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Effect of Phospholipids on Crude Linseed Oil Filtration

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Abstract: Lecithin addition (0 to 10%) in crude linseed oil was used to investigate the effect of phospholipids on oil filtration at 20°C. The addition of lecithin (more than 2%) results in a decrease in the filtration rate, an increase in the cake resistance, and a modification of the filtration mechanism from cake resistance to intermediate blocking. At 20°C the lecithin precipitated on the particles and caused sedimentation of a deposit impermeable to oil that slows down the oil flow through the cake. The magnetic stirring is not an efficient way of filtration improvement on the contrary of filtration at 50°C.

Keywords: Cake resistance, dead-end filtration, filtration mechanism, linseed oil, phospholipids

INTRODUCTION

Linseed oil finds applications in linoleum, inks, varnishes, and other coating devices (1). It is industrially expressed from linseed on screw presses without following solvent extraction. Depending on the expression conditions, two oils with different qualities can be obtained. A first cold pressing oil is of high quality (low phospholipidic content). Whereas the second pressure oil is of lower quality (high phospholipidic and free fatty acid content). The second pressure oil is obtained by screw pressing

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at high temperature (100°C) of the meal issued from the first cold pressing (2). The phospholipids that reflect the oil quality are amphiphilic compounds initially located in the cellular membranes. They represent a wide range of molecules with a glycerol skeleton. Glycerol is esterified by two fatty acids and by a phosphoric group that can be associated with different polar molecules (alcohol or polyol) (3). These phospholipids are responsible for quality deterioration during oil storage (formation of dark-colored substances) (4). Therefore the second pressing oil is also degummed to remove phospholipids from oil. Depending on the phospholipids composition, degumming is performed by water addition or by an acidic treatment followed by water addition. The hydratable phospholipids precipitate with addition of water. Whereas the non-hydratable phospholipids should be converted into hydratable ones by acidulation before water precipitation (4–6). The phospholipids extraction is facilitated by a pressing at elevated temperature. A large amount of phospholipids can be removed by filtration (1,7,8).

In oil processing, filtration is used to remove the solids that are co-extruded in the oil during screw pressing. These solids from disrupted seed material should be separated from oil. Otherwise the enzymes released from the disrupted seeds and the adherent microorganisms can change the oil composition and produce compounds that impair the sensory quality of oil. The solids separation from oil needs two steps. A screening tank is first used to remove large particles. The remaining particles are removed by cake filtration on a "Niagara" pressure leaf filter (9,10). The filter cake serves itself as a filter medium and ensures an efficient oil filtration. 2% wt/wt of phospholipids can remain in oil at the end of the filtration process (5). These compounds are known to negatively impact the oil filtration. However, no study has been conducted on this subject.

The aim of this study is to evaluate the impact of phospholipids on the filtration behavior of linseed crude oil.

MATERIALS AND METHODS

Clarification experiments were carried out using a laboratory test cell (Fig. 1). The filtration pressure was applied via a vertical piston. A food texture analyser (TA-XT2, Stablemicrosystems, UK) was used to apply a constant stress on the fluid. The paper filter medium (Rotilabo 601 P, retention 8 μm, Carl Roth, Germany) had an effective area of 8.3 cm^2. The clarification was performed at a constant pressure of 120 kPa with 50 mL of oil. Two ways of filtration improvement were tested—the filtration at 50°C and the magnetic stirring of suspension during filtration.

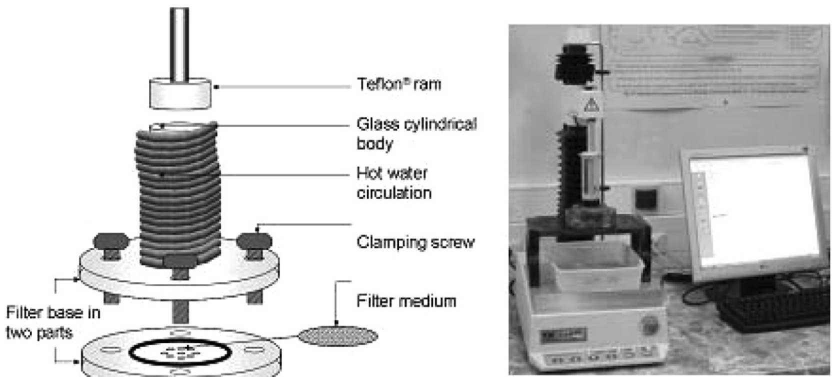


Figure 1. Experimental setup.

