Effect of feed particle size and solvent flow rate on soybean oil extraction in a percolation type extractor

Shejawale Deepali[1], C Murugesh[1], Navin Rastogi[1], and Subramanian Rangaswamy[1]

[1]Central Food Technological Research Institute CSIR

April 28, 2020

Abstract

The influence of particle size and solvent flow rate on the kinetics of oil extraction from soybean (eight fractions from 0.433 to 0.122 mm) was studied using hexane, simulating commercial percolation type extractor. The reduction in particle size from 0.433 mm to 0.141 mm showed an increase in the oil extractability. However, further reduction to 0.129 mm and 0.122 mm affected the extractability due to bed compaction, reducing porosity and contact area. The extractability (21.5%) of the ground mass was similar to the major mass fractions (0.239 - 0.353mm). The rate of extraction increased drastically with the solvent flow rate. The highest flow rate (9.67 mL/min) exhibited the highest mass transfer coefficient (km) 1.27×10-3 s-1 and the diffusion coefficient (De) 1.77×10-12m2/s. At 7.33 mL/min, the yield and the rate of extraction were optimal and no potential benefits were obtained at higher flow rates.

1 Introduction

Vegetable oil processing represents the third-largest segment in the food processing sector in the world. Oilseed is the major source of vegetable oil (Subramanian et al., 2004). Mechanical pressing, pressing followed by solvent extraction and direct solvent extraction are the three methods of extraction used in the commercial-scale (Subramanian & Nakajima, 1997). The direct solvent extraction method is employed for low oil-bearing (<30% oil) materials, and soybean oil is the largest direct solvent-extracted vegetable oil. The very high oil extractability, lower boiling point (66.6°C to 68.9°C), low latent heat of vaporization (335 kJ/kg), low corrosion and an acceptable odour for the defatted meal makes commercial hexane superior to other solvents and preferred choice of solvent. Percolation extractor is the most common type employed in the industry. In this extractor, the solvent percolates down the bed of oil-bearing material by dissolving the oil into the solvent stream. The typical construction provides different stages and the operation ensures counter-current mode of extraction to maximise the extractability.

There have been continuous research efforts towards improvements in solvent-extraction of oil-bearing materials. Even though the principle of extraction is simple, the mass transfer phenomenon is influenced by many factors like type and composition of feed, pre-treatments that affect the cellular structure and size, type of solvent and its temperature as well as solvent-to-feed ratio. Diffusivity is a vital transport property and the estimation of the diffusion coefficient is thus useful in designing efficient extraction equipment (Perez et al., 2011). In this direction, there have been several attempts towards understanding the kinetics of solvent extraction of various vegetable oils employing different solvents.

The kinetics of extraction of rapeseed oil with hexane was studied at 53°C with two different solvent flow rates (0.024 and 0.033 kg-hexane/kg-oilseed/min) in a percolation extractor (Sasmaz, 1996). Although the oil yield was found to increase with the solvent flow rate, the diffusion coefficient was reported to be the same. Baumler et al. (2010) studied the effect of contact time and temperature on the extractability of oil, tocopherols and phospholipids from sunflower collets using hexane in a stirred tank extractor. The extraction

1

followed two-stage kinetics, and the phenomenon was described using a two-stage model derived from Fick's second law of diffusion. In a similar study, Fernandez et al. (2012) reported the extraction kinetics of canola oil and tocopherol at different temperatures (25, 40, 50 and 60°C). They proposed a modified model given by So and Macdonald (1986) based on Fick's second law.

Rodrigues et al. (2011) and Toda et al. (2016) studied the effect of extraction temperature (40 to 60°C) as well as solvent hydration (0.04% to 20.01%, w/w water) on the soybean oil extraction with ethanol employing stirred tank and cylindrical batch extractor, respectively. The increase in temperature was reported to influence the oil extraction yield. In contrast, the increase in the level of hydration suppressed the oil yield (Rodrigues et al., 2011) as well as increased the FFA content (Toda et al., 2016) and the oil extraction was shown to follow the model proposed by So and Macdonald (1986).

