH_3 \longrightarrow ROCH_2\overset{O^-}{\overset{|}{C}}HCH_3$$

slow

$$ROCH_2\overset{O^-}{\overset{|}{C}}HCH_3 + H_2O \longrightarrow ROCH_2\overset{OH}{\overset{|}{C}}HCH_3 + OH^-$$

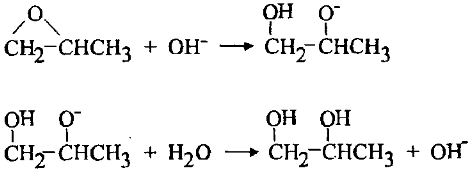
fast

Uncatalysed reaction with starch:



$$ROH + CH_2\overset{O}{-}CHCH_3 \longrightarrow ROCH_2\overset{OH}{\overset{|}{C}}HCH_3$$

Catalysed hydrolysis:



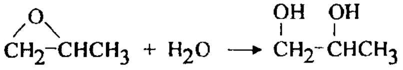
$$CH_2\overset{O}{-}CHCH_3 + OH^- \longrightarrow \overset{OH}{\overset{|}{C}}H_2-\overset{O^-}{\overset{|}{C}}HCH_3$$

slow

$$\overset{OH}{\overset{|}{C}}H_2-\overset{O^-}{\overset{|}{C}}HCH_3 + H_2O \longrightarrow \overset{OH}{\overset{|}{C}}H_2-\overset{OH}{\overset{|}{C}}HCH_3 + OH^-$$

fast

Uncatalysed hydrolysis:



$$CH_2\overset{O}{-}CHCH_3 + H_2O \longrightarrow \overset{OH}{\overset{|}{C}}H_2-\overset{OH}{\overset{|}{C}}HCH_3$$

We have a selectivity problem because propylene oxide may either react with starch or water, leading to the desired product and 1,2 propane diol, respectively. For the reaction kinetics, see [8].

Pilot plant design

The design ofthe continuous pilot was based on the following requirements:

- Range of residence times suitable for obtaining conversions of propylene oxide of over 80 % in the temperature range ofinterest (343 to 373 K);
- Good plug flow characteristics;
- Good temperature control;
- Operation at starch concentrations ofup to 35 mass percent must be possible with regard to maximum allowable pressure drop;
- Possibility of monitoring the course of the reaction in the reactor.

The resulting scheme is shown in figure 4. The starch slurries were prepared in a stirred tank of 50 dm^3 (1). Driven by a Mohno pump (2) these slurries flow via a heating coil (4), a premixer (5) and a heating section (6) into the reactor. Just before the premixer, both an aqueous sodium hydroxide solution and liquid propylene oxide could be added to the starch slurry by two metering pumps. In the premixer, starch slurry, sodium hydroxide and propylene oxide were mixed by 10 Sulzer SMX mixers. Always, sufficient sodium hydroxide was added to get complete gelatinisation of the starch immediately after the premixer. The heating section consisted of a ceramic tube, inserted in a wave pipe of a microwave oven (7). The reactor contained five so-called measurement sections (8) each equipped with a Pt 100 temperature sensor, a pressure sensor and an adapter for the insertion of a radial temperature sensor, consisting of five radially spaced 0.10 mm thermocouples. In each section the reaction mixture could be sampled. The reactor contained four so-called SMX sections (9), consisting of a jacketed tube, filled with 14 Sulzer SMX static mixer elements ($d_{sm} = l_{sm} = 27.3$ mm) to induce plug flow and to enhance heat transfer. The tube was thermostatted with water. The reactor outlet consists of a pressure controlling pneumatic valve (10). Total reactor volume: ± 1 dm^3.

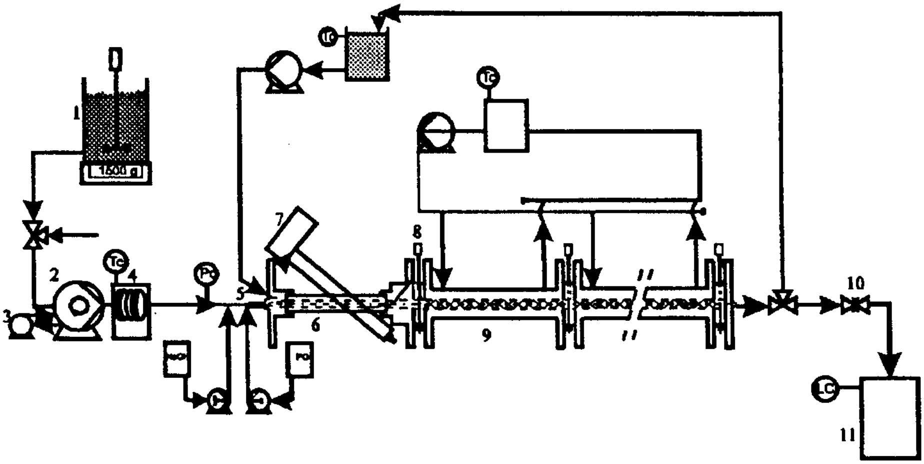


Fig. 4. Flow sheet ofthe static mixer reactor for the continuous chemical modification of concentrated starch pastes.

On chemical analysis methods applied, see [9].