The temperature inside the filtration cell was controlled up to 50°C thanks to a hot water circulation system connected to a water bath. The magnetic stirring during filtration was ensured by a magnetic bar present in the filtration cell.

Crude linseed oil was supplied by the Vandeputte oil factory (Mouscron, Belgium). The solid content of the first pressure oil was estimate at 14% wt/wt by centrifugation. The particles size, determined by light micrographs (magnification X40), ranged from 10 to 30 μm (the largest ones come from the seed coat and the smallest ones from the embryo). Oil from the second pressing had a solid content of 6% wt/wt with a particles size inferior to 10 μm. The oil phospholipidic content was modified by the addition of soy lecithin (Carl Roth, Germany). Soy lecithin was chosen for its high phospholipidic content (≥97%), its oleaginous origin, and its availability. Different lecithin concentrations between 0 and 10% were studied. This lecithin concentration range was adopted in order to surround the remaining concentration in oil after filtration. Since a part of phospholipids is captured into the filter cake during filtration, the higher lecithin concentration was fixed at 10% of lecithin. Lecithin was dissolved under magnetic stirring for one hour in linseed crude oil preheated at 55°C. For room temperature tests, the solution was cooled under magnetic stirring until 25°C. For each experiment at least two repetitions were realized and the presented values are the mean of these two experiments.

Viscosity measurements were realized using a rheometer Haake VT 550 (Swantech International, Villeneuve la Garenne, France). The shear stress was linearly increased from $0.01\,s^{-1}$ to $500\,s^{-1}$ for 150 seconds. As oil is a Newtonian fluid, viscosity can be obtained from the slope of the shear stress shear rate graph. The evolution of oil viscosity according to lecithin concentration and temperature was performed using commercial clarified oil (Mieuxa, Ferrieres en Gatinais, France). The enriched oil was produced with the same dissolution protocol as described above.

EMPIRICAL MODEL

The oil filtration can be described by the same laws as aqueous filtration. The fluid flow through a porous medium is described by Darcy's law. Filtration can occur via different mechanisms covered by the Herman and Bredee relation (Eq. (1)) (11).

$$\frac{d^2t}{dV^2} = k\left[\frac{dt}{dV}\right]^n \tag{1}$$

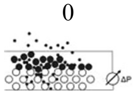
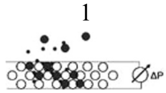
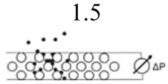
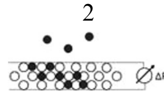
Where the parameter k is a constant and the exponent n characterises the filtration mechanism. Table 1 presents the different filtration mechanisms according to the value of n. For cake filtration, the particles deposit on the filter medium surface. On the contrary, for complete pore blocking they penetrate into the filter medium and prevent fluid flow through this pore. The experimental data can therefore be linearized in different coordinates. For example, the filtration curve in t/V-V coordinates is a straight line for the cake filtration, while for the standard blocking a straight line is obtained in t/V-t coordinates (11, 12).

The integration of Eq. (1) for cake filtration ($n = 0$) results in the Ruth Carman equation (Eq. (2)) (13).

$$\frac{t}{V} = \frac{\mu\alpha\mathrm{w}}{2\Delta PA^2}V + \frac{\mu R_m}{\Delta PA} \tag{2}$$

where αw is the cake resistance. Equation (2) was used to determine the cake resistance in cake filtration experiments. Since in our raw material

Table 1. Characteristics of filtration mechanisms (12)

Filtration mechanism	Cake filtration	Intermediate blocking	Standard blocking	Complete pore blocking
n	0	1	1.5	2
Blocking behavior				
Coordinates of linearization	t/V = f(V)	1/q = f(t)	t/V = f(t)	q = f(V)

the particles contain intrinsically oil, the specific cake resistance α has not been determined. Indeed, there is no possibility to separate just the oil coming from the continuous phase independently of the oil contained in the cells particles.