Subsequently, Rodrigues et al. (2017) investigated the effect of temperature (30 to 90°C) in a semi-batch pressurised liquid extractor on the extraction yield. The equilibrium extraction yield was found to increase from 12.35 to 24.42% with an increase in extraction temperature from 30 to 90°C. The rise in temperature increases the solubility and decreases the viscosity favouring the transport. Solvent flow rate influenced the initial rate of extraction, but not the equilibrium yield. The pressure applied in the process did not independently influence the process.

The above studies revealed that temperature is the primary factor influencing the extraction yield. Researchers have also observed that the extraction proceeds in two stages in the studies carried out in stirred tank extractor which is different from the percolation extractor in practice in the industry. Besides, oil extraction is carried out at the near-boiling point in the commercial extraction and the vital process variable is the solvent flow rate. Accordingly, future studies need greater attention to ensure that near-complete extraction is achieved at the minimum solvent flow rate.

Therefore, a comprehensive study of the kinetics of oil extraction involving different solvent flow rate at the maximum operating temperature (boiling point of solvent) under simulated industry extraction conditions (percolation extractor) would be appropriate to gain valuable insights from the industrial perspective. Further, soybean would be an ideal candidate considering that it is the largest extracted edible oil in the world. Hence, in the present study, the kinetics of soybean oil extraction using the most widely used solvent, hexane at different solvent flow rates was evaluated.

2 Materials and Methods

2.1 Materials

Soybean flakes were obtained from M/s Sakthi Soya Ltd., Pollachi, India. Flakes were stored in polyethylene bags at 5°C and drawn for experimentation as and when required. Hexane was used as an extraction solvent and procured from M/s ACE Rasayan, Bengaluru, India (AR grade, extra pure 85%, BP 65-70°C).

2.2 Size reduction

Soybean flakes (particle size 630±0.58 μm) were ground using a hammer mill (Model: CMC-CM, M/s Cadmach Machinery Co., Ahmedabad, India).

2.3 Sieve analysis and particle size determination

The ground soybean was passed through a series of sieves assembled in the order of decreasing mesh size using a vibratory unit. The volume surface mean diameter (D_s) of the ground material was determined using the following equation.

$$D_s = \left[\sum_{i=1}^{n} \left(\frac{x_i}{D_{\mathrm{pi}}} \right) \right]^{-1} \quad (1)$$

Where 'x$_i$' is the mass fraction in a given sieve, 'n' is the total number of size fractions and D_{pi} is the average particle diameter of individual fraction, taken as the arithmetic average of the smallest and largest particle

diameters in the fraction (McCabe et al., 2005).

2.4 Extraction of soybean oil using modified Soxhlet apparatus

Soxhlet apparatus consisted of 250 mL round bottom flask fitted with butt type extraction tube and condenser. The apparatus was modified to keep the sample in a suspended position to establish flow-through condition instead of solvent submerged condition (as in the conventional method) by introducing a sample holder as illustrated (Fig. 1). This arrangement ensured the flow of solvent through the samplemeetsthe experimental criterion.

The round bottom flask was immersed in a temperature-controlled oil bath (Model No. ONE 29, M/s Memmert, Schwabach, Germany) containing silicon oil (10000 cSt) as the heating medium. The solvent flow rate was varied by adjusting the temperature of the oil bath. Increase in oil bath temperature increased the solvent evaporation and thereby increased the hexane flowrate in the extraction unit (Fig. 2).

