PHYSICOCHEMICAL CHARACTERIZATION OF USED COOKING OIL: ENVIRONMENTAL IMPLICATIONS AND REUSE POTENTIAL

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Improper disposal of waste cooking oil (WCO) poses significant environmental challenges, necessitating effective reuse strategies aligned with circular economy principles. This study aimed to perform the physicochemical characterization of WCO from residential and commercial sources to propose specific management routes based on degradation levels. Analytical determinations included density, acid value, peroxide value, and iodine value, performed in triplicate. The results revealed high heterogeneity and severe degradation, with acidity ranging from 1.15 to 5.82 mg KOH/g and peroxide values reaching 111.92 meq O_2/kg. Notably, density increased compared to virgin oil (0.95 g/mL), reaching up to 1.17 g/mL. Pearson correlation analysis indicated a significant positive association between hydrolytic and oxidative degradation ($r = 0.8349$; $p = 0.0014$). Cluster Analysis using the Gap Statistic method successfully categorized samples into four groups. Based on this, specific valorization routes were proposed: Cluster A (lower degradation) for biotechnological applications (enzymatic hydrolysis); Cluster D (intermediate) for chemical production of esters; and Cluster B (restaurant/high degradation) for energy purposes (biodiesel). These findings demonstrate that physicochemical profiling is a viable tool for directing WCO into appropriate value chains, transforming an environmental pollutant into a sustainable resource.

KEYWORDS: WASTE VALORIZATION; LIPID OXIDATION; TRANSESTERIFICATION; HYDROLYSIS; CHEMOMETRICS.

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1. INTRODUCTION

Vegetable oils are organic compounds predominantly composed of triacylglycerols. These molecules result from the combination of one glycerol molecule with three fatty acids, bonded through ester linkages. The composition of fatty acids can vary in terms of carbon chain length and degree of unsaturation, which directly influences the physical and nutritional properties of the oils (XU ET AL., 2018). In general, vegetable oils have a high proportion of unsaturated fatty acids, which makes them liquid at room temperature and distinguishes them from animal fats.

Vegetable oils are widely used in human nutrition. Soybean oil production accounts for approximately 56% of Brazil's total oil output, with 90% of this volume intended for food consumption (NAIR, 2023). However, when exposed to high temperatures during frying, vegetable oils undergo chemical changes, including hydrolysis, oxidation, and polymerization which affect flavor and odor, reduce nutritional value, and generate toxic compounds (ZHAO ET AL., 2021). Under frying conditions, the deterioration of vegetable oil is influenced by three major chemical reactions: hydrolysis, oxidation, and polymerization (WU, G. ET AL., 2019).

The hydrolysis involves the cleavage of triacylglycerols (TAGs), releasing free fatty acids (FFAs), diacylglycerols, monoacylglycerols, and glycerol (GOU ET AL., 2018). Simultaneously, the thermo-oxidation process is initiated at the double bonds of the unsaturated fatty acids, where interaction with oxygen forms highly unstable hydroperoxides (primary products). These compounds undergo rapid decomposition via cleavage, generating a variety of volatile and non-volatile secondary oxidation products, such as aldehydes, alcohols, and ketones (EL-MAGHRABEY ET AL., 2022). The accumulation of these toxic secondary compounds, along with the subsequent dimerization and polymerization reactions between them and FFAs, leads to the formation of high-molecular-weight species, which increase viscosity and drastically contribute to overall oil degradation (ERICKSON; YEVTUSHENKO; LU, 2022). Consequently, these residual vegetable oils are rendered unsuitable for human consumption and are classified as solid waste.

The high pollution potential of used cooking oil is widely recognized. Although there is no specific federal legislation regarding its disposal, Brazil's National Solid Waste Policy (LAW NO. 12.305/2010) addresses its management indirectly. Improper disposal of this waste into domestic sewage systems can contaminate up to 25,000 liters of water per liter of oil discarded (OLIVEIRA & NASCIMENTO, 2014), directly undermining the achievement of several Sustainable Development Goals (SDGs), such as access to clean water and sanitation (SDG 6), sustainable cities and communities (SDG 11), and the protection of terrestrial and aquatic ecosystems (SDGs 13, 14, and 15). Furthermore, when infiltrated into the soil, oil can reach underground aquifers, threatening sources of drinking water (OLIVEIRA ET AL., 2022). In aquatic environments, the formation of a surface film hinders gas exchange, disrupts ecological balance, and promotes harmful chemical reactions (OSSAI ET AL., 2024). The oxidation of the oil and its deposition at the bottom of water bodies may lead to the death of aquatic organisms and the bioaccumulation of toxic compounds along the food chain (CASTELVETRO ET AL., 2020).