Recently, Grenier (12) derived numerically the volume–time data according to the Herman-Bredee equation (1) and represented these derivates in the logarithmic scale. The slope of this line gives the factor n. This method was used in this study. The filtrate volume was calculated by multiplying the piston displacement and the cell section. The derivatives from the Herman-Bredee equation (1) were obtained by numerical differentiation of data. The numerical differentiation step varied from 0.1 to 2.5 mm depending on the filtration duration. The plot of the second derivatives according to the first one gave straight lines. The factor n that represents the filtration mechanism was determined from the line slope. Even if the numerical differentiation of the data leads to a loss of accuracy, the use of this method gives indication about the modification of filtration mechanism.

RESULTS AND DISCUSSION

Influence of Temperature and Lecithin Concentration on Oil Viscosity

The oil viscosity is influenced by both temperature and lecithin concentration. Viscosity increases with lower temperature and higher concentration of phospholipids. The viscosity increase with temperature follows an Arrhenius law (Fig. 2a). When the temperature is constant, the viscosity is a second order polynomial function of lecithin concentration (Fig. 2b). The parameters of this polynomial model are temperature-dependant. The parameters dependency with temperature follows an exponential

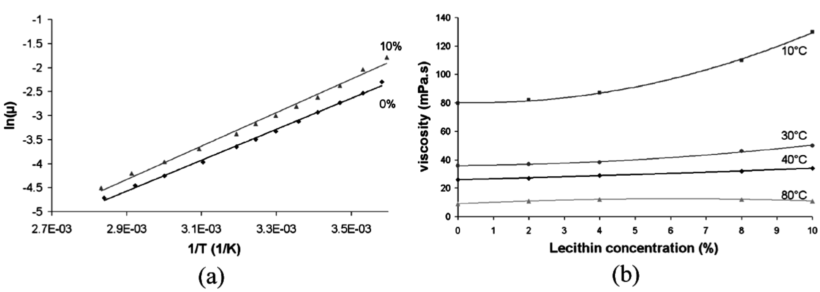


Figure 2. Evolution of oil viscosity μ according to temperature (a) (Arrhenius law) and lecithin concentration; (b) (2nd order polynomial law).

law. Replacement of the parameters in the polynomial model by their exponential expression leads to Eq. (3), which describes the viscosity modification according to both temperature and lecithin concentration.

$$\mu = \exp\left[\frac{5667}{T} - 20.78\right] \times c^2 + \exp\left[\frac{3136}{T} - 6.69\right] \tag{3}$$

The viscosity calculated according to Eq. (3) is in a good agreement with the experiments. The plot of the calculated viscosity values versus the experimental values is linear with a regression coefficient of 0.995.

Such changes in viscosity should be taken into account since filtration is highly influenced by the liquid viscosity.

Identification of Filtration Mechanism

Filtration experiments were conducted at 20°C and 50°C. Additional experiments at 20°C were realized under magnetic stirring. For each experiment, the filtration mechanism was determined by using the derivation of experimental data. The graphic representation of the second volume derivative according to the first derivative gives curves whose slope characterizes the filtration mechanism.

At ambient temperature and without magnetic agitation, the determination of factor n from Eq. (1) highlighted a drastic change in the filtration mechanism with the lecithin concentration. As shown in Fig. 3a, the filtration mechanism changed from a cake filtration ($n = 0$) with 0% of lecithin to an intermediate blocking filtration ($n \approx 1$, 8% wt/wt lecithin). With the addition of 6% wt/wt of lecithin, both mechanisms are present. This unusual behavior occurred when larger particles are

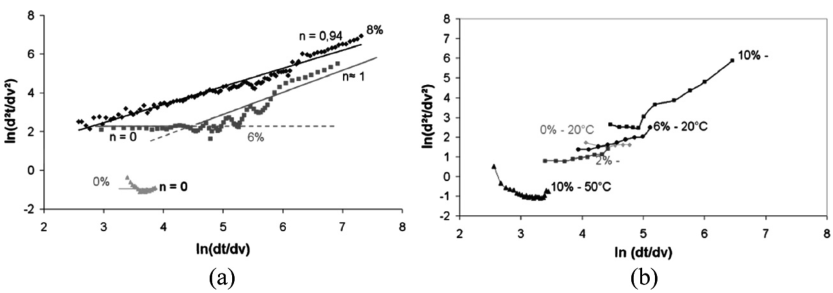


Figure 3. Evolution of filtration mechanism according to lecithin concentration at 20°C without agitation (a), at 20°C with agitation and at 50°C without agitation (b).