2.5 Determination of moisture content

The moisture content of the soybean was determined according to theAOCS official method, Ac 2-41(AOCS, 2009). In brief, 10 g of sample was taken in a moisture dish and dried in a hot air oven at 130 ± 3°Cfor 3 h. After 3 h, the moisture dish with the sample was transferred to a desiccator to cool it to ambient temperature $(27 \pm 2$°C) and the loss in weight was recorded at ambient temperature. The moisture content of the sample was calculated using the following formula:

Moisture content (%)$= \frac{Loss\ in\ weight,\quad g}{Weight\ of\ test\ portion,\quad g} \times 100 (2)$

2.6 Determination of oil content

The oil content was determined according to the AOCS official method, Ac 3-44 (AOCS, 2011). The method involved complete extraction of oil from the test sample using petroleum ether in a soxhlet extraction unit and expressing the oil extracted based on the test sample. In brief, 2 g of the test sample was taken in a thimble and placed it in the extraction tube and the extraction was continued for 5 h. After extraction, the extraction flask was disconnected, and the solvent was evaporated using a water bath and the flask was weighed. The oil content in the test sample was calculated using the following formula:

Oil in the test sample (%)$= \frac{Weight\ of\ oil,\quad g}{Weight\ of\ test\ portion,\quad g} \times 100 (3)$

Oil, moisture free basis (%) $= \frac{\%\ oil\ in\ the\ test\ sample}{100 - \%\ moisture\ in\ the\ test\ sample} \times 100 (4)$

2.7 Determination of mass transfer coefficient (k_m) and diffusion coefficient (D_e)

Considering the exponential approach to equilibrium, mass transfer of oil can be deduced as (Rastogi &Raghavarao, 1995):

$\frac{dM_t}{dt} = -k_m (M_t - M_\infty) (5)$

The plot of rate of change of oil content (dM_t/dt) against average residual oilcontent (M_t),was used to estimate the equilibrium residual oil content ($M_{[?]}$) and the mass transfer coefficient (k_m).

The effective diffusivity or the effective diffusion coefficient (D_e) for the diffusive mass transfer of oil from the solid matrix was estimated using the solution for Fick's second law of diffusion for a spherical configuration (Crank, 1975):

$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_e n^2 \pi^2 t}{a^2}\right) (6)$

Where, M_t and $M_{[?]}$ are the mass of the oil diffused at time t=t and t=[?], respectively. 'D_e' is the diffusion coefficient of oil (m^2/s), 'a' is the radius of the equivalent sphere (m), 't' is the time of diffusion and 'n' is the number of terms in the series.

3

Since the value of the Fourier number (Dt/a^2) is greater than 0.1 in the present case, only the first term in Eq. (6) is significant and other terms can be neglected (McCabe et al., 2005).

Equation (6), therefore, reduces to:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}.\exp\left(-\frac{D_e n^2 \pi^2 t}{a^2}\right) (7)$$

Simplification of the above equation results in:

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\left(\frac{6}{\pi^2}\right) - \frac{D_e \pi^2 t}{a^2} (8)$$

The k_m and diffusion coefficient D_e values were estimated for different solvent flow rates. Details of the parameters involved in the experiment are given in table 1.

3.0 Results and Discussion

The present study was aimed to understand the kinetics of extraction of soybean oil using hexane, simulating percolation conditions of the commercial extraction process. This approach was appropriate but a significant deviation from a large number of extraction studies reported employing stirred tank extractor. Initial experiments were carried out to understand the influence of particle size, subsequent studies were performed with whole ground soybean flakes. Besides, the temperature has a greater influence on oil extractability, but consciously maintained constant at the boiling point of solvent as it is not a variable factor in the commercial extraction. The main focus of the study was on the influence of solvent flow rate which is one of the major variable factors having a bearing on the oil extractability in a percolation extractor.

3.1 Influence of particle size on oil extractability

The ground soy flakes were subjected to sieve analysis (Fig. 3). The fractions with average particle diameter, 0.353, 0.290, 0.239, 0.196, and 0.165 mm were found to constitute the major mass fractions. The volume surface mean diameter (D_s) of the total ground mass was determined to be 0.234 mm, which was close to the average particle diameter (0.239 mm) of the largest mass fraction (0.296). The major mass fractions obtained during sieve analysis were selected along with a few small and large size fractions to study the effect of particle size on the oil extractability.