Improper disposal of these oils harms aquatic and terrestrial biodiversity, alters soil properties, contaminates groundwater, and impairs the operation of water treatment plants (LI ET AL., 2020; YOUSIF ET AL., 2017; MANSFIELD ET AL., 2012). Due to their low biodegradability and chronic toxicity, these oils pose a significant environmental threat, highlighting the urgent need for actions focused on collection, public awareness, and sustainable reuse (OLADUNJOYE & ALUKO, 2024; KNOTHE & STEIDLEY, 2005).

Waste vegetable oils can be repurposed for various applications, thereby mitigating their disposal. Although biodiesel production via transesterification remains the most established pathway, recent studies highlight the potential of these oils as feedstock for high-value-added bioproducts, including biolubricants, biosurfactants, and specific fatty acids obtained through enzymatic hydrolysis (COSTA ET AL., 2023; Teh ET AL., 2025). Acidity quantification indicates the presence of free fatty acids (FFAs), which can be fractionated and directed toward ester production for the pharmaceutical, cosmetic, and food industries.

However, a major bottleneck reported in recent literature is the chemical heterogeneity of the feedstock. Physicochemical alterations in waste vegetable oils depend on various factors, such as exposure time, temperature, and the moisture content of the food types used. Most studies focus on oils from controlled sources (e.g., restaurants), neglecting the complexity of domestic waste, which exhibits greater variability (NASCIMENTO ET AL., 2022). Physicochemical parameters, such as peroxide and iodine values, reflect the degree of oxidative rancidification and unsaturation, respectively. Understanding this variability is crucial, as highly degraded oils may inhibit enzymatic processes or compromise the quality of the final biofuel (DOS SANTOS ET AL., 2024). Consequently, a systematic classification is required to allocate these heterogeneous residues to their most suitable valorization pathway, optimizing the yield of subsequent bioprocesses.

Given this scenario, and the gap regarding the characterization of domestic sample complexity, the present study aims to analyze the physicochemical properties of waste cooking oil from diverse sources. By applying cluster analysis, this work seeks to identify degradation patterns to contribute to repurposing strategies for this waste in sustainable processes, fostering practices aligned with circular economy principles.

2. MATERIALS AND METHODS

The research presented herein was conducted at the Laboratory of Biochemistry and Bioprocesses (LBBIO), Department of Biological Sciences, UNESP – Assis Campus.

2.1 Characterization of Waste Cooking Oil

2.1.1 Waste Oil Samples

A total of 11 Waste Cooking Oil (WCO) samples, totaling 10 L, were collected from heterogeneous sources to ensure the representativeness of this complex residue matrix. Ten samples were sourced from domestic kitchens (Samples 1–7, 9, 10, and one unlisted sample), and one sample (Sample 8) originated from a commercial restaurant. The WCO analyzed was predominantly soybean oil, all generated under uncontrolled thermal conditions (variability in time and temperature) and having been in contact with various food types. Fresh commercial soybean oil COCAMAR® was utilized as the control. All analyses were performed in triplicate.

2.1.2 Acid Value (AV)

The Acid Value (AV), expressed as mg KOH per gram of sample, was determined according to the standards of Official Methods of Analysis of the Adolfo Lutz Institute (2008). Approximately 2.0 g of each sample was weighed and dissolved in 25 mL of a neutralized diethyl ether-ethanol solution (2:1, v/v). The solution was titrated with standardized 0.1 mol/L NaOH using phenolphthalein as the indicator. The AV was calculated according to Eq. 1.

$$AV = \frac{v\ x\ f\ x\ 5{,}61}{P} \qquad (1)$$

Where Acid Value (AV) (mg KOH/g): *V*= Volume of the 0.1 mol/L Sodium Hydroxide (NaOH) solution consumed in the titration (mL). *F*= Standardization factor of the Sodium

Hydroxide solution. *P*= Mass of the sample (g). *5,61*= Constant value resulting from the molar mass of KOH (56.1), used to convert the moles of base consumed into mg of KOH.