deposited on the filter medium. With suspension at 6% wt/wt of lecithin, the large particles are deposited faster than the smaller ones. Afterwards, the small particles, flowing down penetrate the cake pores and block them, exhibiting the intermediate blocking mechanism. Nevertheless, for experiments at lecithin concentrations higher than 6%, the sedimentation of particles during filtration was observed. Yet, the formed cake has been described as impervious to oil (14). This phenomenon could explain the modification of the filtration mechanism. The oil obtained from the second pressing also presents a succession of two filtration mechanisms even without lecithin addition. The first part of the second pressing oil filtration occurs by a filtration mechanism close to the intermediate blocking ($n \approx 0.8$), while the second part follows a cake filtration mechanism ($n \approx 0$).

The filtration mechanism also depends on temperature. At 20°C, the addition of lecithin changes the filtration mechanism. On the contrary at 50°C the filtration occurs via cake filtration at all considered lecithin concentrations (0–10%) as shown in Fig. 3b.

At ambient temperature under magnetic stirring, the derivation of experimental data shows behavior close to cake filtration at low lecithin concentrations. At high lecithin concentrations (>5% wt/wt) the filtration begins with cake filtration and evolved towards an unknown mechanism ($n > 2$). For instance with 8% of lecithin, the slope of the second part of the curve gives $n = 4$ (Fig. 3b). In spite of the magnetic stirring, particles deposit at the surface of the filter medium, which could explain the noticed cake filtration mechanism. This evolution of the filtration mechanism influences the cake resistance and the filtration rate.

Cake Resistance

Figure 4 shows the values of the combined term named cake resistance, $R_c = \alpha w$. The specific cake resistance α was not determined in this study since the solids content in the oil-saturated cake cannot be easily evaluated. The cake resistance R_c decreases for low lecithin concentrations (0.5 to 2% wt/wt) and for lecithin concentrations higher than 2%, R_c increases independently of the filtration conditions. Temperature increase results in cake resistance decrease. Nevertheless this decrease is with no common extent to the increase observed between filtration at 20°C with and without agitation. The cake resistance for experiments under magnetic stirring is near ten times higher than that for experiments without agitation.

The viscosity increase cannot explain this evolution since it was already taken into account in the Ruth-Carman equation. Suspension

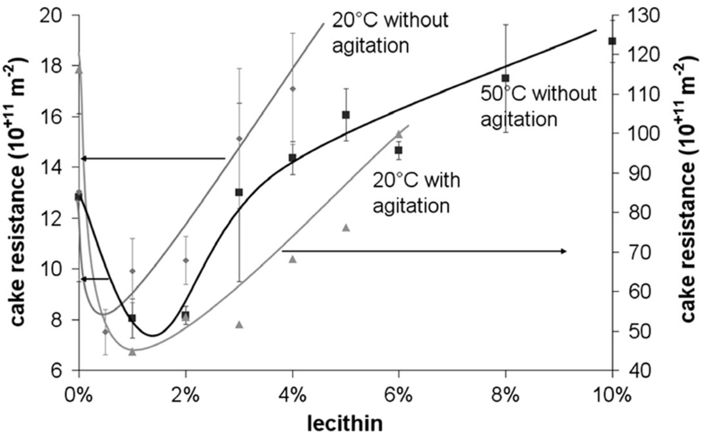


Figure 4. Evolution of cake resistance according to lecithin concentration.