Residence time distribution

Fig. 5 gives some results of residence time distribution measurements together with curves from a model presented elsewhere [7]. Indeed, the reactor shows excellent plug flow behaviour with Peclet numbers of typically: N_{pe}= 100 (or 63 per meter length of reactor) Notice that N_{pe}= 100 is equivalent to a residence time distribution obtained from 50 ideal mixers in series.

For comparison: Van Zuilichem [10] reported for single screw extruders $10 < N_{pe} \leq 20$ only.

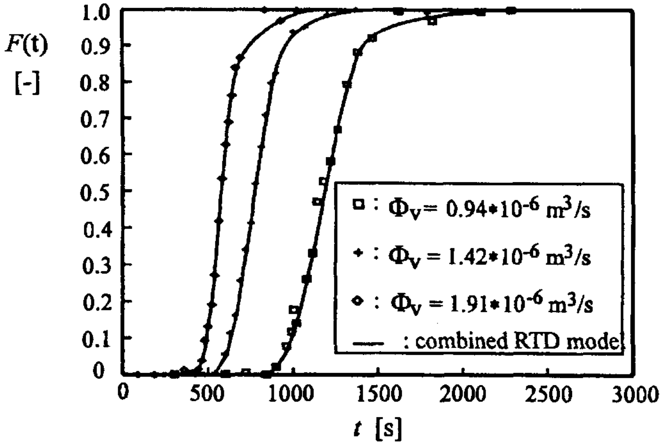


Fig. 5. Experimentally determined cumulative residence time functions for $m_{starch} = 0.28$ at $T = 343.15$ K and results obtained from fitting the experimental data with a residence time distribution model.

Heat transfer

The heat transfer to the wall was measured for starch pastes of various strengths, all as a function of the Peclet number for heat, based on the tube diameter:

$$N_{Pe_{h,t}} = N_{Re} N_{Pr} = \frac{\rho c_p v d_t}{\lambda}$$

$$\text{with} \quad N_{Re} = \rho v d_t / \xi$$

$$N_{Pr} = c_p \xi / \lambda$$

See Fig. 6 for results. All data could be accurately described by:

$$N_{Nu} = 1.87 \left(N_{Pe_{h,t}} \right)^{0.44}$$

This relation nicely agrees with that of Kalbitz and Bohnet [11], whereas the relation of Sulzer [6] appears to be less accurate.

Conversion and selectivity

A set of 9 reaction experiments were carried out with:

$0.15 < m_{starch} < 0.3$ [-]
$250 < c_{NaOH} < 500$ [mol/m^3]
$343 < T < 365$ K
$300 < r < 1200$ s

The observed conversions of propylene oxide conversion toward hydroxy propylated starch are shown in Figs. 7 and 8, respectively, both in relation to theoretical values predicted from a reaction engineering model presented elsewhere [7]. Depending on the values of the operating parameters listed above a practically complete conversion appears to be possible with proven selectivities as high as 80 %. Indeed, this compares favourable, relative to a typical selectivity reported for a classical slurry batch process of 60 % [12].

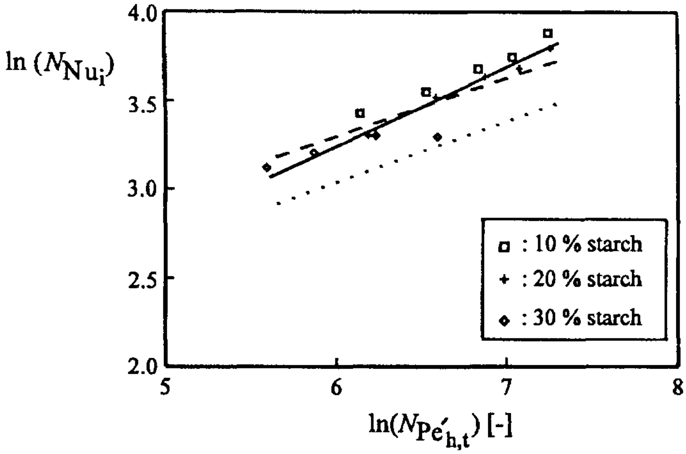


Fig. 6. Experimental data and literature relations for ln(N_{Nu}) as a function of ln($N_{Pe'h,t}$) [9].
– : our relation; -- : Kalbitz and Bohnet [11]; . . . . : Sulzer, [6].

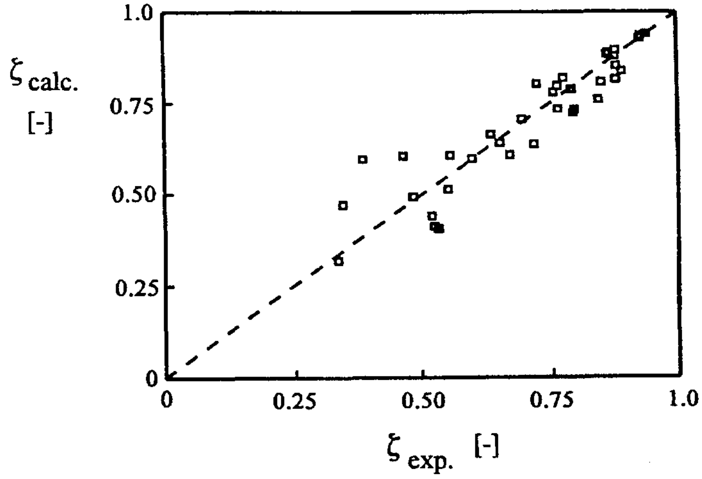


Fig. 7. Parity plot of experimentally determined and calculated propylene oxide conversions.

