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Solid–liquid extraction of rice bran oil using binary mixture of ethyl acetate and dichloromethane

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Abstract: The aim of the study is to investigate the potentials of less hazardous, binary mixtures of ethyl acetate (EA) and dichloromethane (DCM) for rice bran oil recovery. Nine solvent mixtures are used with different volumetric ratios of EA/DCM ranging from 0.11 to 9. Solvent mixture with volumetric ratio of 4 (S_8) has enabled the maximum oil recovery 88.04 %. The oil extraction yield is enhanced from 76.41 to 89.7 % by increasing the preheating temperature from 40 to 65 °C. The other optimized parameters for enhanced oil recovery are: bran particle size <125 μm (obtained with 120 mesh sieve), solvent to bran ratio of 5 mL/g, and stirring time of 15 min. The minimum stirring rate for preventing agglomeration in the mixture and optimized oil recovery is 80 rpm.

Keywords: rice bran oil; solvent extraction; temperature; particle size; contact time; agitation.

INTRODUCTION

Rice bran is obtained during the processing of rice as by-product and it contains 14–20 % oil. Rice bran oil (RBO) has been used as edible oil and pharmaceutical supplement because of associated health benefits. Bran oil is either extracted mechanically or by the solvothermal extraction process.[1] Mechanical extraction is an energy intensive process and the percentage of oil recovery is also very low. Since solvent extraction allows higher percentages of oil recovery, compared to mechanical extraction it is the most widely adapted process for production of RBO.[2]

Solvent selection is critical for the optimized oil recovery and the final product quality. The essential requirements for solvent to be used for RBO recovery involve high extraction yields, low miscibility with water, inertness towards oil, and less hazardous nature. Further, the maximum solvent recovery after extraction is also desirable.[3] Generally, hexane is used for the industrial scale extraction

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of bran oil. However, a number of environmental and safety hazards are associated with the RBO processing using hexane. Moreover, an extensive use of hexane for oil extraction industry has resulted as an increase in its unit price. Therefore, other solvents have also been investigated to reduce these hazards, enhance the product recovery, and quality.

Soares *et al*. and Sparks *et al*. have employed supercritical CO_2, compressed liquefied petroleum gas and liquid propane for RBO extraction.[4,5] Despite the improved oil quality the investment costs of these processes are very high. Hanmoungjai and co-workers have reported low cost recovery of bran oil using aqueous media.[6] However, the quality of the end-product is poor due to rancidity of the oil during extraction process. Additionally, the percentage recovery of oil up to 85 % is obtained only when severe processing parameters are used, such as pH 12, stirring time of 30 min, and stirring rate of 1000 rpm.[6] Recently, Javed *et al*. have investigated the extraction of the RBO using ethanol–acetone solvent mixtures.[7] An enhanced recovery of the RBO has been reported, but the absolute miscibility of solvents with moisture content left in the solid bran may cause rancidity during the extraction. Further, the commercial ethanol is also accompanied with a fractional amount of water content, which may also reduce the quality of extracted oil. Moreover, in order to tackle this problem, the use of absolute ethanol can make the extraction process economically unfeasible. Moreover, the trace amounts of ethanol based solvent systems for the RBO extraction can make the final product susceptible to rancidity after preservation.

In the solid–liquid extraction of the RBO, the nature of solvent system determines the efficacy of process. The extraction process with pure solvents is less complex, compared to the processes that employ binary or ternary solvent mixtures. Generally, the binary mixtures are selected to combine the characteristics of two solvents for higher extractability of oil. A way to improve the use of binary mixtures is to increase their polarity, because it helps the solvent to break the associations between oil and solid bran.[8]

Although in binary mixtures both solvents have nearly equal extraction efficiencies, the one is primarily chosen as an extracting agent, while the other one is added as clearing/sweeping agent. The extractant in mixture recovers the major portion of oil, while the clearing agent retrieves the leftover oil in the solid bran. Therefore, the extracting agent ought to be in excess, compared to the clearing agent in the binary mixture.

