SOLID BED PROPERTIES IN SUPERCRITICAL PROCESSING

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In this work several properties of fixed beds of natural materials are examined with respect to their impact on batch and continuous extraction processes using supercritical fluids. Important properties are, amongst others, compressibility, permeability and pressure propagation in fixed beds. The aim is to develop an understanding of solid bed behaviour in order to estimate its significance for supercritical processing.

INTRODUCTION

Within supercritical processing of solid materials at industrial scale, physical properties of the solid bed like its void fraction and permeability are mostly unknown. In batch extraction, extractor capacity, pressure drop over the bed height, channelling and compaction are related to the mentioned characteristics and depend on moisture, temperature, oil content and compressibility of the solid. Recent investigations are dedicated to develop continuous supercritical extraction processes of solid source materials. Most promising is the use of the extruder technology for feeding the solid into the extraction zone and conveying the extracted solid out of it again. Figure 1 shows a schematic drawing of an extruder prepared for supercritical extraction. Not only mechanical design of the extruder but also performance of the extraction depends on physical material characteristics such as compaction, porosity, pressure distribution and permeability of the solid bed. In order to determine influence of material composition and operating conditions on the most relevant properties it is necessary to study these using simplified geometries like a piston systems. In the following different properties are presented discussing these in the context of feasibility and optimisation of the process. Adapting a model to the process, a parameter study is carried out using relevant data.

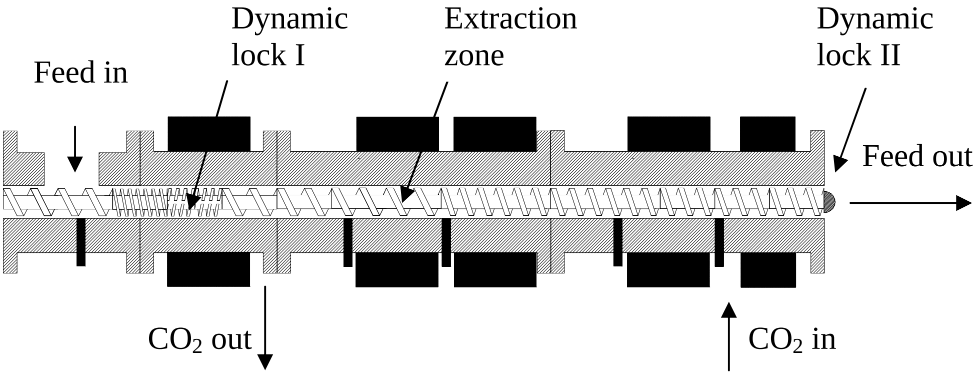

Figure 1: Schematic drawing of an extruder-extractor

I – MECHANICAL COMPACTION

According to Eggers (1996) and (2000) [1,2] special features like fixed bed compaction play an important role in supercritical batch extraction. Especially fine powders with certain moisture content (e.g. wheat gluten) tend to compact during the extraction process, which can lead to low permeability and bad extraction performance as far as blocking. Compaction during extraction is especially a problem when scaling up, probably due to a pre-compaction caused by the higher own weight of the material. Other important factors are particle entrainment and compression due to the pressure difference along the bed axis during extraction.

Today, hop extraction is one of the few profitable applications of supercritical CO_2 -extraction at large scale. Realising a continuous extrusion-extraction process and thus increasing cost-effectiveness in a field where supercritical extraction is already state-of-the-art would be particularly attractive. Contrary to batch extraction, good compressibility behaviour is a feature that is necessary for the feasibility of the process because it enables the formation of dynamic sealing keeping the supercritical CO_2 inside the extraction zone of the extruder.

Therefore, amongst others, compressibility of hop was examined with respect to the extrusion-extraction process. Prior to the experiment the hop was pre-treated in an extruder in order to simulate the conditions of the material that is to form a gas proof plug in the extrusion-extraction process. After being fed into the extruder high shear reduces the particles to a fine powder. To some degree the actual particle size in the plug will depend on factors like moisture, oil content and the configuration of the preceding screws. A test using the same type of hop from different extrusion trials (different PSD) did not show a significant influence. So focus was put on the influence of moisture and temperature.

