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 (S8) has enabled the maximum oil recovery 88.04%. The oil extraction yield is enhanced from 76.41% to 89.7% by increasing preheating temperature from 40oC to 65oC. Other optimized parameters for enhanced oil recovery are: bran particle size <125 µm (obtained with 120 mesh sieve), solvent to bran ratio of 5, and stirring time 15 minutes. 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

RUNNING TITLE:Extraction of Rice Bran Oil

**INTRODUCTION**

Rice bran is obtained during the processing of rice as byproduct 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 solvothermal extraction process[1](#_ENREF_1). Mechanical extraction is an energy intensive process and percentage oil recovery is also very low. Since solvent extraction allows higher percentages of oil recovery compared to mechanical extraction and is the most widely adapted process for production of RBO[2](#_ENREF_2).

Solvent selection is critical for optimized oil recovery and final product quality. 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, maximum solvent recovery after extraction is also desirable[3](#_ENREF_3). Generally, hexane is used for industrial scale extraction 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 product recovery, and quality.

Soares et. al. and Sparks et. al. have employed supercritical CO2, compressed liquefied petroleum gas and liquid propane for RBO extraction[4](#_ENREF_4), [5](#_ENREF_5). Despite improved oil quality the investment costs of these processes are very high. Hanmoungjai and coworkers have reported low cost recovery of bran oil using aqueous media[6](#_ENREF_6). However, quality of the end-product is poor due to rancidity of the oil during extraction process. Additionally, percentage recovery of oil up to 85% is obtained only when severe processing parameters are used such as pH 12, stirring time 30 min, and stirring rate of 1000 RPM[6](#_ENREF_6). Recently, Javed et.al. have investigated extraction of the RBO using ethanol – acetone solvent mixtures[7](#_ENREF_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, 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, 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 solid-liquid extraction of the RBO, nature of solvent system determines the efficacy of process. Extraction process with pure solvents is less complex, compared to the processes that employ binary or ternary solvent mixtures. Generally, binary mixtures are selected to combine the characteristics of two solvents for higher extractability of oil. Another objective of using binary mixtures is to increase their polarity because it helps the solvent to break the associations between oil and solid bran[8](#_ENREF_8).

Although, in binary mixtures, both solvents have nearly equal extraction efficiencies but 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 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, 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. Second mechanism dominates the later phase of extraction when solvent mixture diffuses into the pockets, dissolves the oil within solid bran and brings it to bulk of miscella. The recovery of oil in first mechanism is very little because most of the oil remains bounded within bran particles and maximum oil is therefore, extracted from 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 concentration gradient.

In this study, we have used for the first time the binary mixtures of Ethyl Acetate (EA) and Dichloromethane (DCM) for the extraction of RBO. 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.

**MATERIALS AND METHODS**

*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), n-hexane (CAS No. 110-54-3 , anhydrous 95% , Sigma Aldrich).

*Preparation and analysis of Rice Bran*

The rice bran was first sieved using 60-200 mesh sieves, to remove any unwanted material from it. Moisture content of bran was removed by subjecting it to oven heating at 110oC for 1 h. In order to determine the RBO content, a new approach of multi run solvent extraction method was used. 20 g of bran was mixed with 100 ml of ethanol and preheated at 60oC, followed by stirring at 100 RPM for 15 minutes. 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 60oC to recover solvents and the percentage oil content obtained was calculated using Eq. (1).

  (1)

Where; WB is weight of rice bran used and w1, w2, w3, w4 are the weights of oil content, separately obtained in extraction runs R1, R2, R3, R4 respectively. The oil content in reference bran, obtained with multi run extraction method was 16.45 % and was comparable as obtained using standard soxhlet extraction method i.e. 16.29% [9](#_ENREF_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 1: Volumetric composition of Solvent systems

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Solvent System** | **EA /ml** | **DCM /ml** | **Total Volume /ml** | **Volumetric Ratio** |
| S1 | 5 | 45 | 50 | 0.11 |
| S2 | 10 | 40 | 50 | 0.25 |
| S3 | 15 | 35 | 50 | 0.42 |
| S4 | 20 | 30 | 50 | 0.67 |
| S5 | 25 | 25 | 50 | 1 |
| S6 | 30 | 20 | 50 | 1.5 |
| S7 | 35 | 15 | 50 | 2.33 |
| S8 | 40 | 10 | 50 | 4 |
| S9 | 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 minutes at 60oC in a 200 ml beaker, covered with a lid to prevent solvent loss. The preheated mixture was then subjected to mechanical stirring for 15 minutes, without further heating. Finally, the mixture was filtered through a filter crucible. The filtrate was vacuum distilled at 60oC to separate solvent from oil. The percentage recovery of oil was calculated using following Eq. 2.

 (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, 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 binary mixture. Optimization of the EA/DCM ratio was essential for identification of the extractant and clearing agents in the used solvent system. In order to investigate optimum volumetric ratios of EA and DCM for maximization of RBO recovery, nine solvent systems have been used (). It has been noticed that the lowest oil recovery (69.42%) is achieved using the solvent system S1 with the lowest EA/DCM volumetric ratio of 0.11. It is evident that as the proportion of EA in the binary mixture increases, percentage recovery of the RBO also increases. The maximum oil recovery of 88.04% has been achieved by using the solvent system S8 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 S9. These results indicate that the RBO recovery is improved when EA act as an extractant and DCM as clearing agent. Since the binary mixture S8 affords maximum RBO recovery, the rest of extraction parameters have been studied using this solvent system.

