BLEACHING OF LIPID MATERIALS USING CARBON DIOXIDE AS MODERATOR

Geert F. Woerlee* and Hubert C. Pellikaan
FeyeCon Development & Implementation B.V., Rijnkade 17A,
1382 GS Weesp,The Netherlands
E-mail: geert@feyecon.com, Fax: +31 294 458866

Lipid materials such as triglycerides waxes and fosfolipids all have in common that they are obtained from natural sources in a crude quality which is often unsuitable for human consumption or other commercial uses. Hence such crude lipid raw materials are usually subjected to a sequence of refining and other processing steps to upgrade the quality and/or applicability thereof. A commonly applied process in the upgrading of crude lipid materials includes bleaching.

The new bleaching method was developed starting from the insight that in many existing processing methods, particularly in those cases where a reactive granulate is employed, the rate limiting factor is the rate of diffusion of the reactants in the lipid material. The inclusion of a near supercritical gas was found to be particularly advantageous in processing methods that employ a reactive granulate, such as a catalyst or an adsorbent.

This study shows that the required contacting time for bleaching processes was decreased linear with the decrease of viscosity and its subsequently diffusivity increase. The contacting time could be decreased by a factor ten due to the dissolved carbon dioxide. More surprisingly was the fact the efficiency of the applied reactive granulate was increased by approximately 30%. This is most likely due to the fact that the active sites of the granulate can be reach more easily by the lipid material. An additional advantage of the process is the decrease loss of the material which accumulates on the granulate. The improved filtering quality decreased the loss of lipid materials by 50%.

INTRODUCTION

Lipid materials such as triglycerides, waxes and fosfolipids all have in common that they are obtained from natural sources in a crude quality, which is often unsuitable for human consumption or commercial uses. Hence such crude lipid raw materials are usually subjected to a sequence of refining and other processing steps to upgrade the quality and/or applicability thereof. Processes commonly applied in the upgrading of crude lipid materials include bleaching, deodorisation, fractionation, hydrogenation, interesterification, hydrolysis etc.

The aforementioned methods of processing lipid materials are well known in the art and are normally conducted at elevated temperatures. Conventional methods of processing lipid materials tend to be rather time-consuming, i.e. typically it takes several hours to bring them to completion. This is mainly due to the fact that the chemical phenomena governing these processes occur at a rather slow rate. Given the enormous scale at which these processes are operated, even a slight improvement in terms of processing time may generate very significant benefits, particularly in terms of savings.

The application of supercritical gases in the processing of lipid materials is known in many applications. The known areas of application are extraction from plant materials and isolation of lipid fractions through supercritical separation. Schulmeyer et al. [1] relates to a process for obtaining vegetable oils by extraction with liquid or supercritical carbon dioxide, wherein the solvent flows through the comminuted oil seed or a crude oil and is subsequently passed through a bed of bleaching agent. Stahl et al. [2] concerns a process for the extractive production of waxes from fossil, vegetable or animal starting material, by extraction with a gas at supercritical pressure and temperature conditions wherein the separation of the extract-containing gas is achieved in a separator part by pressure reduction and/or temperature change.

The present method was developed starting from the insight that in many existing processing methods, particularly in those cases where a reactive granulate is employed, the rate limiting factor is the rate of diffusion of the reactants in the lipid material. It was found that the diffusion rates of these reactants could be increased significantly by dissolving into the lipid material a gas at near supercritical conditions. The inclusion of a near supercritical gas was found to be particularly advantageous in processing methods that employ a reactive granulate, such as a catalyst, an adsorbent or a bleaching compounds. In the following we will focus on the bleaching process.

EXPERIMENTAL METHOD AND PROCEDURE

For this study an experimental facility was constructed up to 400 bar. The reaction vessel with volume of 322ml was placed in a thermostatic bath. On top of the reaction vessel an additional vessel (1/2”pipe) was installed to dose the solid material at a specific time. At the bottom of the autoclave a filter was applied to separate the granulate form the lipid material after the bleaching process. The mixing was performed manually. The experimental set-up is shown in figure 1.