The influence of particle size on the extractability of oil was assessed (Fig.4) at a constant solvent flow rate of 7.33 mL/min corresponding to AOCS conditions (~150 drops/min). Reduction in particle size leads to an increase in specific surface area and generally increased the extractability. Particle size showed a significant increase in the oil extractability from 0.433 mm to 0.353 mm, 0.239 to 0.165 mm and 0.165 to 0.141 mm following the general perception that larger the surface area greater is the extractability. However, further reduction in particle size to 0.129 and 0.122 mm caused a significant reduction in the extractability. The reduction in oil extractability may be due to the bed compaction with finer particles reducing the bulk porosity and reducing the exposure area (Corrochano et al., 2015). The maximum extractability (23.7%) was obtained with 0.141 mm particle size fraction but its mass contribution was merely 0.025. The extractability (21.5%) of the unsegregated ground mass (D_s= 0.234 mm) was similar to the extractability of most of the major mass fractions (0.353, 0.290 and 0.239 mm). Therefore, with due practical consideration, the whole ground mass of soy flakes was taken for further studies on extractability at different solvent flow rates.

3.2 Influence of solvent flow rate on oil extractability

The dependence of oil extractability on solvent flow rate was assessed with the whole ground soy flakes (D_s= 0.234 mm) by varying the solvent flow rate (2.67, 3.88, 6.33, 7.33 and 9.67 mL/min). The yield, as indicated by the residual oil content in the meal, increased with time at all solvent flow rates approaching near-total recovery(residual oil content 0.01 g/g, Fig. 5). The results also revealed that the rate of reduction in the residual oil content or in other words, the rate of extraction varied drastically with the solvent flow rate.

Higher solvent flow rates 7.33 mL/min and 9.67 mL/min exhibited the highest extractability in the initial

phase and reduced the residual oil content to ˜30% within 15 min of extraction time. The lowest flow rate used in the study (2.67 mL/min) exhibited the least extractability and reduced the residual oil content only to the extent of ˜64% during the same extraction period. Further, ˜95% of oil could be extracted in ˜45 min at higher solvent flow rates (7.33 mL/min and 9.67 mL/min) while flow rate at 2.67 mL/min took ˜5 h for a similar reduction. A similar observation of higher extractability at higher hexane flow rate was reported in the extraction of rapeseed oil in a percolation extractor (Sasmaz, 1996). In a solid-liquid extraction process, the concentration gradient is the driving force for the diffusion of solute from the solid matrix to the liquid (solvent). The higher solvent flow rate removes extracted oil from the extraction bed more efficiently and keeps the concentration gradient higher, which in turn increases the rate of extraction (Cacace& Mazza, 2006).

3.2.1 Mass transfer kinetics of oil extraction

Evaluation of mass transfer kinetics helps to understand the rate at which the solute moves from the solid matrix to the solvent phase in the case of solid-liquid extraction. Mass transfer coefficient indicates the rate to reach equilibrium, therefore, important in the process design and sizing of extraction vessels. In the present study, the solvent flow rate was found to greatly influence the rate of extraction (Fig. 5). Five different flow rates (2.67, 3.88, 6.33, 7.33 and 9.67 mL/min) were assessed for their effect on the rate of extraction by evaluating the rate of reduction in the residual oil content (Fig. 6). The rate of oil extraction increased with the increase in the solvent flow rate and the flow rates 7.33 mL/min and 9.67 mL/min displayed greater extraction potential to reach the equilibrium. From the analysis, the equilibrium residual oil content (m_e) were obtained at different flow rates and the corresponding mass transfer coefficients (k_m) were estimated (Table 2). Higher-order of oil removal from the solid matrix was observed at higher solvent flow rates; k_m values at 7.33 mL/min ($1.25 \times 10^{-3} s^{-1}$) and 9.67 mL/min ($1.27 \times 10^{-3} s^{-1}$) were 2-fold higher than the value obtained at 2.67 mL/min ($0.53 \times 10^{-3} s^{-1}$).