2.1.3 Peroxide Value (PV)

The Peroxide Value (PV), expressed as mEq of O_2 per kg of sample, was determined by the standards of the American Oil Chemist's Society (A.O.C.S) Cd8-53. A 2.0 g of the sample was dissolved in 30 mL of an acetic acid–chloroform solution (3:2, v/v). Subsequently, 0.5 mL of saturated KI solution was added, and the mixture was incubated in the dark for exactly 1 minute. Then, 30 mL of distilled water was added, and the liberated iodine was titrated with standardized 0.01 mol/L sodium thiosulfate solution ($Na_2S_2O_3$) under constant stirring until the yellow coloration disappeared. Finally, 0.5 mL of starch indicator solution was added, and the titration continued until the complete disappearance of the blue color. The PV was calculated according to Eq. 2.

$$PV(mEq/kg) = \frac{(A - B)\ x\ N\ \ x\ 1000}{P} \qquad (2)$$

Where Peroxide Value: *A* = Volume of 0.1 (or 0.01 N) sodium thiosulfate ($Na_2S_2O_3$) solution consumed in the sample titration (mL). *B* = Volume of 0.1 (or 0.01 N) sodium thiosulfate ($Na_2S_2O_3$) solution consumed in the blank titration (mL). *N* = Normality of the sodium thiosulfate solution ($Na_2S_2O_3$) (Eq/L). *P* = Mass of the sample (g).

2.1.4 Iodine Value (IV) by the WIJS Method

The Iodine Value (IV), expressed in g of I_2 per 100 of sample, was determined using A.O.C.S. Official Method Cd1-25 (Wijs Method). A 0.25 g of the sample was mixed with 10 mL of cyclohexane and 25 mL of Wijs solution. After homogenization, the mixture was kept in the dark for 30 minutes. Subsequently, 10 mL of 15% (w/v) potassium iodide solution and 100 mL of distilled water were added. The solution was titrated with 0.1 mol/L sodium thiosulfate ($Na_2S_2O_3$) until the faint yellow color disappeared. Finally, 1–2 mL of 1% (w/v) starch indicator solution was added, and titration continued until the blue color completely disappeared. The IV was calculated according to Eq. 3.

$$Iodine\ Value = \frac{(Vb - Va)\ x\ M\ x\ 12{,}69}{P} \qquad (3)$$

Where IV: *M* = Molarity of the $Na_2S_2O_3$ solution. *Vb* = Volume consumed in the blank titration (mL). *Va* = Volume consumed in the sample titration (mL). *P* = Mass of the sample (g).

2.1.5 Moisture and Volatile Matter Determination (MVM)

The Moisture and Volatile Matter (MVM) content was determined according to the standards of Official Methods of Analysis of the Adolfo Lutz Institute (2008). A 2.0 g sample was weighed into a previously tared beaker. The material was heated for 3 hours at 105 ± 2°C, cooled in a desiccator, and then weighed. This process was repeated until a constant weight was achieved. The MVM was calculated based on the percentage of weight loss.

2.1.7 Refractive Index (RI)

The Refractive Index (RI) was determined according to the A.O.C.S. Official Method Cc7-25, using an Abbé refractometer (Biosystems Digit). The prism temperature was rigorously controlled at 40ºC via a thermostatic circulating system. The oil sample was subjected to mandatory filtration to ensure an anhydrous state and the complete removal of impurities. After application, the sample was allowed to stabilize (1 to 2 minutes) before the instrument was adjusted. The RI was recorded in triplicate, requiring a maximum variation of 0,002 (Note:0.002 is too large; double-check the required precision of the method) between readings, with the final result expressed as the mean.

2.1.8 Relative Density Determination

The Relative Density Determination (RD) was determined according to the A.O.C.S. Official Method Cc 10a-25. The sample was previously melted and subjected to mandatory filtration for the removal of impurities and moisture traces. A 2 mL capacity pycnometer was carefully filled, avoiding air bubbles. The pycnometer was capped and immersed in a thermostatically controlled water bath at 25 ± 0.1°C for 30 minutes to achieve thermal equilibrium. After stabilization, excess oil was removed, and the pycnometer was weighed. The RD was calculated according to Eq. 4.

$$RD = \frac{A-B}{C} \qquad (4)$$

Where A = mass of the pycnometer containing the oil sample (g). B = mass of the empty pycnometer (g). C = mass of water at 25 °C (g).