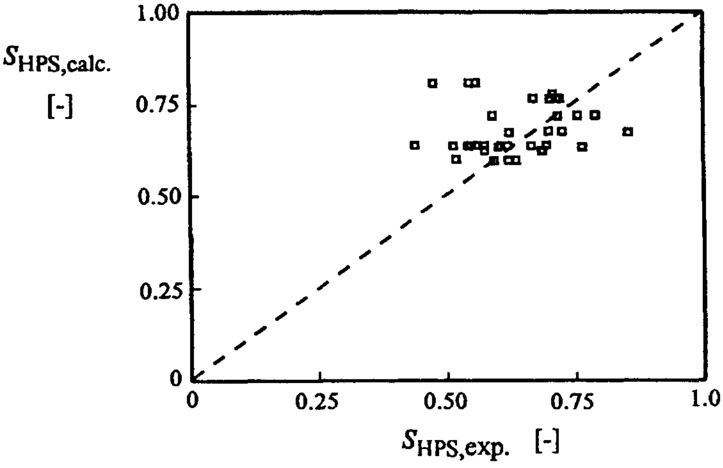


Fig. 8. Parity plot of experimentally determined and calculated selectivities toward hydroxypropyl starch.

Scale-up

Based on the experimental data of the pilot reactor we made a preliminary design for a plant having an annual production capacity of 3500 tons dry hydroxy propyl starch.

We considered both adiabatic operation with SMX mixers and isothermal operation with SMR mixers. It turned out that no significant gain in selectivity could be realised by applying isothermal operation. Hence we propose adiabatic operation. Figure 9 and 10 show the calculated required reactor volume and propylene oxide

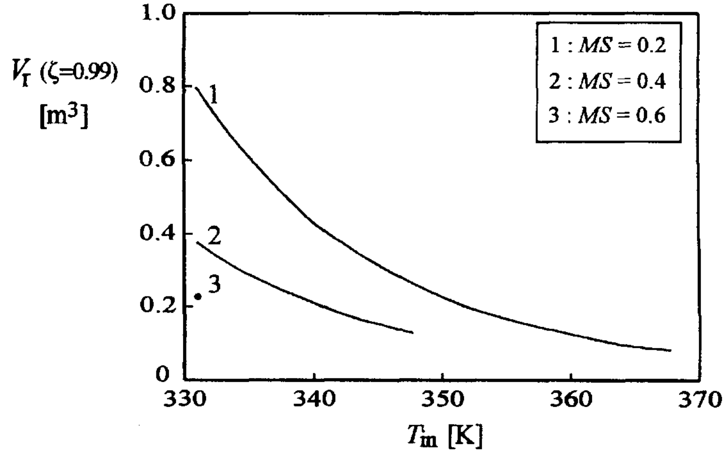


Fig. 9. Required reactor volume for 99 % propylene oxide conversion as a function of reactor inlet temperature (adiabatic operation, $m_{starch} = 0.45$).

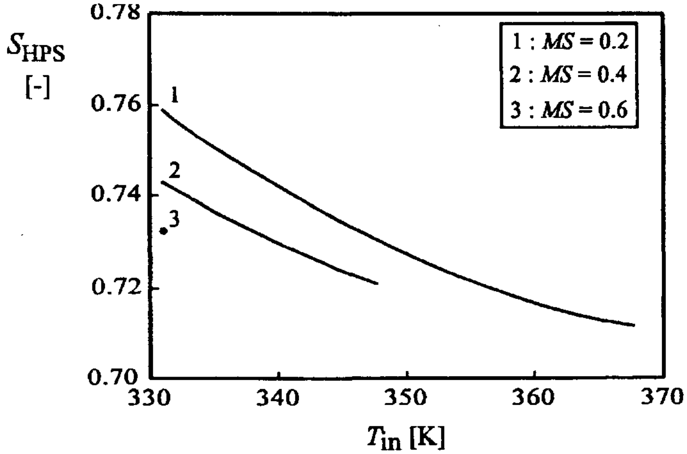


Fig. 10. Overall reaction selectivity as a function of reactor inlet temperature (adiabatic operation, m = 0.45).

selectivity, respectively, both on the basis of 99 % PO conversion as a function of degree of Molar Substitution (MS) and reactor inlet temperature. Even at a relatively low inlet temperature of 330 K the required reactor volume remains substantially below 1 m^3 and selectivities expectedly will be above 72 %.

The stirred Vibrating Fluidized Bed Reactor

In order to retain its easy flow and handling properties and to avoid excessive drying costs, it is attractive to modify starch while saving its granular structure wherever possible. Low substituted starch derivatives (MS < 0.1) are usually manufactured by modifying starch in aqueous suspensions. However, this has some disadvantages such as a low selectivity of the process and a low reaction rate due to a limited hydroxide concentration and reaction temperature (typically below 55°C), both to prevent gelatinization of the suspended starch particles, see Kuipers [13). Because the granule gelatinization temperature lowers with increasing MS, there is a maximum MS in aqueous slurry reactions where above the granular form of the starch gets lost.