In the case of solid-liquid extraction, turbulence is unlikely to occur in the matrix to improve the rate of mass transfer, hence molecular diffusion of solute from the matrix to the solvent acts as the rate-controlling step (Aguilera 2003). In the present study,D_e increased with increase in solvent flow rate (Fig. 7) during the extraction of oil from ground soybean flakes; the D_e at 2.67 mL/min ($0.58 \times 10^{-12} m^2/s$) increased by 3-fold to reach $1.77 \times 10^{-12} m^2/s$ at 9.67 mL/min (Table 2). Sasmaz (1996) reported a D_e value of $3.4 \times 10^{-12} m^2/s$ during rapeseed oil extraction at two different hexane flow rates.

3.2.1.1 Mass transfer coefficient (k_m) and diffusion coefficient (D_e)

Mass transfer coefficient (k_m) indicates the rate of mass transfer on unit change in concentration. Concentration difference is the only independent factor considered in the calculation of the mass transfer coefficient. The change in concentration can be due to simple washing of solute from the surface of the solid matrix to the solvent or due to diffusion of solute from the interior of the solid matrix to the solvent or due to the combined effect. While the effective diffusion coefficient (D_e) depends mainly on solid geometry and physical properties (porosity and tortuosity) of the solid matrix, it is not expected to change with extraction conditions.

In the present study, both k_m and $D_e$were found to increase with the increase in the solvent flow rate (Table 2). The mass transfer coefficient k_m can be estimated for any case of solid-liquid extraction either surface washing controlled or diffusion controlled. The D_e value varied from 0.58 to 1.77 m^2/s and it did not increase substantially beyond the flow rate of 7.33 mL/min. However, D_e value is expected to be nearly constant for a solute of defined geometry. The results revealed that the diffusion coefficient for solid-liquid extraction has to be estimated only under appropriate boundary conditions. Accordingly, the diffusion coefficient estimated for the solvent flow rates of 7.33 mL/min and 9.67 mL/min were considered to be suitable (Table 2).

3.3 Conclusion

Reduction in particle size and increase in solvent flow rate increased the rate of extraction as well as the oil yield. Mass transfer coefficient was found to increase with an increase in flow rate. Based on the study, 7.33

mL/min of solvent flow rate was found to be suitable for the extraction of soybean oil in a percolation type extractor. The results obtained in the study would be useful in optimizing the operating conditions of the extraction plant in maximizing the oil yield.

References

Aguilera, J. M. (2003). Solid-liquid extraction. Marcel Dekker, Inc., NY.

AOCS. (2009). Official methods and recommended practices of the American Oil Chemist's Society, Champaign.

AOCS. (2011). Official methods and recommended practices of the American Oil Chemists' Society, Champaign.

Baumler, E. R., Crapiste, G. H., & Carelli, A. A. (2010). Solvent extraction: kinetic study of major and minor compounds. Journal of the American Oil Chemists' Society, **87** :1489-1495. https://doi.org/10.1007/s11746-010-1637-3.

Cacace, J. E., & Mazza, G. (2006). Pressurized low polarity water extraction of lignans from whole flaxseed. Journal of Food Engineering,**77** :1087-1095. https://doi.org/10.1016/j.jfoodeng.2005.08.039.

Corrochano, B. R., Melrose, J. R., Bentley, A. C., Fryer, P. J., & Bakalis, S. (2015). A new methodology to estimate the steady-state permeability of roast and ground coffee in packed beds. Journal of Food Engineering, **150** :106-116. https://doi.org/10.1016/j.jfoodeng.2014.11.006.

Crank, J. (1975). The mathematics of diffusion. Oxford: Clarendon Press, UK.

Fernandez, M. B, Perez, E. E, Crapiste, G. H, & Nolasco, S. M. (2012). Kinetic study of canola oil and tocopherol extraction: Parameter comparison of nonlinear models. Journal of food engineering,**111** :682-689. https://doi.org/10.1016/j.jfoodeng.2012.01.036.

McCabe, W. L., Smith, J. C., &Harriott, P. (2005). Unit operations of chemical engineering (7th ed.). New York: McGraw-Hill967–1000.