2.1.9 Data Analysis

Statistical analysis was conducted using OriginPro® 8.0 software. Prior to mean comparisons, data normality was assessed using the Shapiro-Wilk test. Mean comparisons were subsequently performed via Analysis of Variance (ANOVA), followed by the Tukey's post-hoc test for multiple comparisons. The significance level set at 95% ($p<0.05$). Cluster analysis was performed using Jamovi® software to identify degradation patterns.

3. RESULTS AND DISCUSSION

3.1 Physicochemical analyses of waste oil samples

This study aimed to perform the physicochemical characterization of waste cooking oil to contribute to sustainable reuse strategies and promote practices aligned with the circular economy. Ideally, the evaluation of the degradation level of waste oils through physicochemical parameters allows for the classification of this material, assisting in waste management.

The results indicate that the waste oil samples exhibited significant changes in acidity, peroxide, and iodine values when compared to virgin oil. These alterations reflect physical and chemical degradation processes that compromise oil quality and stability, rendering it unsuitable for reuse in food applications. Consequently, proper management strategies are required, targeting either safe disposal or alternative industrial applications (Table 1).

In the analyzed waste oil samples, acidity values ranged from 1.15 to 5.82 mg KOH/g. These figures are significantly higher than the maximum limit established for refined soybean oil, which is 0.6 mg KOH/g (ANVISA; CODEX ALIMENTARIUS). Such elevated values indicate intense degradation of triglycerides, primarily due to the hydrolysis of ester bonds and the release of free fatty acids. These processes are intensified by the prolonged and repeated use of oil during frying (LIU ET AL., 2021). Given that these waste oils are often improperly discarded, the high acidity and elevated content of free fatty acids (FFA) promote water contamination. The presence of these FFAs and degradation by-products affects the water's surface tension and demands high levels of oxygen for biodegradation, which subsequently leads to eutrophication and severely impacts aquatic life (THUSHARI; BABEL, 2022).

Peroxide values up to ten times higher than the acceptable limits were detected in the waste oil samples, ranging from 20.86 to 111.92 meq O_2/kg, whereas the maximum recommended limit for edible vegetable oils is 10 meq O2/kg (CODEX ALIMENTARIUS). These results demonstrate a high degree of lipid oxidation resulting from the repeated and prolonged exposure of oils to high temperatures. The formation of peroxides represents the initial phase of oxidative rancidity, indicating the presence of unstable hydroperoxides that degrade into secondary compounds, such as aldehydes and ketones, which possess potential toxic effects. When discarded into the environment, vegetable oil residues present a significant ecotoxicological risk due to their high concentration of peroxides and highly reactive secondary by-products (aldehydes and ketones). These chemical compounds not only exhibit direct toxicity to microorganisms and aquatic organisms, but their high chemical reactivity can also critically interfere with biochemical processes and natural cycles within ecosystems (PATEL; SINGH, 2025).

The iodine value analysis revealed an average of approximately 32 ± 1.76 g I2/100 g fat for all waste oil samples. This value is 25% lower than that observed in virgin oil (43.11 ± 0.03 g I2/100 g fat). Therefore, used oil presents a significantly lower degree of unsaturation in fatty acids compared to unused oil, confirming that cooking conditions directly affect this parameter. However, the origin of the oil, whether domestic (generally milder usage with less reheating and shorter exposure) or commercial (typically more intense), did not result in statistically significant differences in the degradation level (ABRANTE-PASCUAL ET AL., 2024). This suggests that usage origin is not a definitive parameter for guiding waste oil management strategies. The quantification of unsaturation within triacylglycerol chains is a critical parameter for guiding the sustainable management and adequate distribution of these residues. Since the iodine value directly reflects the quantity of double bonds, its reduction is highly correlated with the enhanced oxidative stability of the final product. Consequently, this analysis serves as an essential screening tool for waste management strategies, enabling the samples to be appropriately directed toward the most suitable valorization pathway—such as transesterification—which capitalizes on the lower degree of unsaturation (KUMAR ET AL., 2025).