If the substrate is a gas, such as in hydroxyethylation or hydroxypropylation, a gas-solid modification process seems attractive because it does not suffer from these disadvantages. The low moisture content of (semi) dry starch might favour the desired reaction relative to the hydrolysis of the alkeneoxide while the reactivity might be increased by application of higher temperatures than are possible in the conventional slurry process. An additional, potentially very interesting, advantage of the gas-solid hydroxyalkylation of starch possibly is the extension to products with a higher degree of substitution without loss of the granule structure. An economic evaluation of the two processes showed that the estimated production costs can be lower for the novel gas-solid process relative to the slurry process (Van Warners [14]). However, for sufficient reactivity and diffusivity, the starch granules must contain some water, typically between 15 and 25 wt % d.b. With increasing moisture content, starch becomes increasingly cohesive thus tuming from a so-called A into a C-powder. An emperical measure for powder cohesiviness is the so-called Hausner Ratio (HR) which is the ratio between the lowest and the highest density of a powder as measured by a standardized technique. Fig. 11 shows our experimental results, indicating starch of the desired moisture percentage to be at the transition from A into C powder.

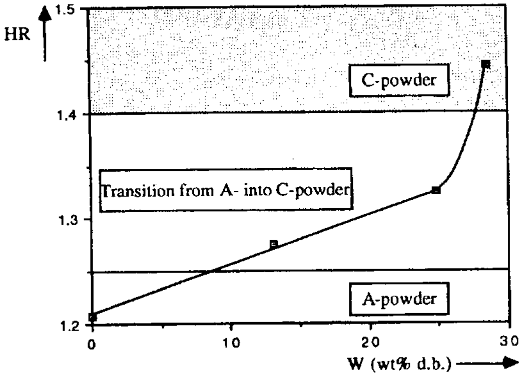


Fig. 11. Influence of moisture content W of potato starch on its Hausner ratio, HR, at T= 293 K.

AC and C powders are known to be too sticky to be processed into conventional gas-solid contactors such as a fixed bed, a moving bed or a gas-solid trickle flow reactor.

Indeed, in these reactors a poor gas-solid contact is obtained due to particle agglomeration. This results in an inferior product quality [13].

Based on $\rho_p = 1500$ kg m^{-3} and $R_p = 25$ μm, dry potato starch can be classified as an A-powder which is very suitable for dense phase fluidization as is confirmed by a patent (Thompson [15]).

In contrast, semi dry potato starch of W 10 wt % d.b. cannot be fluidized by aeration (Stigter [16]). Apparently, such a low W is already sufficient to get channelling, which is a characteristic for a C-powder. So, starch changes from an A- to a C-powder with increasing W from 0 to 10 wt % d.b.. Fluidization of cohesive powders can often be improved by the use of mechanical stirrers, vibrators or by the addition of sub-micron particles. In most chemical reactions, such as the hydroxyethylation of-granular potato starch, addition of sub-micron silica is not desired because of both difficulties in processing and purity requirements of the product.

Therefore, we focused on the effects of stirring and/or vibration of an aerated bed of potato starch.

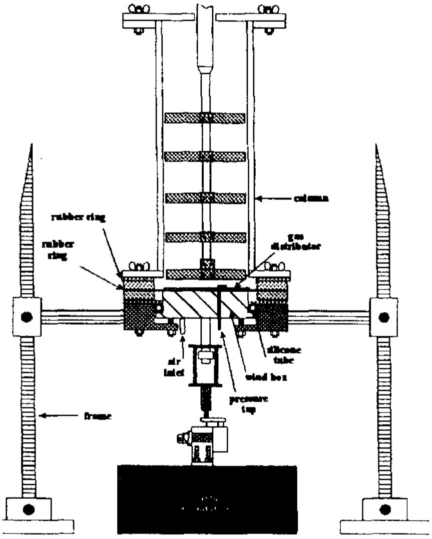


Fig. 12. Scheme of the aerated stirred vibrating fluidized bed.

Experimental

The experimental set-up is shown in Fig. 12. The bed has an inner diameter of 29 cm and a height of 1.35 m. The gas distributor, consisting of porous stainless steel, could be brought in vibration with variable frequency ($0 < f < 90$ s^{-1}) and amplitude $0 < x_0 < 1.5$ mm. Stirring of the bed with a various number of blades $1 \leq n \leq 15$ was possible at various rates $0.8 < N < 4.2$ rev/s. Always the relative humidity of the gas fed to the bed was in equilibrium with the moisture content of the starch in the bed.

The aerated bed without stirring and vibration

Kuipers [13] showed that even an aerated bed of relatively dry potato starch of W = 6 wt % d.b. cannot be fluidized without mechanical energy input. Initially, the pressure drop across the fixed bed increases proportionally with increasing air velocity. With increasing air rate, large horizontal cracks appear in the bed. The latter tends to lift as a plug (see Fig. 13a). At higher air velocities stable channels are formed in the static bed. Due to channelling and cracking, the behaviour of the bed is very unstable which means that no reproducible results are obtained after repetition of the experiment. The

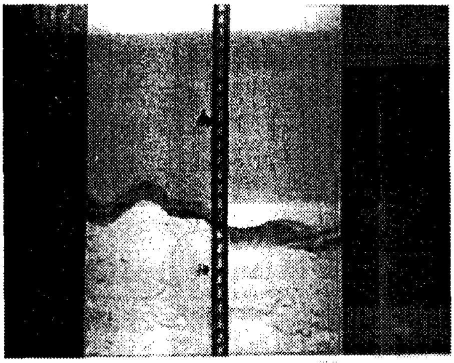


Fig. 13a. Channelling in an aerated bed of potato starch. W = 10.2 wt % d.b., H_0 = 0.76 m.