Perez, E.E., Carelli, A.A. and Crapiste, G.H. (2011). Temperature-dependent diffusion coefficient of oil from different sunflower seeds during extraction with hexane. Journal of Food Engineering, **105** :180-185. https://doi.org/10.1016/j.jfoodeng.2011.02.025.

Rastogi, N. K., & Raghavarao, K. S. M. S. (1995). Kinetics of osmotic dehydration of coconut. Journal of Food Process Engineering,**18** :187–197.

Rodrigues, C.E.C., Longo, N.M., Silva, C., Aracava, K.K & Garavazo, B.R. (2011). Ethanolic extraction of soybean oil: Oil solubility equilibria and kinetic studies. Chemical Engineering Transactions,**24** :811-816. https://doi.org/10.1155/2015/871236.

Rodrigues, G.M, Cardozo-Filho, L. & Silva, C. (2017). Pressurized liquid extraction of oil from soybean seeds. The Canadian Journal of Chemical Engineering, **95** :2383-2389.

Sasmaz A. D. (1996). Evaluation of diffusion coefficient of rapeseed oil during solvent extraction with hexane. Journal of American oil Chemists,**73** :669-671. https://doi.org/10.1007/BF02518126.

So, G. C., & MacDonald, D. G. (1986). Kinetics of oil extraction from canola (rapeseed). The Canadian Journal of Chemical Engineering,**64** :80-86.

Subramanian, R., & Nakajima, M. (1997). Membrane degumming of crude soybean and rapeseed oils. Journal of the American Oil Chemists' Society, **74** :971-975. https://doi.org/10.1007/s11746-997-0013-4.

Subramanian, R., Nakajima, M., Raghavarao, K. S. M. S., & Kimura, T. (2004). Processing vegetable oils using nonporous denser polymeric composite membranes. Journal of the American Oil Chemists' Society,**81** :313-322. https://doi.org/10.1007/s11746-004-0901-z.

Table 1 Experimental extraction parameters employed in the kinetics studies[a]

S. No.	Variables	Levels
1	Solvent flow rate (mL/min)	2.67, 3.88, 6.33, 7.33, 9.67
2	Time (h)	0.25, 0.50, 0.75, 1, 1.5, 2, 3, 4, 5

[a]Conducted with whole ground mass of soy flakes

Table 2 Kinetic coefficients at different solvent flow rates

S. No.	Solvent flow rate	Equilibrium residual oil content (m_e)	Mass transfer coefficient (k_m)	Diffusion coefficient	Diffusion coefficient	Diffusion coefficient
				(D_e)	Percolation rate	Remarks
	(mL/min)	(g/g)	(s^{-1})	(m^2/s)	Drops/min	
1	2.67	0.0183	0.53×10^{-3}	0.58×10^{-12}	26	Low
2	3.88	0.0168	0.61×10^{-3}	0.77×10^{-12}	66	Low
3	6.33	0.0062	0.74×10^{-3}	1.07×10^{-12}	117	Low
4	7.33	0.0039	1.25×10^{-3}	1.72×10^{-12}	156	Appropriate
5	9.67	0.0002	1.27×10^{-3}	1.77×10^{-12}	168	Appropriate