Finally, density is a crucial physical property for the characterization of vegetable oils. While typical densities of pure oils generally range from 0.91 to 0.93 g/mL (CHOE & MIN, 2006), the virgin oil analyzed in this study presented a baseline density of 0.95 g/mL. In contrast, the waste oil samples exhibited a consistent increase in density, with values ranging from 0.98 to 1.17 g/mL. It is noteworthy that the majority of the analyzed samples exceeded 1.0 g/mL. According to FRANKEL (2012), density values surpassing this threshold indicate a significant accumulation of contaminants and degradation products, such as moisture, solid residues, and polymerization compounds formed during thermal stress. These results confirm that the prolonged use of the oil altered its physical composition, resulting in a denser material due to the formation of higher molecular weight compounds.

3.2 Statistical Analysis of the Physicochemical Composition of Waste Oils

Given the heterogeneity of waste oil composition resulting from diverse usage conditions, statistical techniques were employed to categorize the samples based on their physicochemical profiles, thereby facilitating more efficient management strategies. Specifically, Pearson correlation analysis and Cluster analysis using the Gap Statistic method were applied to identify patterns and relationships within the dataset.

TABLE 1 – PHYSICOCHEMICAL ANALYSES OF WASTE COOKING OIL SAMPLES AND VIRGIN OIL

PARAMETERS	**WASTE COOKING OILS**										
	AM1^{A}	**AM2^{D}**	**AM3^{D}**	**AM4^{A}**	**AM5^{A}**	**AM6^{D}**	**AM7^{A}**	**AM8^{B}**	**AM9^{A}**	**AM10^{A}**	**VIRGIN OIL^{C}**
Quality and degradation											
Acidity Index (%oleic acid)*	2,35±0,04	2,93±0,03	2,56±0,03	2,08±0,03	2,93±0,08	1,07±0,04	1,18±0,04	4,15±0,02	0,82±0,04	1,13±0,08	0,90±0,06
Peroxide Index (meq/kg)*	36,92±9,69	61,22±3,74	71,94±13,11	31,86±6,11	44,28±4,39	52,23±9,77	23,50±5,53	111,92±1,42	20,86±3,14	31,42±3,83	3,48±1,12
Iodine Index (g $I_2 \cdot 100^{-1}$ g fat)	30,43±0,03	31,45±0,02	33,98±0,04	34,49±0,03	32,46±0,01	34,49±0,03	29,92±0,02	30,94±0,05	30,43±0,02	32,96±0,02	43,11±0,03
Physicochemical properties											
Density (g/mL at 25 °C)*	0,98±0	1,17±0	1,11±0	1,07±0	1,12±0	1,08±0	1,13±0	1,06±0	1,07±0	1,17±0	0,95±0
Soluble compounds											
Brix (°Bx)*	1,47±0	1,47±0	1,47±0	1,47±0	1,47±0	1,47±0	1,47±0	1,47±0	1,47±0	1,47±0	1,47±0

*Values represent the mean ± standard deviation of analyses performed in triplicate.

A, B, C, and D: Cluster profiles according to cluster analysis.

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3.2.1 Pearson Correlation

Pearson correlation analysis was conducted to elucidate the interrelationships among the evaluated parameters, addressing a limitation of the Gap Statistic method used in cluster analysis, which does not explicitly identify the specific variables driving the grouping. Therefore, correlation analysis provides insight into the factors influencing sample variability and supports the interpretation of the formed clusters.

The results revealed a strong and statistically significant positive correlation between acid value and peroxide value ($r = 0.83491$; $p = 0.00138$). This indicates that the increase in free fatty acids (hydrolytic degradation) is directly associated with the accumulation of lipid oxidation products. This finding corroborates previous studies reporting that hydrolytic and oxidative degradation processes often occur concurrently in vegetable oils subjected to thermal stress (COSTA ET AL., 2019; SHAHIDI & AMAROWICZ, 2016).

Conversely, the other analyzed variables, iodine value, density, and soluble solids content (Brix), did not exhibit statistically significant correlations with each other or with the degradation indicators. This suggests that these parameters vary independently within the waste oil samples and do not show a linear dependency in the studied dataset.

3.2.2 Cluster Analysis and Group Characterization

Cluster analysis based on the Gap Statistic metric identified that a four-cluster solution (Table 1) was the most appropriate model for the dataset, ensuring high stability and low intra-group variability. This segmentation aligns with the natural structure of the data, allowing for the identification of specific patterns within complex datasets, a technique widely applied in food characterization and quality control (JOLLIFFE & CADIMA, 2016). Following the grouping, analysis of variance (ANOVA) and Tukey's test were applied to validate the formation of the clusters and identify the specific physicochemical variables responsible for the distinctions between groups.