Results of uniaxial compression trials on hop (Hallertau Perle) in a cylindrical vessel (d_i = 40 mm, $L_{Bed} \cong$ 400 mm) are shown in **Figure 2**.

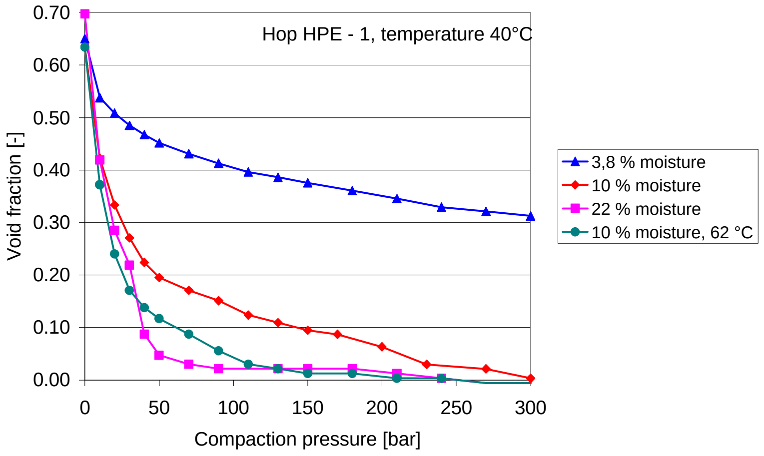

Figure 2: Influence of temperature and moisture on material compressibility

There is a clear tendency of the material being more compressible at higher temperatures. This is supposed to be due to a decrease in viscosity of the resins contained in hop. Moisture content however shows to be the most important parameter. Water as a binder promotes the formation of bridges between the particles and through its polarity enhances dipole interactions and capillarity effects. Moreover water wets the surface and partly the pores of the particles leading to a softening of the material.

These types of interactions are much weaker in case of oil showing much less influence in respective experiments using caraway with different oil contents.

With respect to the extrusion-extraction process this means that above all moisture content has to be controlled. Even if all oil/resin is removed during extraction, sufficient compressibility and thus gas tightness can be reached. The impact of temperature control however should not be neglected.

II – PERMEABILITY

Table ***1*** gives an overview on the solid bed behaviour of different natural materials depending on pre-compaction. After pre-compaction CO_2 is passed through the bed , which is in a cylindrical device (d_i = 40 mm, $L_{Bed} \cong$ 400 mm). Pressure difference is obtained by measuring inlet and outlet pressure by the use of manometers. Small pressure differences can be measured via a pressure difference gauge. In a certain range of mass flow and corresponding pressure drop a definite value of permeability can be calculated according to Darcy's law for laminar flow (eq. 1), where $\dot{M}_{CO_2}$ is CO_2 mass flow, h dynamical viscosity, B bed permeability and A_{cyl} the cross-sectional area of the cylinder.

$$\dot{M}_{CO_2} = -r_{CO_2} A_{cyl} \frac{B}{h} grad(P)$$

eq. 1: Darcy's law for laminar flow

Table 1: Permeability of different materials depending on pre-compaction pressure

	$P_{compress}$ [bar]	Void fraction [-]	Permeability B [m²]	M_{CO2} [kg/h]
Caraway	70	0.05	-	0
	40	0.08	~7.8E-19	~0.0012
	30	0.2	~4.2E-17	~0.06
Hop (Hallertau Perle)	165	0.1	-	0
	65	0.2	1.70E-18	0.0046
	35	0.3	~6E-16	~1.3
Hop (H.H. Magnum)	~150	0.1	-	0
	40	0.2	-	0
	25	0.3	2.40E-16	~0.6
Cocoa	~250	0.15	1.80E-16	0.6
	60	0.25	beyond measuring range	

The first column of the table gives the axial pressure applied for pre-compaction. The second column shows the resulting void fraction of the fixed bed. The permeability given in the third column is calculated using the CO_2 flow measured at the outlet of the fixed bed given in the fourth column. A CO_2 flow of "0" means that no value could be measured i.e. that flow is much lower than the lower limit of the measuring range (0,0002 kg/h) of the flowmeter and that no flow could be discerned by other means either. In some cases an evolution of permeability with time could be observed. So caraway with a void fraction of 0.08 at first proved to be gas proof but became permeable after a while. Mechanical de-oiling of the material through the pressure difference plays a role in this. In other cases permeability decreases with time for various reasons, e.g. mutual solubility effects and swelling. However in all cases the maximum value that has been measured is recorded.