modification due to lecithin addition may be responsible for this evolution. In nonpolar liquid, phospholipids may form inverse micelles. In inverse micelles the polar groups of the surfactants (phosphate head) are concentrated in the interior and the lipophilic groups (fatty acid) extend towards and into the nonpolar solvent (oil). In soy crude oil, the critical micellar concentration (CMC) for phospholipids is around 1020 mg/kg. The CMC is the minimum concentration for micelle appearance (15). The micelle's size ranges from 3.56 to 4.70 nm but the presence of hydrophilic impurities also influences the micelle's size. Seed particles can be considered as hydrophilic impurities, so lecithin may produce inverse micelles around these particles. However, the studied phospholipids concentrations are much higher than the CMC reported for the appearance of inverse micelles. Then, the micelles formation cannot explain the change in filtration behavior. However, lecithin solubility seems to be a determining factor. At ambient temperature, lecithin can precipitate and modify the particles.

For experiments performed at ambient temperature under agitation, the filtrate viscosity was measured. These measurements were made in order to quantify the effectively dissolved lecithin. The obtained values were compared to those of commercial linseed oil enriched in lecithin. Figure 5 presents this evolution.

The lower filtrate viscosity at 0% of lecithin compared to commercial oil could be explained by an influence of raw material. According to this, the concentration of lecithin in the filtrate is below 2% for addition of less than 5% of lecithin. For addition of 6 to 10% of lecithin, 3 to 4% is really dissolved in the filtrate. So, a part of the lecithin remained in the filter cake with the particles.

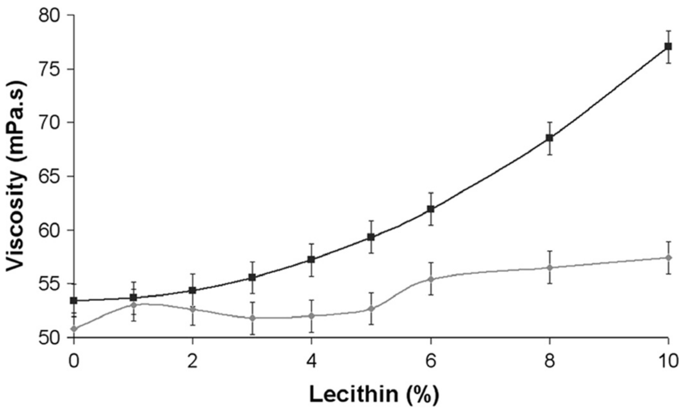


Figure 5. Evolution of filtrate viscosity (◆) compared to standard made with commercial oil (■).

Light Micrographs

In order to evaluate the impact of lecithin addition and its possible precipitation, light micrographs of oil with different lecithin concentrations were realized.

At 20°C, particles are clearly dispersed, while at 6% and 8% lecithin concentration, the particles are aggregated. For experiments performed at 50°C with 8% of lecithin, the particles are individualized in the same way as for experiments without lecithin (Fig. 6). The viscosity

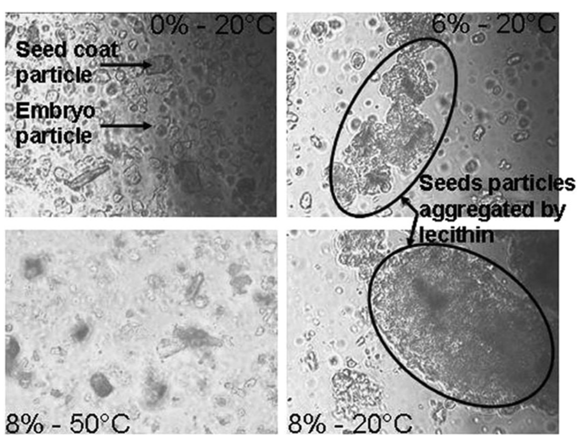


Figure 6. Light micrographs (magnification $\times$ 40) of linseed oil suspensions at 0, 6 and 8% lecithin.

measurements have shown that a part of the lecithin remain in the filter cake after filtration. Moreover, at high lecithin concentrations particles are aggregated. These observations can be related to a precipitation of lecithin at ambient temperature.

The precipitation of lecithin changes the size and the form of seed particles. As shown in Fig. 6, the lecithin precipitation causes an aggregation phenomenon that results in a cake formation quite impermeable to the oil flow. In addition, the agglomerates have a tendency to decant at the bottom of the filtration cell. This phenomenon appeared at high lecithin concentration. Once the particles are deposited, the supernatant oil is filtrated through the cake at very low flow rate.