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Figure 1: Volumetric compositions of solvent systems and their corresponding oil extraction yields at Preheating temperature 60oC (3 min), Particle Size (<149 µm obtained with 100 mesh sieve), Solvent to Bran ratio 5, and Stirring 100 RPM (15 min)

*The effect of preheating temperature*

The temperature applied during 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 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 increase. The solubility of oil in solvent system at variable temperatures can be explained in terms of Hildebrand’s solubility parameter, Eq. (3).

  (3)

Where,

δ = Hildebrand solubility parameter, J1/2m-3/2

ΔH= Enthalpy of vaporization, J/Kg

R= Gas constant, J/mol/K

T= Temperature, K

Vm= Molar volume of solvent system, m3/mol

The temperature effect on the percentage oil recovery is graphically demonstrated in . It has been observed that oil recovery increases gradually from 76.4% to 89.7% as preheating temperature is raised from 40oC to 65oC. As temperature increases, the processing solvent gets closer to the state where it vaporizes. At that state, kinetic energy of solvent molecules increases and their ability to dissolve 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 decreased concentration gradient of oil between bran and bulk of miscella.

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Figure 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, and Stirring 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, energy efficient RBO recovery can be achieved when bran particle size is optimized. In order to examine the influence of bran particle size on oil extraction, a plot between variable particle sizes and their corresponding oil yields has been shown in , keeping the rest of the processing parameters uniform.

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Figure 3: Effect of bran particle size on oil recovery with solvent system S8, Preheating Temperature 60oC (3 min), Solvent to Bran ratio 5, and Stirring 100 RPM (15 min)

As a general trend, it has been noticed that when the larger particles are used, percentage recoveries of oil are lower compared to the ones, obtained with smaller particles. For instance when particle size is <250 µm (obtained with 60 Mesh sieve), the extraction yields of oil is only 81.37%. The reason is, when bran with large particle size is used, the ability of solvent to dissolve the RBO is reduced for two reasons. First, heat transfer to the inbound oil is decreased and thus secretion of the oil from the solid bran becomes negligible. Second, the penetration distance for solvent to reach oil pockets is also increased and ultimately recovery of oil declines. When 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 particle size is decreased to 88 µm, the extraction yield decreases to 89.71% and this declining trend in the oil recovery continues, even after. The cause of this depressed oil recovery is that, too small a particle size will increase agglomeration tendency among bran particles. Therefore, a significant amount of stirring energy is consumed in distorting such agglomerates and thus 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 bran with particle size from <125 to <105 µm results in the highest RBO recovery at the given processing conditions .

*The effect of the solvent to bran ratio*

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

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Figure 4: Effect of Solvent to Bran ratio on oil recovery with solvent system S8, Preheating Temperature 60oC (3 min), Particle Size (<149 µm obtained with 100 Mesh sieve), and Stirring 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](#_ENREF_10), presented in Eq. (4).

 (4)

Where,

dC/dt = Rate of change of concentration, K/gm3/s

k = diffusion coefficient, m2/s

A = area of solid liquid interface, m2

Cs = Concentration of the saturated solution in contact with solid particles, Kg/m3

C = concentration of solute in bulk of solution at time t, Kg/m3

b = Thickness of liquid film surrounding the particles, m

V = total volume of solution, m3

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

*The effect of the stirring rate*

Stirring is primarily done to avoid the formation of bran agglomerates. Hixson and Baum studied the influence of stirring rate on dissolution of solute in solvents at variable degrees of agitation using a dimensionless number[11](#_ENREF_11), represented in Eq. (5).

 (5)

Where,

N = number of revolutions of stirrer per unit time

d = diameter of stirring vessel, m

ρ= density of liquid, Kg/m3

µ = viscosity of liquid, Ns/m2

The above correlation clearly suggests that dissolution of oil will increase at higher stirring rates. Therefore, the effect of stirring rate on oil recovery is illustrated in . When agitation rate employed to the solvent bran mixture is 60 RPM, the percentage oil recovery is 82.57%. However, when agitation rate is increased to 80 RPM, extraction of oil rises to 87.31%. This suggests that at 60 RPM, bran particles tend to agglomerate because of insufficient kinetic energy needed to swirl the solvent in the processing mixture. Further, the dissolved oil in 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 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 extraction yields become smaller and smaller. This is due to the reason that higher stirring rates add little energy to the solvent molecules which may lower viscosity of solvent system. Therefore, these results are again in agreement with the Eq. (5), indicating that dissolution of solute may increase when viscosity of solute is decreased.

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Figure 5: Effect of Stirring rate on oil recovery with solvent system S8, Preheating Temperature 60oC (3 min), Particle Size (<149 µm, obtained with 100 Mesh sieve), Solvent to Bran ratio 5, and Stirring Time (15 min)

*The effect of the stirring time*

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

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Figure 6: Effect of Processing/Stirring Time on oil recovery with solvent system S8, Preheating Temperature 60oC (3 min), Particle Size (<149 µm, obtained with 100 Mesh sieve), Solvent to Bran ratio 5, and Stirring 100 RPM (15 min)

It has been observed that after 5 min of stirring, the extraction yield is 78.33%. For agitation times of 10 and 15 min, the oil recoveries are grown to 84.92 and 88.04% respectively. However, when stirring time is further increased, percentage increase in the RBO recoveries becomes less significant. This can be explained as follows; the initial concentration gradient of oil between bran and bulk of miscella is high and therefore extraction of oil increases sharply. However, as the mass is transferred from solid bran to solvent phase, concentration gradient decreases causing reduced increase in the oil recoveries[10](#_ENREF_10) . This is also in accordance with the mass transfer Eq. (4).

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Figure 7: Concentration gradient of oil between solid bran and bulk of miscella at variable times

**CONCLUSION**

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

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