To understand the mechanism of solid–liquid extraction of oil, the particulate nature of the bran particles is important to comprehend. The RBO is contained in pockets present within the bran particles and is extracted by two mechanisms. The first one is characteristic for the preheating phase, whereby the oil becomes less viscous with volumetric increase. This volumetric increase causes the RBO to secret out from the oil containing pockets, which were damaged

during the milling process of the solid bran. The released oil forms a layer over the solid surface of bran particles, from where solvent dissolves it. The second mechanism dominates the later phase of extraction, when the solvent mixture diffuses into the pockets, dissolves the oil within solid bran and brings it to bulk of miscella. The recovery of oil in the first mechanism is very little because most of the oil remains bounded within bran particles and maximum oil is therefore extracted from the second mechanism involving solvent diffusion. The RBO is dissolved into solvent because of viscosity gradient that exists between solvent and RBO. However, the rate of oil transfer from bran particles to miscella is governed by the concentration gradient.

In this study, we have used the binary mixtures of ethyl acetate (EA) and dichloromethane (DCM) for the extraction of RBO for the first time. Nine binary mixtures of EA and DCM have been employed in order to maximize RBO recovery. The effects of the bran particle size, preheating temperature, stirring rate, and stirring time on the extraction yields have been discussed.

EXPERIMENTAL

Materials

The rice bran (local rice processing mill), acetone (CAS No. 67-64-1, 99.9 %, Merck Millipore), dichloromethane (CAS No. 75-09-2, anhydrous 99.8 %, Sigma–Aldrich), ethanol (CAS No. 64-17-5, analytical standard, Sigma), ethyl acetate (CAS No. 141-78-6, anhydrous 99.8 %, Sigma–Aldrich) and *n*-hexane (CAS No. 110-54-3, anhydrous 95 %, Sigma–Aldrich) were used.

Preparation and analysis of rice bran

The rice bran was first sieved using 60–200 mesh sieves, to remove any unwanted material from it. The moisture content of bran was removed by subjecting it to oven heating at 110 °C for 1 h. In order to determine the rice bran oil (RBO) content, a new approach of a multi-run solvent extraction method was used. 20 g of bran was mixed with 100 ml of ethanol and preheated at 60 °C, followed by stirring at 100 rpm for 15 min. The mixture was filtered, and the filter cake was again treated with 100 ml of hexane, acetone and dichloromethane separately. The filtrates were vacuum distilled at 60 °C to recover solvents and the percentage oil content obtained was calculated using Eq. (1):

$$\text{Oil content} = 100\frac{w_1 + w_2 + w_3 + w_4}{W_B} \quad (1)$$

where W_B is weight of rice bran used and w_1, w_2, w_3 and w_4 are the weights of oil content, separately obtained in extraction runs R_1, R_2, R_3 and R_4, respectively. The oil content in the reference bran, obtained with the multi run extraction method was 16.45 % and was comparable as obtained, using the standard soxhlet extraction method, *i.e.*, 16.29 %.[9]

Preparation of binary mixtures

Binary mixtures of ethyl acetate (EA) and dichloromethane (DCM) were prepared using variable volumetric ratios of these solvents. The details of binary solvent systems are given in the TABLE I.

TABLE I. Volumetric composition of solvent systems

Solvent system	Volume of EA, ml	Volume of DCM, ml	Total volume, ml	Volumetric ratio
S_1	5	45	50	0.11
S_2	10	40	50	0.25
S_3	15	35	50	0.42
S_4	20	30	50	0.67
S_5	25	25	50	1
S_6	30	20	50	1.5
S_7	35	15	50	2.33
S_8	40	10	50	4
S_9	45	5	50	9

RBO extraction procedure

Rice bran oil was extracted using 10 g of stabilized bran and 50 ml of solvent. In every experiment, solvent and bran mixtures were preheated for 3 min at 60 °C, in a 200 ml beaker, covered with a lid to prevent the solvent loss. The preheated mixture was then subjected to mechanical stirring for 15 min, without further heating. Finally, the mixture was filtered through a filter crucible. The filtrate was vacuum distilled at 60 °C to separate solvent from oil. The percentage recovery of oil was calculated using following Eq. (2):

$$\text{Oil recovery} = 100\frac{\text{Weight of oil extracted}}{\text{Weight of oil content in bran}} \quad (2)$$

To determine the RBO concentration in the solid bran and miscella, 10 samples of rice bran were simultaneously processed. The RBO concentration in miscella was calculated by measuring its percentage recovery after regular time intervals of 1 min, from 1 to 10 min. Similarly, the concentration of RBO in solid bran was also calculated using subtraction method.