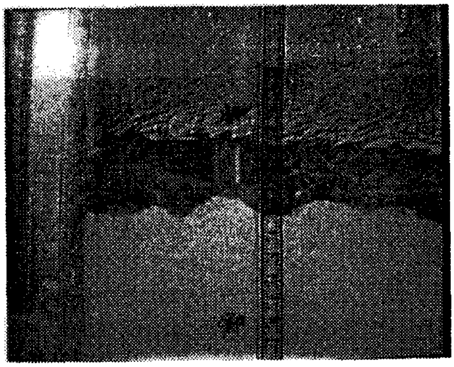


Fig. 13b. Agglomerates and flocks at the bed surface of an aerated and stirred bed of potato starch. W=10.2 wt %, H_0=0.76 m, δ_0 = 124 mm and N = 1.67 rps.

Fig. 13c. Channelling at 10 cm above the gas distributor in an aerated and vibrated bed of potato starch. W = 13.1 wt % d.b., $H_0 = 0.76$, $x_0 = 0.83$ mm and $f = 30\ s^{-1}$ (G = 3).

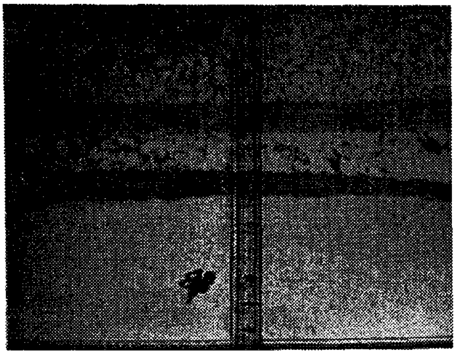


Fig. 13d. Elimination of channels and agglomerates (flocks) even at the surface in a stirred vibrating fluidized bed of potato starch. W=13.1 wt % d.b., $H_0 = 0.74$ m, $\delta_0 = 124$ mm, N = 1.67 rps, $x_0 = 0.83$ mm (G = 3) and $f = 30\ s^{-1}$.

gas-solid contact in such a bed is poor and inhomogeneous. Therefore, a conventional fluidized bed is not a suitable reactor for C-powders such as semi-dry granular starch.

The same conclusion follows from the Fluidisation Index ($FI = \Delta pA/Mg$) which should be one for good fluidization. Fig. 14 shows both the instability of the bed and the poor fluidisation ($FI < 0.9$) for a conventional fluid bed of relatively dry starch of W = 10 wt % d.b. With increasing humidity fluidizability further deteriorates.

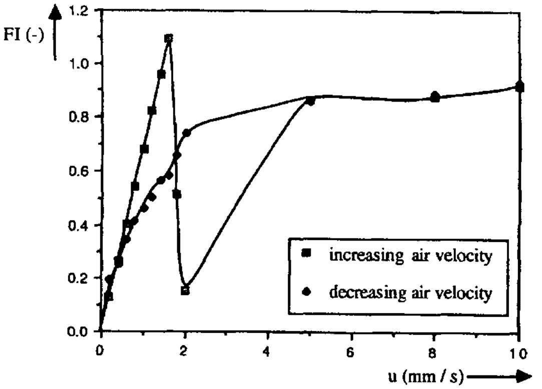


Fig. 14. Fluidisation index FI of potato starch without vibration and stirring versus gas velocity. W = 10.2 wt % d.b. and $H_0 = 0.76$ m.

The stirred fluidized bed

Stirring the bed with a single stirrer has a positive effect on fluidisation only if the stirrer is close to the bottom plate. (see Fig. 15). Applying multiple stirrers gives a further improvement (see fig. 16). The optimal blade distance and stirring speed appeared to depend on the moisture content. For 10 wt % d.b. moist a maximal value of FI can be realized with an interblade distance $\delta_b \leq 16$ cm and $N \geq 1.7$ rps.

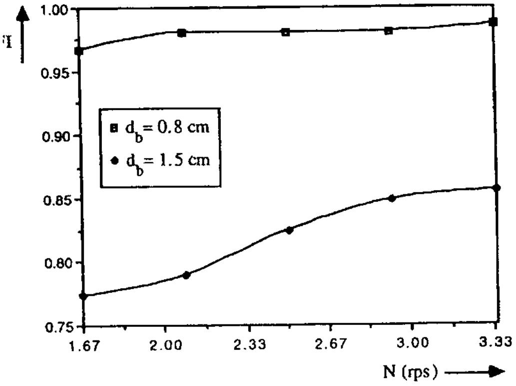


Fig. 15. Effect of stirrer position on the fluidization index FI of a stirred bed of potato starch as a function of stirrer speed N for a single stirrer. $H_0 = 0.09$ m, $W = 10.2$ wt % d.b., $u/u_{mf} \approx 2.9$.

