CHAPTER 2

Extraction and Physico-chemical Properties of Non-edible Vegetable Oils

Non-edible vegetable oils (NEVOs) hold a significant value in various industrial applications, including biodiesel production, lubricants, cosmetics, polymers, and pharmaceuticals.[1,2] NEVOs are extracted from their seed through various methods like solvent extraction, mechanical pressing, or innovative techniques like microwave-assisted extraction (MAE). NEVOs possess distinctive physicochemical properties crucial for their diverse applications.[3] Generally; NEVO extracted through mechanical pressing is particularly valuable in the synthesis of polymers. Pressing, a mechanical extraction method, involves applying pressure to seeds to extract the oil without the use of solvents, ensuring both purity and environmental friendliness.[4,5]

The physico-chemical properties of NEVOs play a significant role in their suitability for polymer synthesis. Properties such as FA composition, iodine value (IA), saponification value (SV), and hydroxyl value (HV) directly impact the polymerization process and the characteristics of the resulting polymers. In particular, NEVOs extracted through mechanical pressing show better density, viscosity, flash point, SV, and oxidative stability, which ensures the quality of the synthesized polymers.[6]

These physico-chemical properties make NEVOs sustainable alternatives in polymer synthesis, contributing to reduced environmental impact and resource conservation.[7–9] The renewable and eco-friendly nature offers a pathway to replace petroleum-based resources, making them particularly valuable in the synthesis of high-performance polymers. By leveraging the unique properties of NEVOs, industries can develop polymer materials with enhanced characteristics, thus reducing their ecological footprint and fostering innovation in material science.

By utilizing mechanical pressing extraction methods and understanding the physicochemical properties of NEVOs, industries can develop their potential for polymer synthesis, specifically PU polymers, driving forward innovation and sustainability in materials science and manufacturing processes.

Two indigenous oils, Castor oil (CO) and Mahua oil (MO), are extracted and characterized for their further applications as polyol in the PU synthesis.

2.1. Extraction of NEVOs

2.1.1. Extraction of CO

Castor plants are very common in India and mostly grow in tropical and subtropical regions. Castor seeds (obtained through castor plants) were collected from Sabarkantha district of Gujarat state, India. The CO extraction from castor seeds is mainly done here using

the mechanical pressing method. This process entails crushing the seeds and then reducing their moisture content through gentle heating in a steam-jacketed vessel. The crushed seeds are then placed into a pressing machine, where mechanical force is applied to extract the oil. The CO obtained through mechanical pressing exhibits a light color and contains low levels of free FAs (Fatty acids). However, using this method typically extracts only around 45–50% of the oil, leaving the remainder in the pressed cake. **Figure 2.1** shows the extraction of CO.