RESULTS AND DISCUSSIONS

The effect of solvent composition

The maximum extraction of the RBO cannot be achieved without optimizing the composition of solvent that formulates the binary mixture. The optimization of the EA/DCM ratio was essential for the identification of the extractant and the clearing agents in the used solvent system. In order to investigate the optimum volumetric ratios of EA and DCM for the maximization of RBO recovery, nine solvent systems have been used (Fig. 1). It has been noticed that the lowest oil recovery (69.42 %) is achieved using the solvent system S_1 with the lowest EA/ /DCM volumetric ratio of 0.11. It is evident that as the proportion of EA in the binary mixture increases, the percentage recovery of the RBO also increases. The maximum oil recovery of 88.04 % has been achieved using the solvent system S_8 having EA/DCM volumetric ratio of 4. However, a slight decrease in the recovery of oil has been noticed when EA proportion in the mixture is further increased, as in the case of S_9. These results indicate that the RBO recovery is improved when EA act as the extractant and DCM as the clearing agent. Since the

binary mixture S_8 affords the maximum RBO recovery, the rest of extraction parameters have been studied using this solvent system.

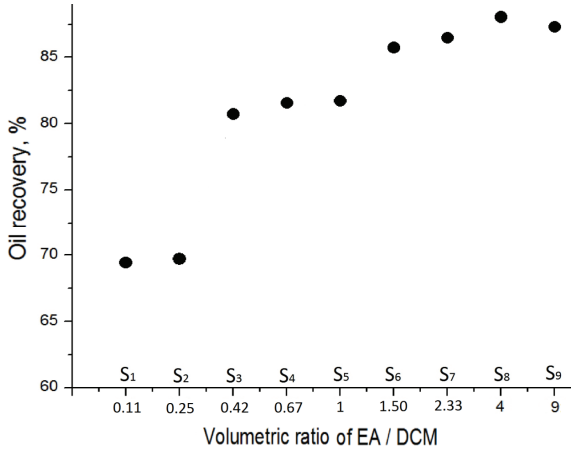

Fig. 1. Volumetric compositions of solvent systems and their corresponding oil extraction yields at preheating temperature, 60 °C (3 min), particle size, <149 μm (obtained with 100 mesh sieve), solvent to bran ratio, 5 mL/g, and stirring speed 100 rpm (15 min).

The effect of preheating temperature

The temperature applied during the extraction process may significantly alter the recovery of the RBO. The heat supplied to the solvent-bran mixture not only forces the oil to secrete out from solid bran, but also lowers the viscosity of the solvent. The reduced viscosity of solvent enables its penetration into the remote pockets of the bran particles, which gives rise to the oil recovery. Further, the oil solubility in the solvent system also increases with the temperature rise. The solubility of oil in the solvent system at variable temperatures can be explained in terms of Hildebrand's solubility parameter, Eq. (3):

$$\delta = \sqrt{\frac{\Delta H - RT}{V_m}} \tag{3}$$

where δ = Hildebrand solubility parameter, ΔH = enthalpy change of vaporization, R = *G*as constant, T = temperature, V_m = molar volume of solvent system.

The temperature effect on the percentage oil recovery is graphically demonstrated in Fig. 2. It has been observed that the oil recovery increases gradually from 76.4 to 89.7 % as preheating temperature is raised from 40 to 65 °C. As temperature increases, the processing solvent gets closer to the point when it vaporizes. At that state, the kinetic energy of solvent molecules increases and their ability to dissolve the solute is enhanced, thus increasing the recovery of oil. The preheating temperature increase results only in a minor increase of the RBO recovery. This reduced increase in the RBO recovery can be justified in terms of the decreased concentration gradient of oil between the bran and the bulk of miscella.

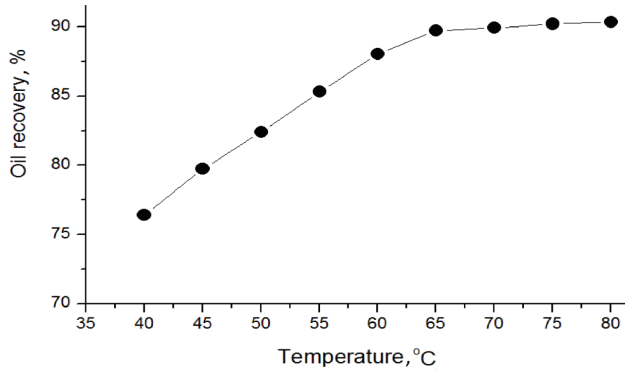

Fig. 2. Effect of preheating temperature on oil extraction yields with solvent system S8, preheating time 3 min, particle size <149 μm (obtained with 100 mesh sieve), solvent to bran ratio 5 mL/g and stirring speed 100 rpm (15 min).