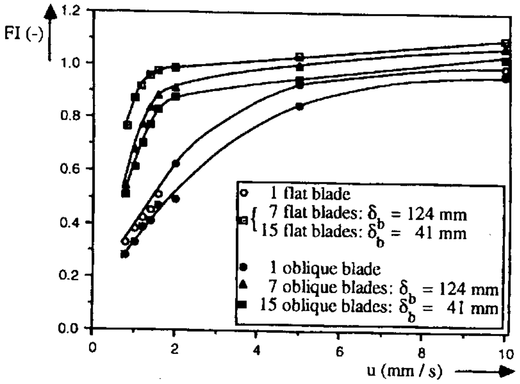


Fig. 16. Influence of interblade distance and stirrer design on FI of a stirred aerated bed of starch. $H_0 = 0.76$ m. $W = 10.2$ wt % d.b. and $N = 1.67$ rps.

Starch of higher moisture content asks for a slightly lower optimal interblade distance (e.g. 12 cm for $W = 22$ wt % d.b.) though no higher optimal stirring speed is required (see Fig.17a). With increasing stirring speed, bed expansion, and thus bed porosity (ε) increases and as a result the torque per stirrer blade (T') decreases, see Fig. 17. By applying the optimal stirring conditions mentioned above, it appeared possible to eliminate any channeling in the bed. However, stirring alone is not effective in destroying large starch particle agglomerates which remain present in the fluid bed. This can be nicely seen in Fig.13b showing large agglomerates at the bed surface, resulting in a "mountaneous landscape" where a flat surface is preferred.

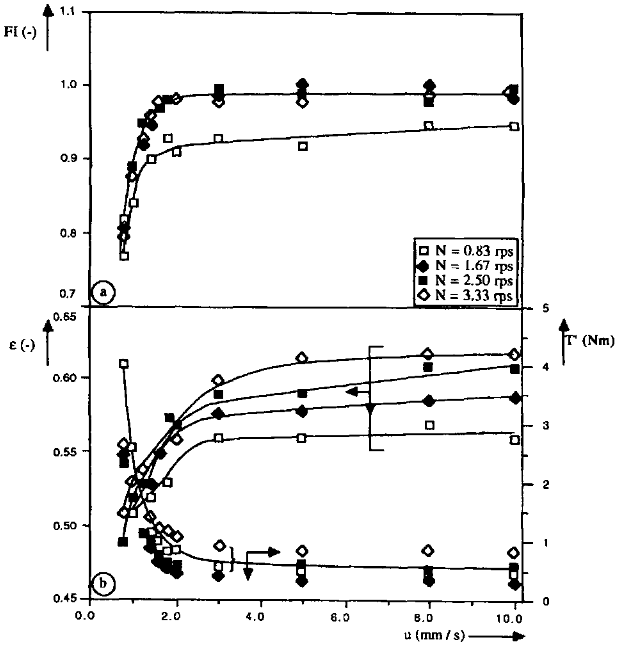


Fig. 17. Fluidisation of a stirred bed of starch of W = 22.4 wt % d.b., δ_b = 124 mm and H_0 = 0.84 m.

a) FI as a function of u for various N,

b) ε and T' as a function of u for various N.

Agglomerate, or flock formation is undesired because it may result in inhomogeneous derivatisation due to insufficient gas-solid contact in the center of the flocks.

Therefore, stirring alone is not sufficient to get at good fluidisation at the scale of the particles.

The vibrating fluidized bed

Bed vibration is characterized by frequency (f) and amplitude (x_0), often combined in a dimensionesless acceleration intensity G:

$$G = \omega^2 x_0/g$$

with $\omega = 2\pi f$ rad/s.

In our experiments G and f varied as follows: $1 \leq G \leq 8$; $30 \leq f \leq 90$ s^{-1} with starch of W = 13 wt % d.b.

By vibration of an aerated bed of potato starch, the channels in the lower part (about 0.1 m) of the bed are eliminated only. The vibration is not sufficient to eliminate channeling in the entire bed. As a result, a relatively low bed expansion is obtained. A minimum amplitude and frequency must be exceeded to balance the weight of the bed by the pressure drop over the bed. Nevertheless, at gas velocities above 2 mm·s^{-1} always cracks and channels appeared in the upper part of bed (see Fig. 13c), independent of the values of G and f. The channels cause part of the gas to bypass the bed, thereby reducing the gas-solid contact. However, vibration with sufficient intensity causes the agglomerates to break down, even in the upper part of a bed of H = 0.76 m.

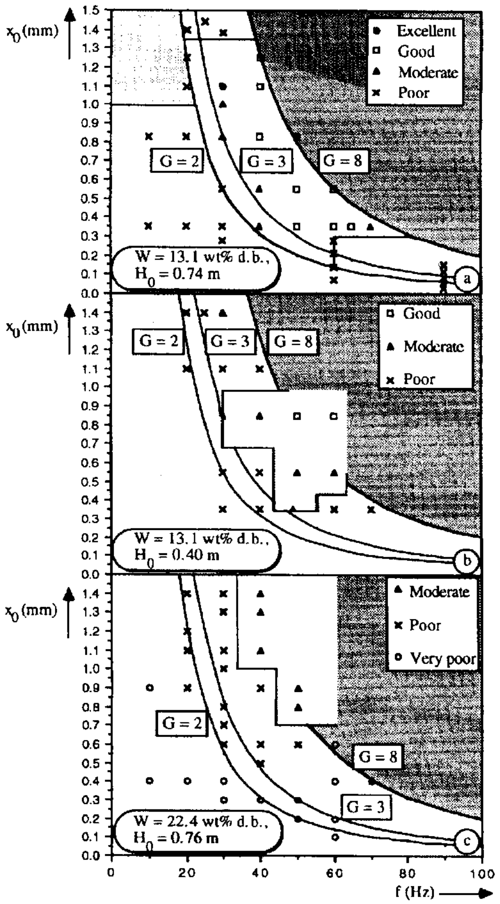


Fig. 18. Fluidisation quality chart showing the amplitude x_0 and frequency f range for which both channels and agglomerates are eliminated in an aerated stirred vibrating fluidized bed of starch with u = 2mm·s^{-1}, δ_b = 124 mm and N = 1.67 rps.