Regarding the variables driving the segmentation, the results revealed that the acidity content (Figure 1) did not differ significantly among the clusters ($p = 0.1227$). This suggests that acidity was not a determining factor in the grouping, indicating a certain homogeneity in free fatty acid levels across the analyzed waste oils. In contrast, the peroxide value (Figure 2) exhibited highly significant differences ($p < 0.001$), emerging as the primary discriminator among the groups. This highlights the role of peroxide as a sensitive marker of oxidative stability. Similarly, the iodine value showed statistical significance ($p = 0.0034$), contributing to the separation of groups based on the degree of unsaturation of fatty acids, with distinct differences observed between clusters A and C, D and C, and A and B.

The samples were classified into four distinct clusters with specific chemical profiles. Cluster C represents the control group, consisting of the unused virgin oil, serving as the reference for optimal quality. Cluster B comprises the single sample from the restaurant (sample 8). Due to intense usage conditions, likely involving higher temperatures and prolonged frying cycles, this sample exhibited the highest signs of degradation. It presented a two-fold increase in acidity compared to residential oils and a peroxide value 3.5 times higher than Cluster A and 1.8 times higher than Cluster D.

Finally, the residential waste oils were split into Cluster A (samples 1, 4, 5, 7, 9, 10) and Cluster D (samples 2, 3, 6). While these residential samples did not differ significantly regarding acidity, density, or iodine value, they were segregated based on oxidation levels. Cluster A, representing the majority of samples (60%), presented a lower peroxide average (31.5 ± 8.6 meq/kg), suggesting this is the most common profile for domestic waste. Conversely, Cluster D comprised samples with significantly higher oxidation (61.8 ± 9.8 meq/kg). This indicates that while origin (residential) is a common factor, handling practices vary, resulting in different degradation levels. Therefore, the chemical profile of Cluster A could serve as a baseline parameter for environmental management strategies and public policy development for domestic oil collection.