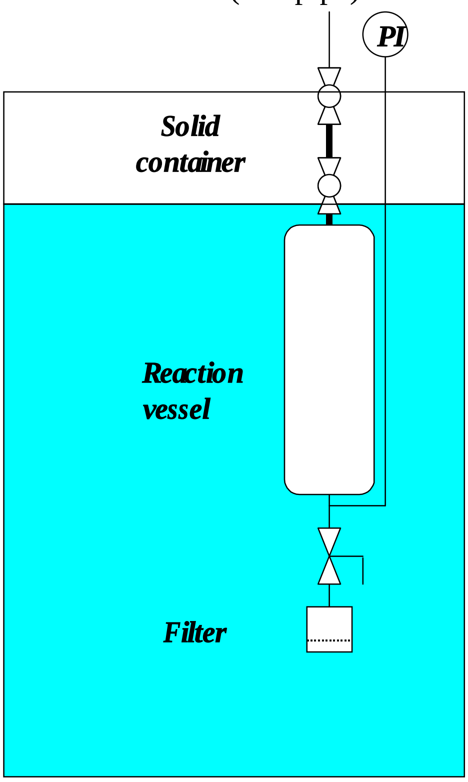

Figure 1: Experimental set-up.

The bleaching experiments were carried out by contacting approximately 100gram of lipid material with 2.5%wt of bleaching earth and 1%wt of activated coal. The applied temperature was 75°C, while the normal reaction time was taken as 20 minutes.

The color change of the lipid material was measured according to the (L, a, b) coordinate system. In this system the (L) represent the black and white axis, (a) de red-green colour axis and (b) de yellow-bleu colour axis. The colour difference is calculated as the absolute difference in this colour space as:

$$\Delta E_{ab} = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} .$$

For bleaching the most important parameter is the yellowness (b) of the material.

EXPERIMENTAL RESULTS

Firstly, the solubility of CO_2 in the lipid material was measured. This was done by weighing an amount of CO_2 and lipid material in the autoclave. After mixing and reading the pressure the dissolved amount of CO_2 could be calculated by solving the component balances and assuming no solubility of the lipid material in the CO_2 phase. Figure 2 shows the measured solubility and of the CO_2 as function of the gas density at an reaction temperature of 75°C.

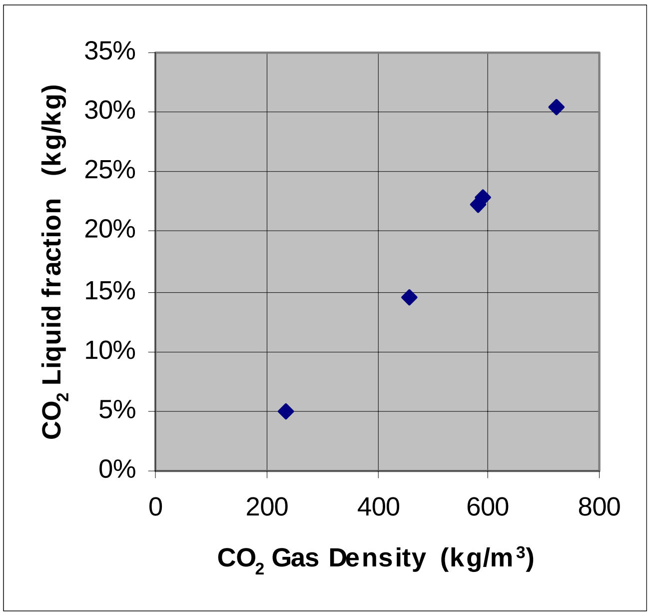

Figure 2: The relative amount of dissolved CO_2 in the lipid material as function of the gas density.

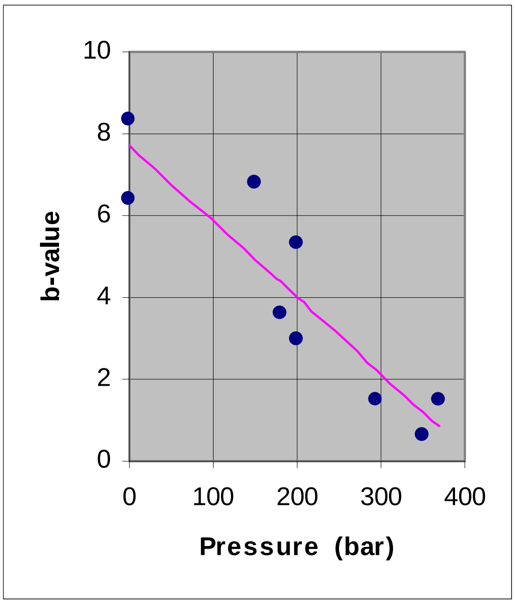

Figure 3: Decrease of the yellowness as function of the applied CO_2 pressure at 75ºC.