a) W = 13.1 wt % d.b., H_0 = 0.74 m.
b) W = 13.1 wt % d.b., H_0 = 0.40 m.
c) W = 22.4 wt % d.b., H_0 = 0.76 m.

The stirred vibrating fluidized bed

Simultaneous vibration and stirring of an aerated bed of starch was investigated to determine what, if any, advantages can be gained this way. To guarantee elimination of channels in a bed of 0.74 m (W = 13.2 wt % d.b.), flat stirrer blades were used with δ_b = 124 mm. Experiments were performed at frequencies of 30, 60 and 90 s^{-1} whereas

G ranged from 1 to 8. The vibration intensity appears to be too low at G = 1 to break down the starch agglomerates at the surface of the bed. At G = 5 these flocks are still present for f = 90 s^{-1} but not at 60 s^{-1}. A further decrease of f at G = 5 is accompanied by the creation of slugs at $u > u_{mf} \approx 1.7$ mm/s. At G = 3 the agglomerates disappear at 60 s^{-1} only. These results show that not only G but also f influences the quality of fluidisation.

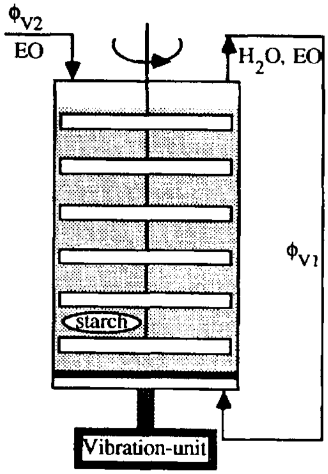


Fig. 19. Gas-solid hydroxyethylation of potato starch in a stirred vibrating fluidized bed.

Fig. 18 shows the results obtained in form of a fluidisation quality chart for three moisture contents and $u/u_{mf} = 1.1$. In the white region, moderate to good fluidisation is realized. The higher the moisture content of the starch the higher the minimal G value is for which good fluidisation is obtained.

Here, moderate, to good means a fluidisation nearly to completely free of both channels and agglomerates. An example is shown in Fig. 13d. The picture shows a completely flat surface, indicating complete break-up of agglomerates whereas no channels are visible. As soon as the vibration is stopped the agglomerates return. No measurements at G > 8 were performed due to (power) limitations in the vibrating system.

The lowest energy consumption at a particular G is obtained with the highest x_0. Therefore the upper left corner of the white regions is the preferred mode of operation.

Gas-solid hydroxyethylation of potato starch in a stirred vibrating fluidized bed

In this section a preliminary design is presented of a stirred vibrating fluidized bed reactor for producing 1 ton/hr Hydroxy-Ethylated Starch HES) of Molar Substitution of 0.1 by reaction with ethyleneoxide. In this system the same 4 reactions occur as discussed above for propylene oxide. The design was based on the reaction kinetics reported by Kuipers et al [17].

Figure 19 schematically shows a potential set-up of a stirred vibrating fluidized bed reactor for the batch-wise hydroxyethylation of potato starch. A volumetric recycle flow ϕ_{V1} is used to fluidize the starch. For fluidization the superficial gas velocity u must be minimally 0.002 $m \cdot s^{-1}$, resulting in $u/u_{mf} \geq 1.2$. For a bed already having the desired moisture content, only EO has to be added to the reactor provided no vent is applied. The pressure in the reactor is kept constant by a time-dependent feed rate ϕ_{V2}

Table 1

Optimal operation parameters for hydroxyethylation of semi-dry potato starch in a stirred vibrating fluidized bed reactor (H_{bed} =1 m) for a desired MS of 0.1 with a capacity of 1000 kg hydroxyethyl starch/h.

	Unalkalized potato starch	Alkalized potato starch
c_{NaOH} (mmol/mol AGU)	0	40
T (K)	368	333
W (wt % d.b.)	9.9	14.2
p_{EO} (kPa)	1190.5	495.1
p_{H_2O} (kPa)	32	5
S_{HES} (-)	> 0.48	0.72
t (ks)	1.2	0.9
D_b (m)	0.84	0.73
ϕ_{vl} (m^3s^{-1})	0.0011	0.00084

of pure EO which balances the EO conversion rate. So, the concentration of EO remains constant in the gas phase of the reactor.

Based on obtaining an optimal selectivity with respect to HES, the result is shown in Table 1 for both unalkalized (= not catalysed) and alkalized (= catalysed) starch. For further details, see [17]. Due to the higher temperatures possible in the dry process, hydroxyethylation seems possible without addition of hydroxide.