Generally speaking, it is possible to form gas proof plugs with extruded caraway as well as the two types of hop that were examined. The minimum compaction pressure required to reach this is higher for hop than for caraway. For cocoa it was not possible to obtain such a gas tight plug. Processing (extrusion) of cocoa proved to be very difficult anyway. This might be due to the relatively low water content of the original material.

Measurements with extracted material (results not shown) made clear that a certain moisture content is required to enable sufficient compression and - as permeability is strongly related to the degree of compaction - to obtain a gas proof lock.

III – RADIAL TO AXIAL PRESSURE RATIO, PRESSURE PROPAGATION

For process feasibility it is important that the material plugs remain stable and are not “shot” out of the extruder because of the CO_2 pressure in the extraction zone. In this the pressure distribution in the solid bed expressed by the radial to axial pressure ratio plays an important role. The radial to axial pressure ratio of, amongst others, caraway is measured in an apparatus, the working principle of which is shown in Figure 3. By applying a certain axial pressure using the piston and measuring the radial pressure at different axial locations of the fixed bed, the product of friction coefficient, m, and radial to axial pressure ratio, l, can be derived applying force balances [6].

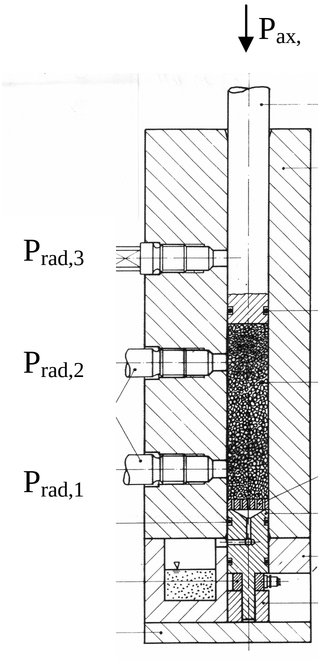

Figure 3: Schematic drawing of experimental apparatus

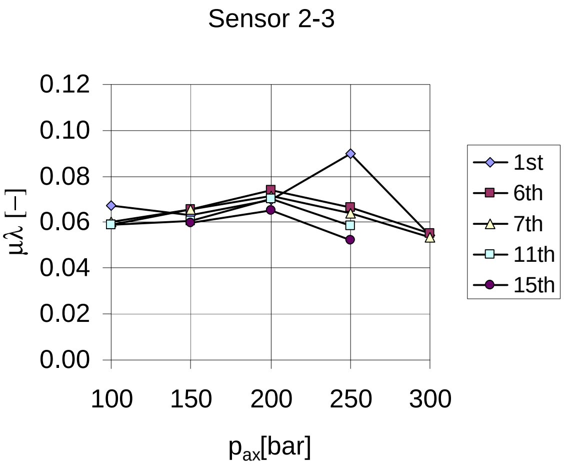

Figure 4: Product friction coefficient and pressure ratio as a function of applied pressure

Figure 4 shows $m \cdot l$ as a function of the applied axial pressure for the upper part of the bed for extruded caraway at room temperature. For each pressure step the trial was repeated several times in order to analyse dynamic behaviour. It may be deduced that at these conditions successive compaction does not change principle behaviour regarding friction and pressure ratio. Typically, the coefficient of friction for loose powders is higher than for compacted solids [7]. On the other hand pressure distribution behaviour in the compacted state may change to a more liquid-like behaviour (higher radial to axial pressure ratio) so that the product of the two factors does not change significantly in this case. However it is assumed that this depends on the material and on processing conditions like temperature and moisture as well.

IV – MODELLING

Modelling of supercritical solid bed batch extraction has been carried out as a function of solid material properties by different authors [3, 4, 5].

In case of continuous extraction within an extruder the solid is compacted at the inlet in order to form a gas tight plug. This mechanical treatment takes influence on the solid characteristics within the following extraction zone like the size of solid agglomerates which on its turn determines extraction efficiency. Further little is known about possible solvent loading. Whether or not experience from batch extraction may be applied depends on distribution of the solid within the extraction zone and phenomena like channelling.