The effect of the bran particle size

The particle size of bran may also govern the percentage recovery of the RBO, substantially. Further, the energy efficient RBO recovery can be achieved when the bran particle size is optimized. In order to examine the influence of the bran particle size on oil extraction, a plot between variable particle sizes and their corresponding oil yields has been shown in Fig. 3, keeping the rest of the processing parameters uniform.

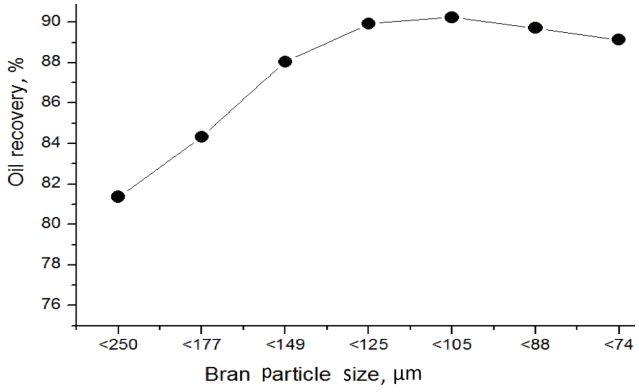

Fig. 3. Effect of bran particle size on oil recovery with solvent system S8, preheating temperature 60 °C (3 min), solvent to bran ratio 5 mL/g and stirring speed 100 rpm (15 min).

As a general trend, it has been noticed that when the larger particles are used, the percentage recoveries of oil are lower compared to the ones obtained with smaller particles. For instance when the particle size is <250 μm (obtained with 60 mesh sieve), the extraction yields of oil is only 81.37 %. The reason is, when the bran with large particle size is used, the ability of a solvent to dissolve

the RBO is reduced for two reasons. First, the heat transfer to the inbound oil is decreased and thus the secretion of the oil from the solid bran becomes negligible. Second, the penetration distance for a solvent to reach the oil pockets is also increased and ultimately the recovery of oil declines. When the particle sizes are reduced from <250 to <125 μm, the observed extraction yield increases to 89.92 %. However, when the bran particle size is further reduced to <105 μm, only a minor percentage increase in the oil recovery is obtained. Moreover, when the particle size is decreased to 88 μm, the extraction yield decreases to 89.71 % and this declining trend in the oil recovery continues with the further decrease of the particle size. The cause of this depressed oil recovery is that too small a particle size will increase the agglomeration tendency among the bran particles. Therefore, a significant amount of stirring energy is consumed in distorting such agglomerates and thus the availability of energy for the solvent penetration into the bran particles is decreased and a poor oil recovery is obtained. It can be concluded that the bran with particle size from <125 to <105 μm results in the highest RBO recovery at the given processing conditions, Fig. 3.

The effect of the solvent to bran ratio

The solvent to bran ratio may also determine the extractability of oil content. In order to investigate the influence of the solvent-bran ratio on the extraction yields, different ratios have been plotted against the percentage oil recoveries in Fig. 4.

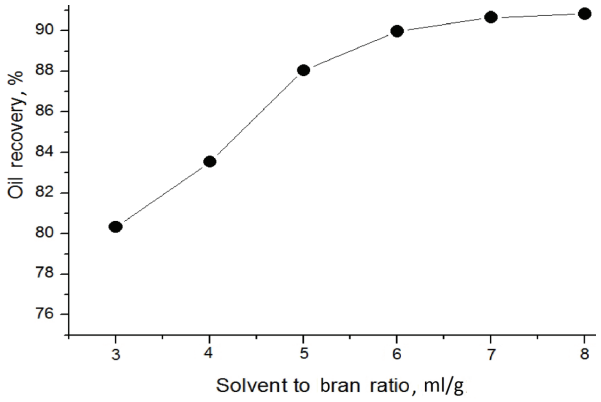

Fig. 4. Effect of solvent to bran ratio on oil recovery with solvent system S8, preheating temperature 60 °C (3 min), particle size <149 μm (obtained with 100 mesh sieve) and stirring speed 100 rpm (15 min).