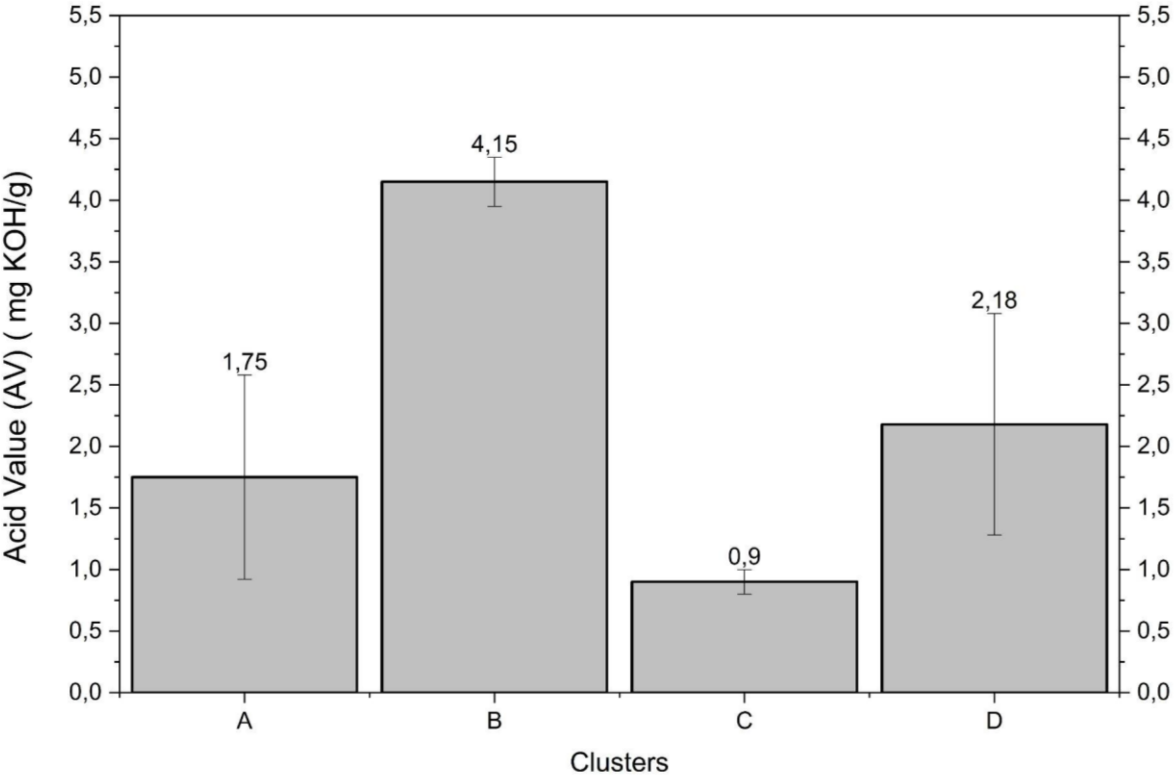

FIGURE 1. COMPARISON OF ACID VALUE (AV) AMONG THE CLUSTERS FORMED BY CLUSTER ANALYSIS. THE BARS REPRESENT THE MEAN ± STANDARD DEVIATION (SD) OF ANALYTICAL TRIPLICATES (N=3), EXPRESSED IN MG KOH/G. CLUSTER COMPOSITION: CLUSTER A (SAMPLES 1, 4, 5, 7, 9, AND 10); CLUSTER B (SAMPLE 8); CLUSTER C (VIRGIN OIL); AND CLUSTER D (SAMPLES 2, 3, AND 6). NOTE: NO STATISTICALLY SIGNIFICANT DIFFERENCES WERE OBSERVED AMONG THE CLUSTERS (ANOVA, P > 0.05).

