A Novel Azeotropic Mixture for Solvent Extraction of Edible Oils

D. Bera[2], D. Lahiri[2], Antonella De Leonardis[1], K.B.De[3] and A. Nag[3*]
[1] Department of Agricultural, Food, Environmental and Microbiological Science and Technologies (DiSTAAM). University of Molise, via De Sanctus, 86100 Campo basso, ITALY
[2] Rural Development Centre, Indian Institute of Technology, Kharagpur, INDIA
[3] Natural Product Laboratory, Chemistry Department, Indian Institute of Technology, Kharagpur, INDIA

[*]Corresponding author: A. Nag
Natural Product Laboratory
Chemistry Department,
Indian Institute of Technology,
Kharagpur-721302, INDIA

ahinnag@chem.iitkgp.ernet.in

ABSTRACT

Hexane, the common solvent for extraction of edible oils from seeds is no more considered safe due to the presence of solvent in oil and also solvent vapour, a hazardous air pollutant. We have carried out the experiments with bahera (*Terminalia bellerica* Roxb) and flax seed (*Linum usitatissimum*) oil as these oils are highly used in food for their nutraceutical values. The extraction of edible oil was performed with different solvents and their azeotropic mixtures such as azeotrope solvent Ethyl acetate + water (91.53%+8.47%) and Ethanol + water (95.4% +4.4%).

Of many protic organic solvents such as methanol, ethanol, isopropanol and ethyl acetate, mixture of ethanol and ethyl acetate were found to be of advantageous as organic impurities are minimum compare to absolute non-protic organic solvent extracted oil.

The oil extraction was temperature dependent. The properties such as refractive index, density, saponifiation and free fatty acid values were also affected by type of solvent used in the extraction process.

Keywords: Azeotropic mixture, seed oil (*Terminalia bellerica* Roxb and *Linum usitatissimum)*

1. INTRODUCTION

Edible oil extracted by conventional mechanical press (called Ghani in India) bears many impurities such as free fatty acids, coloured and others gummy materials which are known to be detrimental to oil flavor and stability (Bera et al., 2004). Generally hexane is used as solvent for the extraction of oil but a question arises about its safety (Bera et al., 2004) due to the presence of solvent (Lusas et al., 1991) in oil and also solvent vapour which is a hazardous air pollutants. Ethanol, methanol and acetone have been recommended as solvents for extraction of vegetable oils. Extraction with a solvent at temperatures and pressure above its critical point is known as supercritical fluid extraction (SCFE) with carbon dioxide as the extraction solvent has been tried as an alternative deacidification process for high FFA containing oils. Several researchers (Lusas et al., 1991; Turkay et al., 1991; Brunetti et al., 1989) have demonstrated the suitability of supercritical carbon dioxide (SC- $C0_2$) as a solvent for extraction of seed oils. But the extract oils contain high FFA, phospholipids and other complex substances; therefore they require a degumming step. Hence the present investigation is to use other solvents than n-hexane and also preserve oil qualities.

2. MATERIALS AND METHODS

All the chemicals used were of analytical grade. Solubility test was performed with different solvents as well as azeotrope mixture. Flax seed and bahera seed oils were purchased from local market because they contain high amount of ω-fatty acids beneficial to health. The oil was extracted from oil seed by using pure solvent at their boiling point and azeotrope solvent at their critical solution temperature by soxhlet apparatus at different time and the result for rate of extraction is given in Table 1.

Table 1.Rate of oil extraction from oil seed by using absolute solvent and azeotrope solvent at different time.

Name of solvent	Rate of extraction (%)				
	2h	4h	6h	8h	10h
n-Hexane	66	84	93	95.5	95.5
Ethanol	66	86	93	95	95
Isopropanol (IPA)	68	89	93	95.5	95.5
Ethyl acetate	66	81	92	95	95
Ethanol + water (95.4+4.4)(azeotrope)	49	62	76	90	94
Isopropanol (IPA) + water(87.8+12.2) (azeotrope)	51	63	79	90	95
Ethyl acetate + water (91.53+8.47) (azeotrope)	48	59	76	89	95
Ethanol + ethyl acetate (40 +60) (azeotrope)	56	66	82	91	95
Isopropanol (IPA) +Ethyl acetate (25+75) (azeotrope)	54	64	79	90	95

Oils and solvents were mixed 2:1 ratio (w/w) by a mechanical shaker for 1/2 hr. The mixture was allowed to settle for 1 hr. About 10 ml of the clear supernatant were drawn and weighed. The solvent was evaporated and the residue oil sample was again weighed. The difference of their weight would give the amount of oil present in the solvent. These data were used to calculate the percentage of solubility of oil in solvents. Nitrogen, phosphorous, protein, refractive index, saponification value, iodine value, peroxide value, free fatty acid were all determined by the standard methods (Official and Recommended Methods of American Oil Chemists Society, 4th edition, edited by D. Firestone, 1995, Champaign, IL: AOCS Press). At the same time residue solvents were analyzed, measured (Gandhi et al., 2001) in each case. All the experiments were performed triplicate and the average values were noted.