Filtration Rate

The filtration rate is influenced by lecithin concentration, the temperature, and the agitation. Figure 7 shows the modification of the filtration rate according to these three parameters. Without agitation, the filtration is faster at 50°C than at 20°C. The filtration rate at 50°C is up to ten times higher than the filtration rate at 20°C. Nevertheless, at 20°C the difference between the experiments with and without agitation is less obvious.

At low concentration of lecithin (0 to 1%) filtration is faster without agitation but for higher concentration (more than 5% lecithin) filtration with agitation is faster.

Higher solubility of lecithin at 50°C accounts for this behavior. The reduction of viscosity due to temperature increase may also have an effect

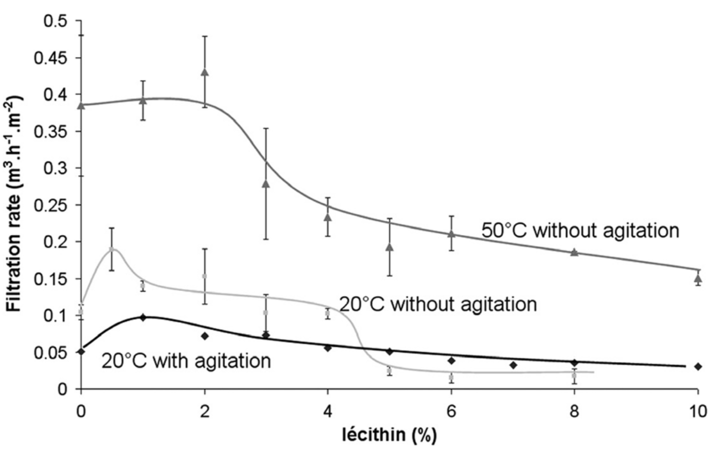


Figure 7. Evolution of the filtration rate according to the lecithin concentration.

on the filtration rate. With 8% wt/wt of lecithin, the filtration at 20°C is almost impossible without agitation. Indeed, after sediment deposit, only a few milliliters of oil are filtrated in one hour. The agitation avoids this sedimentation phenomenon.

The filtration rate for the second pressing oil is lower than for the first pressing oil. It is around $1.56 \cdot 10^{-2}\,m^3 \cdot h^{-1} \cdot m^{-2}$.

CONCLUSION

Filtration of crude linseed oil at ambient temperature without agitation is highly influenced by lecithin concentration. A low lecithin concentration (0.5 to 2% wt/wt) improves filtration as it decreases cake resistance. On the contrary, a higher concentration of lecithin (more than 5% wt/wt) decreases the filtration rate and modifies the filtration mechanism from a cake filtration to a filtration with intermediate blocking. The filtration at 50°C is interesting as it gives a higher filtration rate and a lower cake resistance. These differences could be explained by the solubility of lecithin in oil, which increases with temperature. At ambient temperature, a precipitation of lecithin acts like a binder on the particles. Then the particles loaded with lecithin decant and build a filter cake which is quite impermeable to the flow. Filtration of oil at 50°C reduces all these drawbacks but still remains difficult at high lecithin concentrations. The agitation of suspension at 20°C is not really interesting compared to filtration at 50°C without agitation. The negative impact of agitation could be explained by a blocking of filter medium with smaller particles. Without agitation these particles are retained by the filter cake. With agitation they penetrate the filter medium and could reduce its permeability.

NOTATION

α Specific cake resistance ($m \cdot kg^{-1}$)
A Filtration area (m^2)
B Permeability ($m^3 \cdot s^{-1} \cdot m^{-2}$)
c Lecithin concentration
K Constant
n Factor of the Hermans Bredée equation
q Filtration rate ($m \cdot s^{-1}$)
ΔP Pressure drop (Pa)
R_m Membrane resistance (m^{-1})
R_c Cake resistance (m^{-2})

t Time (s)
μ Liquid viscosity (Pa · s)
T Temperature (K)
V Filtrate volume (m^3)
w Mass of solid per unit of filtrate volume ($kg \cdot m^{-3}$)
z Sediment height (m)

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