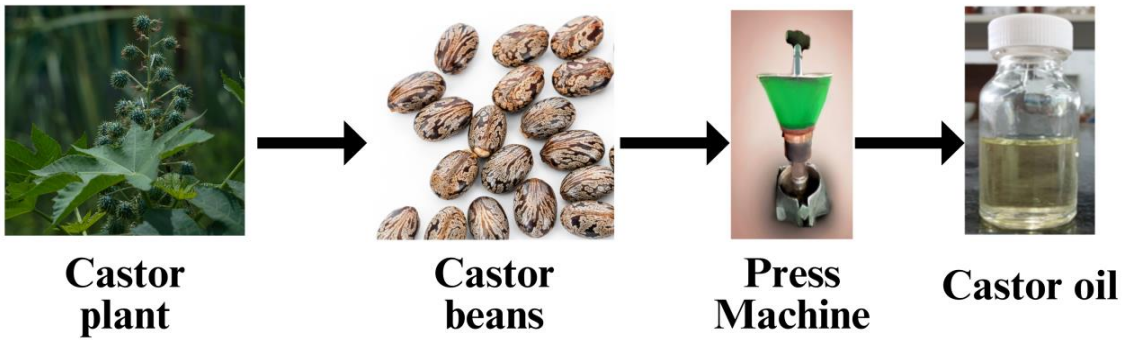

Figure 2.1. Extraction route of the CO

2.1.2. Extraction of MO

Figure 2.2 shows the extraction of MO using the mechanical pressing method**.** Mahua seeds were collected after proper ripening on a mahua tree from the Valsad district of Gujarat state, India. The collected seeds are cleaned to remove any dirt, debris, or foreign particles. The cleaned seeds are dried to reduce their moisture content. Lower moisture content helps in better oil extraction and prevents spoilage during storage. The dried Mahua seeds are then crushed into smaller particles, which increase the surface area, making it easier to extract oil during pressing using a mechanical press machine. After pressing, the MO is separated from the solids through filtration processes. The extracted MO may undergo further purification to remove any remaining impurities. The obtained clear and pure MO is then stored for further use.

The oil extraction waste from both sources, such as seed cake, which contains high carbon content, may be utilized as a biofertilizer. This option is not only eco-friendly but also cost-effective compared to expensive fertilizers.

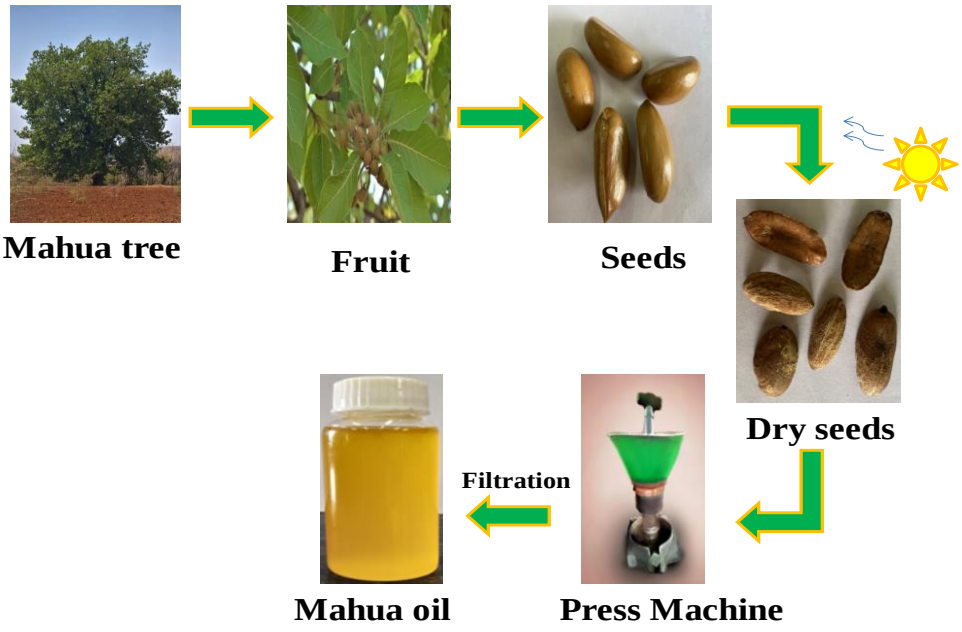

Figure 2.2. Extraction route of the MO

2.2. Determination of physico-chemical properties of NEVOs

Determination of various physico-chemical properties of NEVOs like acid value (AV), hydroxyl value (HV), iodine value (IV), saponification value (SV) and specific gravity (SG) are well-known and established methods and here referred using Mandal, S.[6]