For superior selectivity however, also relative to the classical slurry process, pre-

Table 2

Advantages of the gas-solid process relative to the classical slurry process

Variable	Gas-solid hydroxyethylation	Classical slurry process
Temperature, T	T > 323K is advantageous for high S and reactivity. Diffusion limitation occurs at too high T, pending on c_{NaOH}, W and a_{EO}.	T < 323K due to gelatinization of the starch. This results in relatively long reaction times.
Selectivity S_{HES}	$S_{HES} \approx 0.72$ for ungelatinized alkalized starch.	< 0.62 [14]
Na_2SO_4 addition	No Na_2SO_4 has to be added	Na_2SO_4 is added to reduce gelatinization
Molar Substitution	MS of 0.5 possible without loosing the granular structure.	MS < 0.1. Higher MS results in purification problems due to loss of the granular structure.
Residence time, t	0.9 ks	58 ks

alkalining the starch is helpful. Spectacular too is the expected reduction in residence time, and thus in reactor volume, required for the gas-solid process. Table 2 compares the two processes. Here, the slurry data were taken from van Warners [14]. If our calculations can be proven in a pilot plant, the dry process will have a bright future.

Conclusions

Two novel continuous processes for the chemical derivatisation of starch have been developed. A gas-solid fluidized bed process for modifications with gaseous substrates and a gel process in a static mixer reactor for handling concentrated pastes. Based on results obtained with hydroxyethylation (dry-process) and hydroxypropylation (gel-process) it can be concluded that both processes are very attractive relative to the classical slurry process due to improved reaction selectivity, much shorter residence times and superior controlability and safety.

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Notation

c_{NaOH} = mmol NaOH/mol AGU
$c_{p,fl}$ = specific heat of a fluid [J/kg K]
d_i = inside tube diameter [m]
d_{sm} = diameter of a static mixer element [m]
d_e = diameter of the bed [m]
$D_{e,z}$ = effective axial mass dispersion coefficient [m^2/s]
f = frequency of sinusoidal vibration [s^{-1}]
4f = fanning friction factor [-]
F(t) = cumulative residence time distribution function [-)
FI = fluidization index, FI = $\Delta pA/(Mg)$ [-]
G = dimensionless vibrational acceleration: G = $(\omega^2 x_0/g)$ [-]
g = gravitational constant: g = 9.81 [ms^{-2}]
H_0 = settled bed height [m]
l_{sm} = length of a static mixer element [m]
L = length [m]
m_{starch} = mass fraction starch in reaction mixture [-]
M = mass of bed [kg]
MS = molar substitution [-]
n = number of stirrers in the bed [-]
N = stirring speed, [rev s^{-1}]

$N_{Nu_i} = \frac{\alpha_{i,1} d_i}{\lambda_{fl}}$, Nusselt number [-]

$N_{Nu,av} = \frac{\alpha w d_i}{\lambda}$, = average Nusselt number [-]

$N_{Pe} = \frac{vL}{D_{e,z}}$, Péclet number for axial dispersed flow region [-]

$N_{Pe_{h,t}} = N_{Re} N_{Pr} = \frac{\rho_{fl} c_{p,fl} v d_i}{\lambda_{fl}}$, Peclet number for heat based on the tube diameter [-]

$N_{Pr} = \frac{c_{p,fl} \eta_{fl}}{\lambda_{fl}}$, Prandtl number [-]

$N_{Re} = \frac{\rho v d_i}{\eta}$ = Reynolds number [-]

p_{EO} = partial pressure of ethylene oxide [Pa]
p_{H_2O} = partial pressure of water [Pa]
S_{HES}, = selectivity of the reaction toward hydroxyethyl and hydroxypropyl starch,
S_{HPS} respectively
t = time [s]
T = temperature [K]
T' = torque per stirrer blade, [kg m^2 s^{-2}]
u = superficial gas velocity [m s^{-1}]
u_{mf} = minimum fluidization velocity [m s^{-1}]
v = superficial fluid velocity [m/s]
V_r = reactor volume [m^3]
W = moisture content of the starch [wt % d.b]
x_0 = amplitude of sinusoidal vibration [m]
$\alpha_{i,1}$ = inside wall heat transfer coefficient [W/m^2 K]
α_w = wall heat transfer coefficient [W/m^2 K]
δ_b = interblade distance [-]
Δp = pressure drop over the bed [N m^2]
ε = porosity of the bed [-]
ξ_{PO} = conversion of propylene oxide [-]
λ = thermal conductivity [W/m K]
η = viscosity [Pa s]
ρ = density [kg/m^3]
σ_0 = standard deviation at inlet of mixer [-]
σ_{mix} = standard deviation due to incomplete mixing [-]
Φ_v = volumetric flow rate [m^3/s]
ω = angular frequency of sinusoidal vibration: $\omega = 2\pi f$ [rad s^{-1}]

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Streszczenie

Wprowadzono dwa nowe ciągłe procesy do chemicznej derywatyzacji skrobi. Są to: proces w gazowo-stałym złożu fluidalnym do modyfikacji z udziałem substratów gazowych i proces żelowy w statystycznym reaktorze z mieszadłem do otrzymywania stężonych past. Na podstawie wyników w hydroksyetylowaniu (proces suchy) i hydroksypropylowaniu (proces żelowy) dochodzi się do wniosku, że oba procesy są korzystniejsze od odpowiednich klasycznych procesów prowadzonych z zawiesinami pod względem selektywności, krótszego czasu przebiegu, bezpieczeństwa i doskonałej kontroli ich przebiegu.