Initially, when the solvent to bran ratio is 3 ml/g, the percentage oil recovery is 80.33 %. Further, as the solvent to bran ratios are increased from 4 to 6 ml/g, extraction yields also increase significantly from 83.53 to 89.97 %. The enhanced oil recovery can be explained in terms of mass transfer,[10] presented in Eq. (4):

$$\frac{dc}{dt} = \frac{DA(c_s - c)}{bV} \quad (4)$$

where dc/dt = rate of change of concentration, D = diffusion coefficient, A = area of solid liquid interface, c_s = concentration of the saturated solution in contact with solid particles, c = concentration of solute in bulk of solution at time t, b = thickness of liquid film surrounding the particles, V = total volume of solution, m^3.

Higher interfacial area between the two phases, as well as the concentration gradient causes, increased the RBO recovery. Further, the agitation gets more efficient, reducing the probability of agglomeration and thus giving rise to higher oil recoveries. However, increasing the solvent to bran ratio above 6 did not result in any significant increase in RBO recovery. This is due to the diminished oil content present within the solid bran and therefore the increase in oil recovery becomes less significant.

The effect of the stirring rate

The stirring is primarily done to avoid the formation of the bran agglomerates. Hixson and Baum studied the influence of stirring rate on the dissolution of solute in solvents at variable degrees of agitation using a dimensionless number,[11] represented in Eq. (5):

$$\text{Dimensionless No.} = \frac{Nd^2\rho}{\mu} \quad (5)$$

where N = number of revolutions of stirrer per unit time, d = diameter of stirring vessel, ρ = density of liquid, μ = viscosity of liquid.

The above correlation clearly suggests that the dissolution of oil will increase at higher stirring rates. Therefore, the effect of the stirring rate on the oil recovery is illustrated in Fig. 5. When the agitation rate employed to the solvent bran mixture is 60 rpm, the percentage oil recovery is 82.57 %. However, when the agitation rate is increased to 80 rpm, the extraction of oil rises to 87.31 %. This suggests that at 60 rpm, the bran particles tend to agglomerate because of the insufficient kinetic energy needed to swirl the solvent in the processing mixture. Further, the dissolved oil in the solvent increases its viscosity, which facilitates agglomeration, making the stirring rate insufficient. At an increased agitation rate of 80 rpm, the provision of kinetic energy becomes adequate to sustain the aggregation free solvent bran mixture. Therefore, at 80 rpm, the oil recovery has been reasonably increased. However, when stirring rates are further raised, the percentage growths in the extraction yields become smaller and smaller. This is due to the fact that higher stirring rates add little energy to the solvent molecules, which may lower the viscosity of solvent system. Therefore, these results

are again in agreement with the Eq. (5), indicating that the dissolution of solute may increase when the viscosity of solute is decreased.

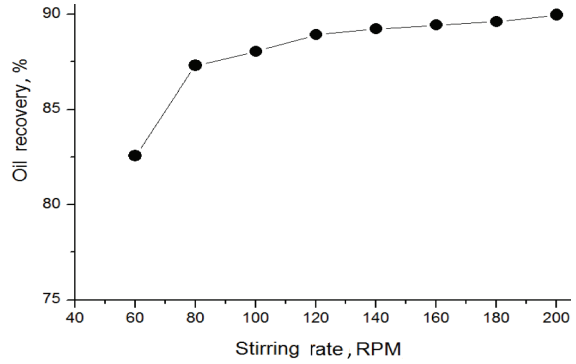

Fig. 5. Effect of stirring rate on oil recovery with solvent system S8, preheating temperature 60 °C (3 min), particle size <149 μm (obtained with 100 mesh sieve) and solvent to bran ratio 5 mL/g.

The effect of the stirring time

The stirring time is also a controlling parameter for the determination of the extraction yield of the RBO. Therefore, the control of stirring time over the percentage recovery is illustrated in Fig. 6.