3. RESULTS AND DISCUSSION

Table 2 shows the properties of flax seed and bahera seed oils. These oils are highly used because they contain high amount of unsaturated fatty acids and have nutraceutical values (Bera et al 2004).

Table 2. Properties of flax seed oil and bahera oil

Properties	Flax seed oil	Bahera oil
Refractive index	1.2	1.1
Density at 20^0C (g/ml)	0.889	0.845
Saponification value (mg/g)	220.0	170
Iodine value (g/100g)	82.0	80
Peroxide value (mg/g)	5.2	5.09
Palmitic acid, $C_{16:0}$	6.0%	21.5%
Stearic acid, $C_{18:0}$	7.1%	7.9%
Oleic acid, $C_{18:1}$	22.2%	57.1%
Linoleic acid, $C_{18:2}$	14.2%	7.8%
Linolenic acid, $C_{18:3}$	50.4%	5.7%
Free fatty acid(mg/g)	2.0	1.62

Table 3 shows that the solubility of oil in n-hexane is high at room temperature as well as at high temperature. Solubility of the oil decreases in polar solvents at room temperature while rising the temperature solubility of the oil increases.

Table 3.Solubility of oil percentage in different absolute solvents and different azeotrope solvents at different temperature ^{0}C

Name of solvent	Solubility of oil (w/w %) at different temperatures ^{0}C							
	30	40	50	60	70	80	90	100
n-Hexane	M							
Ethanol	4.4	21	41	74	M			
Isopropanol (IPA)	67	83	M					
Ethyl acetate	M							
Ethanol + water	2.5	12	25	40	55	65	M	
Isopropanol (IPA) + water	35	50	60	65	M			
Ethyl acetate+ water	35	50	60	70	75	M		

M - miscible, IPA - Isopropyl Alcohol.

n-hexane (bp = 69 ^{0}C), ethyl alcohol (bp = 78.3 ^{0}C), isopropyl alcohol (bp = 82.5 ^{0}C) and ethyl acetate (bp = 77 ^{0}C) azeotrope solvents show higher critical solution temperature (Rao et al., 1957) and indicates the better possibility of extraction of oil from seeds (table 1).

In the azeotropes, the loss of solvent is minimum because the boiling point of the azeotrope is lower than pure solvent and offers economical benefit.

The extraction of oil in isopropyl alcohol is better but as a safety measure one can use an ethanol and ethyl acetate azeotrope mixture. This isopropyl alcohol at higher temperature forms ketonic compound (Lusas et al., 1991) which is harmful to human health.

Table 4. Comparison of some properties of flax seed oil and bahera seed oil after extraction with absolute solvent (n-hexane) and an azeotrope solvent [Ethyl acetate + water (91.53%+8.47%)]

Properties	Absolute solvent (n-hexane)		Azeotrope solvent (Ethyl acetate + water (91.53%+8.47%))	
	Flax seed oil	Bahera seed oil	Flax seed oil	Bahera seed oil
Refractive index	1.2	1.1	0.8	0.6
Density at 20^0C (g/ml)	0.889	0.845	0.80	0.75
Saponification value (mg/g)	220.0	170.0	230.0	180.0
Peroxide value (mg/g)	5.2	5.09	6.2	5.45
Free fatty acid (mg/g)	2.0	1.62	2.2	1.7

The properties of the extracted oil were analyzed and are presented in Table 4. From the Table 4 it is found that the extracted oil by using azeotropic mixture of ethyl acetate + water (91.53%+8.47%), shows less refractive index value and the density of the oil also is lower than for extracted oil using n-hexane. It indicates small amount of gummy materials present in azeotrope extracted oils and other essential free fatty acids remaining the same, but due to the presence of water in azeotrope solvent the free fatty acid value increases and peroxide value and saponificaion value are higher.

4. CONCLUSIONS

The following conclusions can be drawn from the experiments

1.Isopropyl alcohol, ethanol and ethyl acetate were equally effective for the extraction of oil compared with n-hexane.

2.The aqueous solvent and the respective azeotropes are also effective but added advantage with the higher content aqueous solvent in azeotrope solvent, it reduces the amount of organic solvent.

3.The azeotrope solvent reduced the organic gummy materials in solvent extracted oil.

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