Figure 3 shows that when increasing the pressure the effectiveness of the bleaching process also increases. This probably means that more active sites of the bleaching earth become available. This has to do with the amount of carbon dioxide that is dissolved in the liquid lipid phase, which decreases the viscosity of the liquid dramatically.

Clearer is the decrease of the required process time to bleach the lipid material when carbon dioxide is used as moderator. Figure 4 shows the yellowness as function of the process time for a process operated at 180bar and 75ºC. The figure shows an exponential decrease of the yellowness with a certain end value. This end value is determined by the effectiveness of the process as shown in figure 3. The exponential decrease is such that after 210 seconds 99% of the bleaching capacity is reached. When this process is performed at atmospheric conditions the required time would have been 1200 seconds, while only reaching an b-value of 7.5.

The decrease in the required process time can be connected with the decrease of the viscosity and the increase of the diffusion coefficients in the lipid liquid material. Figure 5 shows the estimation of the liquid viscosities as function of the pressure at 75ºC. The decrease of the viscosity has the same order of magnitude as the decrease of the required process time.

An additional advantage of this process is caused by the fact that the amount of lipid material that remains in the filtrate decrease substantially. This is due to better filter properties due to the lower viscosity and the fact that the material filtered is partly CO_2. This advantage is especially usefull when expensive lipid materials are processed.

CONCLUSIONS

A process applying carbon dioxide as moderator has been presented as alternative for the current bleaching process [3]. The process as developed will increase the efficiency and decrease the equipment size due to the fact that the bleaching process appears linear dependent with the transport properties of the liquid material. Next to this the amount of lipid material wasted will decrease due to the better characteristics of the filtrate.

The process can be applied for various lipid materials in which reactions are carried out. In for the process itself it will be most advantages to dissolve as much as possible CO_2. However, when decreasing the amount of CO_2 the required pressure is increased as well. This will lead to an economic optimum at a given pressure. This optimum is dependent on pressure, raw material and granulates costs.

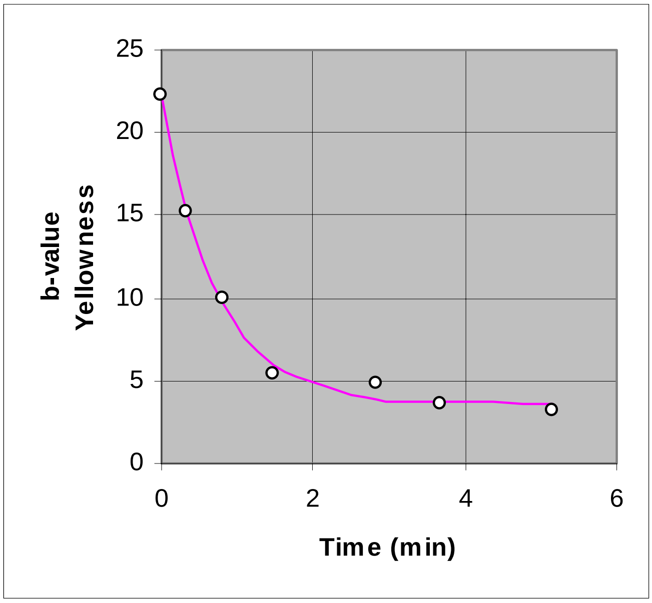

Figure 4: Yellowness as function of process time.

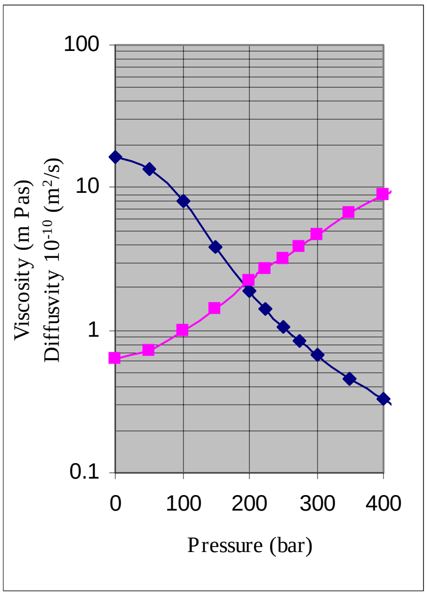

Figure 5: Diffusivity and viscosity of the liquid mixture as function of the applied pressure.

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