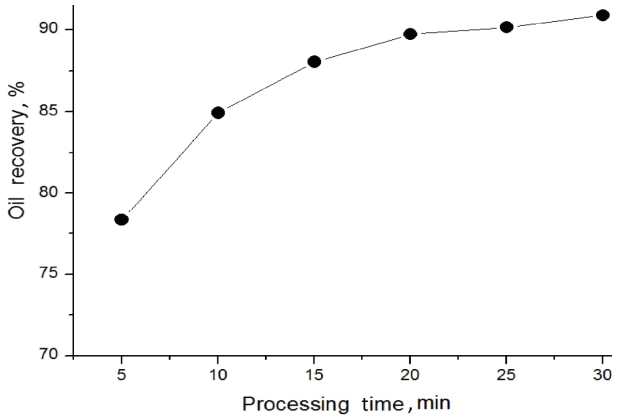

Fig. 6. Effect of processing/stirring time on oil recovery with solvent system S8, preheating temperature 60 °C (3 min), particle size <149 μm (obtained with 100 mesh sieve) solvent to bran ratio 5 mL/g and stirring speed 100 rpm (15 min).

It has been observed that after 5 min of stirring, the extraction yield is 78.33 %. For the agitation times of 10 and 15 min, the oil recoveries are grown to 84.92 and 88.04 %, respectively. However, when the stirring time is further increased, the percentage growth in the RBO recoveries becomes less significant. This can

be explained as follows: the initial concentration gradient of oil between the bran and the bulk of miscella is high and therefore the extraction of oil increases sharply. However, as the mass is transferred from the solid bran to the solvent phase, the concentration gradient decreases causing the reduced increase in the oil recoveries,[10] Fig. 7. This is also in accordance with the mass transfer equation, Eq. (4).

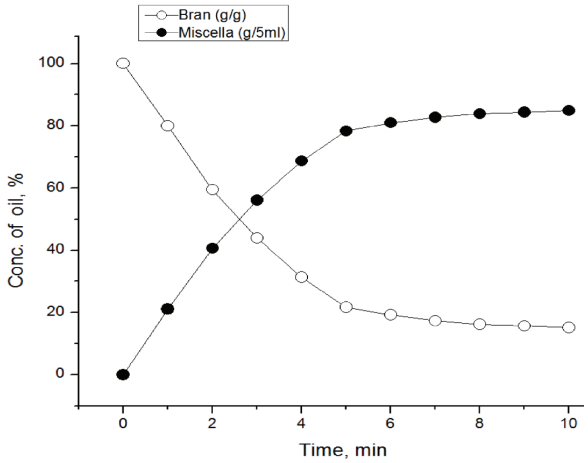

Fig. 7. Concentration gradient of oil between solid bran and bulk of miscella at variable times.

CONCLUSION

This study is the first report on the feasibility of the solvent extraction of RBO using the binary solvent mixture (DCM/EA) to achieve high oil recovery (~90 %). It is concluded that the extraction yields of oil are greatly influenced by the preheating temperature, the bran particle size, the solvent to bran ratio and the stirring time. However, the stirring rate does not significantly increase the oil extraction beyond 80 rpm. The study has shown promising results about the rice bran oil recovery (89.97 %) using the binary mixture of ethyl acetate and dichloromethane at the optimal volumetric ratio of 4, preheating temperature of 60 °C, particle size of <149μm and stirring rate above 80 rpm.

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ИЗВОД

ЧВРСТО–ТЕЧНО ЕКСТРАКЦИЈА УЉА ИЗ ПИРИНЧАНИХ МЕКИЊА ДВОКОМПОНЕНТНОМ СМЕШОМ ЕТИЛ-АЦЕТАТА И ДИХЛОРМЕТАНА

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Циљ рада је испитивање потенцијала мање штетних, двокомпонентних смеша етил-ацетата (EA) и дихлорметана (DCM) за добијање уља из пиринчаних мекиња. Кориш-

ћено је девет смеша са различитим запремиским односима EA/DCM у опсегу од 0,11 до 9. Коришћењем смеше растварача са запреминским односом 4 (C_8) остварује се максимални принос уља од 88,04 %. Екстракциони принос се повећава од 76,41 до 89,7 % са порастом температуре предгревања од 40 до 65 °C. Остали оптимизовани параметри за повећање приноса уља су: величина честица мекиња <125 μm (добијена помоћу сита 120 mesh), однос растварач:мекиње од 5 mL/g, и време мешања од 15 min. Минимална брзина мешања потребна за спречавање агломерације у смеши и постизање оптималног приноса уља је 80 o/min.

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