2.2.1. Acid Value (AV) determination

"Weigh an accurately appropriate amount of the oil sample in a 250 mL conical flask. Add 50 mL of freshly neutralized hot ethyl alcohol and about 1 mL of phenolphthalein indicator solution. Heat the mixture for 15 min in a water bath at 75°–80°C. The mixture was titrated with alkali (KOH) to the end point using the phenolphthalein indicator, which shall be from colorless to light pink (persisted for 15 sec). The weight of the NEVO taken for the estimation and the strength of the alkali used for titration shall be such that the volume of alkali required for the titration does not exceed 10 mL. The acid value was calculated with the following equation:

$$\text{Acid Value} = \frac{56.1 \times V \times N}{W}$$

Where, V= volume of alkali used; N= Normality of alkali; W = sample weight;**"**

2.2.2. Hydroxyl Value (HV) determination

"Weigh exactly 0.5 gm of NEVO and transfer it into a 250 mL acetylation flask, followed by the addition of exactly 5 mL of the acetylating mixture (acetic acid with pyridine). Dissolve the oil sample completely, and if required, add 20 mL of organic solvent (chloroform). Reflux the contents for 30 min on a low flame. Cool the flask to RT and add 50

mL of distilled water slowly from top of the reflux condenser. Allow the contents to RT and titrate the free acetic acid using a 0.1 N KOH solution and phenolphthalein as an indicator. The appearance of the red color of the solution and should persist for at least 1 min is considered a titrating reading (T, mL). Carry out a blank determination, excluding the oil sample (B, mL).

$$\text{Hydroxyl Value} = \frac{56.1 \times (B - T) \times N}{W}$$

Were, W= weight of sample, N= Normality of KOH"

2.2.3. Iodine Value (IV) determination

"The iodine value of the NEVO sample was measured through titration using a 0.1N sodium thiosulfate ($Na_2S_2O_3$). A mixture of 15 mL chloroform and 25 mL iodine solution (Wij's solution) was added to the oil sample in an iodine flask, which was then closed and manually shaken for a few min. Following this, 15 mL of a 10% KI solution and 100 mL of distilled water were added to the mixture. The titration was carried out using a 0.1 N $Na_2S_2O_3$ solution until the solution turned yellow. At that point, 2–3 drops of starch solution were introduced as an indicator, which turned the solution into blue; titration continued until the blue color disappeared. Three measurements were performed on the sample, and the IV for the NEVO sample was calculated with the following equation:

$$\text{Iodine Value} = \frac{12.69 \times (V_0 - V_1) \times N}{W}$$

Where, V_0 = volume of $Na_2S_2O_3$ for blank; V_1 = volume of $Na_2S_2O_3$ required for oil sample; N = Normality of $Na_2S_2O_3$; W = Weight of sample."

2.2.4. Saponification Value (SV) determination

"The SV of the NEVO sample was measured as follows: a 1 gm oil sample was weighed into a conical flask, to which 25 mL of 0.5 N ethanolic KOH was added. The flask was then connected to a reflux condenser and heated in a water bath for 1 hr. Afterward, 3–4 drops of phenolphthalein indicator were added to the hot solution, which was titrated with 0.5 N HCl. The same method was applied to a blank sample, and three measurements were taken for the oil sample, and the SV for the NEVO sample was calculated with the following equation:

$$\text{Saponification Value} = \frac{56.1 \times (V_0 - V_1) \times N}{W}$$

Where, V_0 = volume of acid required for blank; V_I = volume of acid required for sample; N = Normality of acid; W = Weight of sample."

2.2.5. Specific Gravity (SG) determination

"A clean, dry pycnometer was first weighed (V_0), then filled with the oil and weighed again (V_1). A second pycnometer, filled with distilled water, was also weighed (V_2). The SG for the NEVO sample was calculated with the following equation:**"**

$$\text{Specific Gravity } = \frac{(V_1 - V_0)}{(V_2 - V_0)}$$

As shown in **Figure 2.3**, the CO and MO were extracted using a mechanical press method, showing a light yellow and yellow color appearance with characteristic odor. The high oil content (40-45% CO and 40-42% MO) in both castor and mahua seeds is a significant factor, making these oils economically viable and suitable for the purpose of polymer synthesis.