A simplified model based on the idea of a cascade of ideally mixed tanks was developed in order to describe the continuous counter current process. In future work this model will be adapted to extraction experiments in a pilot extrusion-extractor. At this stage it can be used in order to study the influence of different process parameters. Figure 5 shows the influence of CO_2-flow at constant feed flow of 5 kg/h for hop extraction. Figure 6 shows the influence of particle size at the same feed flow and a solvent flow of 10 kg/h. The number of stirred tanks was fixed to 3 i.e. that non-ideal behaviour such as axial dispersion is considered even though at this moment it could not be accurately quantified yet.

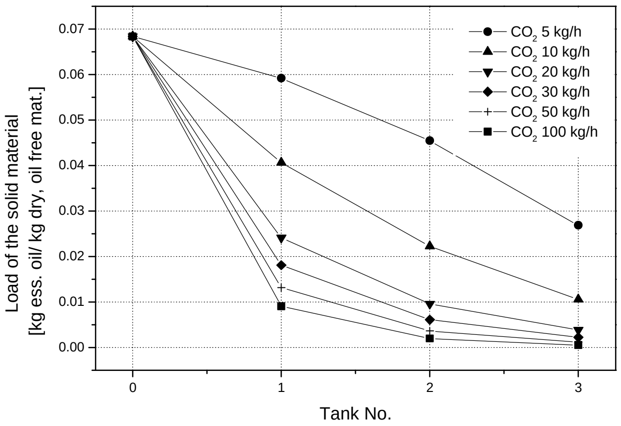

Figure 5: Influence of solvent flow on extraction performance

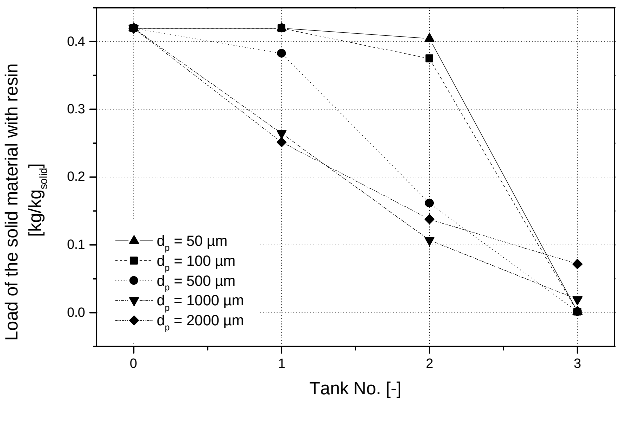

Figure 6: Influence of particle size on extraction performance

Figure 5 shows a typical curve of a counter current contactor as also known from heat transfer. Here, the de-oiling of solid is depicted as a function of the axial position in terms of theoretical stages. At low CO2 – flow entering the contactor from the right hand side, solvent capacity is limiting for the de-oiling process. Thus the solid being retrieved (at the right hand side) still has a relatively high oil content. A critical solvent mass flow exists, at which the concentration curve is bent to the opposite side being the available oil the limiting factor for extraction arriving at relatively low rest oil content within less stages.

In an analogous way, particle size takes influence on the extraction performance (Figure 6): in case of small particles the solvent is saturated quickly with no net mass transfer happening in the last stage whereas large particles lead to high mass transfer resistance requiring the complete extraction zone for sufficient de-oiling to take place.

CONCLUSION

The fixed bed properties compressibility, permeability and pressure propagation for natural material (hop, caraway, cocoa) were examined with respect to supercritical batch and continuous extraction processes. Extraction modelling of continuous supercritical extraction in an extruder-extractor was introduced.

In terms of process feasibility the most important processing variables having a huge impact on the mentioned fixed bed properties were found to be moisture and temperature. For batch extraction fine material has to be sufficiently dry in order to prevent from compacting and inefficient extraction. In extrusion extraction however compaction is the principle of sealing the extraction zone, thus a minimum moisture content is required. Temperature has an effect as well, though less pronounced. Adapting temperature and moisture with respect to the desired compaction behaviour however can have disadvantageous effects on extraction kinetics, so in each case an optimum solution has to be found.

Acknowledgements

We thank the European Union for their financial support in the context of the project CREX and our project partners for their contribution to our scientific work.

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