Figure legends

Fig. 1 Conventional and modified (flow-through) Soxhlet extractor

Fig. 2 Solvent flow rates at different oil bath temperature

Fig. 3 Particle size distribution of ground soy flakes
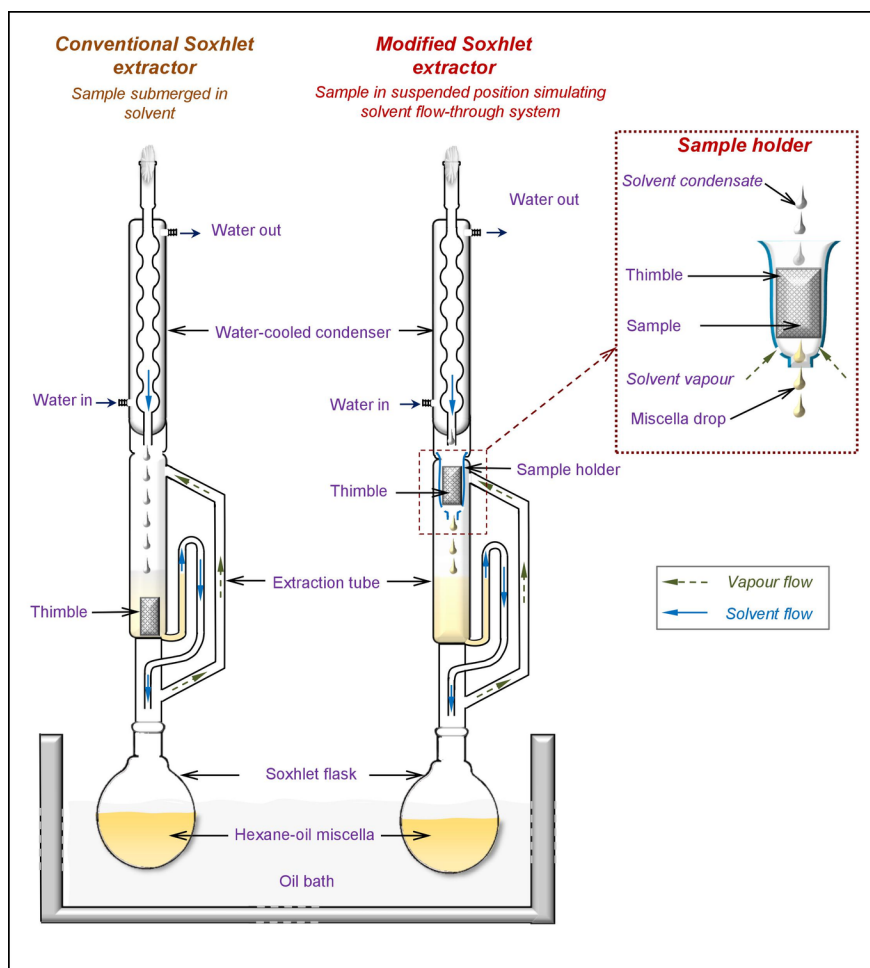
Fig. 4 Effect of feed particle size on oil extractability

Values are expressed as mean $\pm$ standard deviation, n=3. Mean values,denoted by different letters are significantlydifferent (p[?] 0.05) from each other

Fig. 5 Residual oil content in meal during extraction at different solvent flow rate

Fig. 6 Rate of oil extraction at different solvent flow rate

Fig. 7 Plot of $\ln(1-M_t/M_{[?]})$ Vs time

Hosted file

Figure 2.docx available at https://authorea.com/users/307843/articles/438790-effect-of-feed-particle-size-and-solvent-flow-rate-on-soybean-oil-extraction-in-a-percolation-type-extractor

Hosted file

Figure 3.docx available at https://authorea.com/users/307843/articles/438790-effect-of-feed-particle-size-and-solvent-flow-rate-on-soybean-oil-extraction-in-a-percolation-type-extractor

Hosted file

Figure 4.docx available at https://authorea.com/users/307843/articles/438790-effect-of-feed-particle-size-and-solvent-flow-rate-on-soybean-oil-extraction-in-a-percolation-type-extractor

Hosted file

Figure 5.docx available at https://authorea.com/users/307843/articles/438790-effect-of-feed-particle-size-and-solvent-flow-rate-on-soybean-oil-extraction-in-a-percolation-type-extractor

Hosted file

Figure 6.docx available at https://authorea.com/users/307843/articles/438790-effect-of-feed-particle-size-and-solvent-flow-rate-on-soybean-oil-extraction-in-a-percolation-type-extractor

Hosted file

`Figure 7.docx` available at https://authorea.com/users/307843/articles/438790-effect-of-feed-particle-size-and-solvent-flow-rate-on-soybean-oil-extraction-in-a-percolation-type-extractor