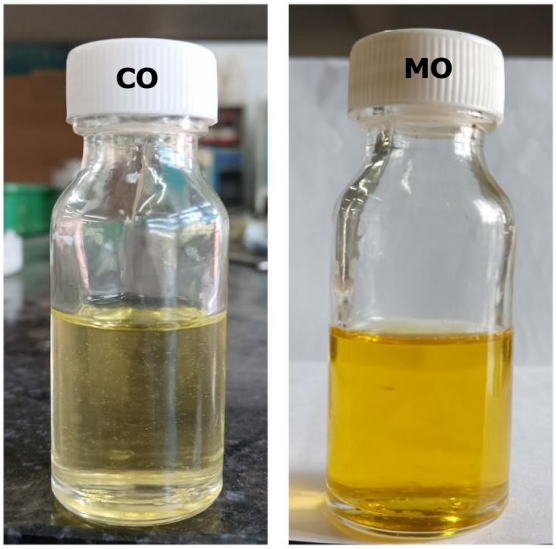

Figure 2.3. Real images of extracted CO and MO.

The physico-chemical properties of CO and MO determined through appropriate methods are listed in **Table 2.1.** It clearly indicated that the measured physico-chemical properties align well with the standard values reported in the literature,[6,10–12] which confirms the suitability of these oils for industrial use and polymer synthesis.

Table 2.1. Physico-chemical properties of CO and MO

Properties	Castor oil	Mahua oil
Appearance	Light yellowish liquid	Yellowish liquid
Acid value (mgKOH/g)	0.83	8.33
Hydroxyl value (mgKOH/g)	162	-
Iodine value (mgI_2/100 g)	83.42	63.78
Saponification value	176	196
Specific gravity @30°C	0.958	0.892

2.3. Chemical Analysis

The composition of FAs present in the studied NEVOs was determined by a gas chromatograph-mass spectrometer (GCMS-QP 2010 plus, Shimadzu, Japan) equipped with HP capillary column and He carrier gas using the standard fatty acid methyl esters (FAMEs). The column temperature was set at 120˚C with an increment of 3˚C per min for 57 min, whereas the injector and detector temperatures were programmed at 260˚C and 280˚C. The retention time and peak height/area were taken in qualitative and quantitative determination of the component present in the NEVOs.

The chemical analysis of studied CO and MO consists of a mixture of saturated and unsaturated FAs, but their specific compositions differ, which influences their behavior in chemical processes.[13] The FA compositions present in the studied CO and MO are reported in **Table 2.2**.

Table 2.2. The FA composition present in the NEVOs

Fatty acids	Castor oil (Wt %)	Mahua oil (Wt %)
Palmitic	0.92	22.53
Stearic	0.85	17.80
Oleic	3.21	39.62
Linoleic	4.70	18.33
Ricinoleic	89.73	-
Linolenic	0.78	-

As per the values seen in **Table 2.2**, the most prominent component is ricinoleic acid, which constitutes ~ 89.73% of its total FAs in the CO. This high concentration of ricinoleic acid is significant because it contains a -OH group at the 12th C position, making CO highly reactive and suitable for polymer synthesis, especially in producing polyurethanes (PUs). In addition to ricinoleic acid, small amounts of other fatty acids, such as oleic acid (3.21%) and linoleic acid (4.70%), are present, contributing to the oil's versatility in industrial applications.[14]

MO, on the other hand, is characterized by a high concentration of oleic acid, which accounts for 39.62% of its FA content. Oleic acid is a monounsaturated FA, and its high presence is common in seed oils of plant origin, making MO valuable for industrial applications requiring stability and flexibility, such as in lubricants and polymers.[15] Additionally, MO contains significant amounts of palmitic (22.53%) and stearic acids (17.80%), which are saturated FAs that enhance the oil's oxidative stability, making it

suitable for use in long-lasting products.[16,17] It was clearly understood that for the synthesis of PU polymers, MO is required to modify as polyol with various potent synthetic routes.

The presence of both saturated and unsaturated FAs in these NEVOs, as shown in **Table 2.2**, indicates their ability to participate in different chemical and polymerization reactions.

2.4. References

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