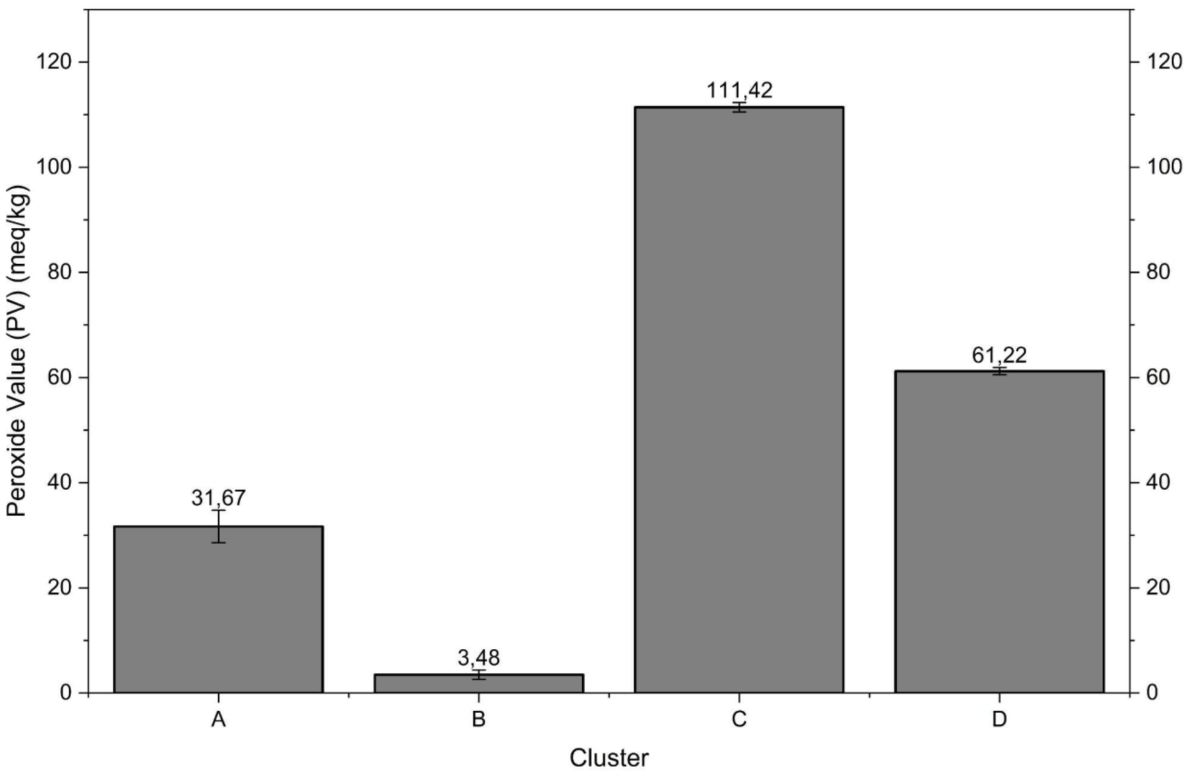

FIGURE 2. COMPARISON OF PEROXIDE VALUE (PV) AMONG THE CLUSTERS FORMED BY CLUSTER ANALYSIS. THE BARS REPRESENT THE MEAN ± STANDARD DEVIATION (SD) OF ANALYTICAL TRIPLICATES (N=3), EXPRESSED IN MILLIEQUIVALENTS OF ACTIVE OXYGEN PER KILOGRAM OF OIL (MEQ O2/KG). CLUSTER COMPOSITION: CLUSTER A (SAMPLES 1, 4, 5, 7, 9, AND 10); CLUSTER B (SAMPLE 8); CLUSTER C (VIRGIN OIL); AND CLUSTER D (SAMPLES 2, 3, AND 6). DIFFERENT LETTERS ABOVE THE BARS (A, B, C, D) INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES (ANOVA FOLLOWED BY TUKEY'S TEST, P < 0.05).

3.3 Waste oil management strategies based on cluster analysis

Considering the characteristics of the analyzed oils and their classification into four clusters, specific management strategies can be proposed, as illustrated in Figure 3. The potential applications for these waste oils were determined based on the concentration of triacylglycerols, free fatty acids, peroxide levels, and the presence of contaminants.

Saponification via alkali treatment represents the simplest application, being largely independent of the physicochemical composition of the samples. However, this process yields a product with low value-added and necessitates the use of caustic and toxic reagents, resulting in soap that is often unattractive to the modern consumer market (ABERA ET AL., 2023). Consequently, this alternative was not considered in the advanced management strategies proposed in this study.

Conversely, free fatty acids, particularly unsaturated ones such as oleic (omega-9), linoleic (omega-6), and linolenic (omega-3) acids, are of significant interest to the food and pharmaceutical industries due to their essential role in cardiovascular health (XU ET AL., 2025). Waste oils exhibiting low peroxide values present potential for the recovery of these fatty acids, as low oxidation levels preserve the integrity of the carbon chains. A sustainable and emerging alternative for this recovery is enzymatic hydrolysis (SANTOS ET AL., 2025). This process operates under mild temperature and pressure conditions, thereby reducing energy costs and minimizing thermal degradation. Chemically, hydrolysis involves the catalytic cleavage of ester bonds in triacylglycerol (TAG) molecules via the addition of water, releasing glycerol and free fatty acids (HU ET AL., 2025). Therefore, oils from Cluster A, which present low peroxide values and lower contaminant content, are identified as ideal candidates for this biotechnological route.

Saturated fatty acids, regardless of chain length, are also highly valued for applications in the chemical and pharmaceutical sectors. These acids serve as raw materials for esterification reactions with alcohols, generating a diverse range of products (ZHANG; ZHANG, 2025). For instance, the esterification of short-chain fatty acids with short-chain alcohols produces volatile esters widely used as aroma compounds (fruit, floral, cheese, or butter notes). Alternatively, long-chain saturated fatty acids, such as palmitates and stearates, can be esterified to produce waxy substances used as bases for creams, shampoos, lotions, and lipsticks (BHATNAGAR; KHURANA, 2024). Consequently, waste oils from Clusters A and D can be fractionated to separate saturated from unsaturated fatty acids, directing them toward these specific industrial applications.

Finally, for biodiesel production, the objective is to obtain esters with high ignition quality (cetane number). These can be produced by the esterification of free fatty acids or the transesterification of acylglycerols with methanol or ethanol. The most common method involves transesterification in the presence of a catalyst (basic, acidic, or enzymatic). For this specific application, peroxide values and the presence of contaminants are less critical compared to food or pharmaceutical standards, provided that proper purification steps are applied (MONTEIRO ET AL., 2022). Therefore, oils included in Clusters B and D are suitable for this purpose. While highly deteriorated oils are unsuitable for sectors requiring high purity, the biodiesel industry represents the highest value-added option for heavily used oils with high oxidation levels, such as the restaurant samples (Cluster B).

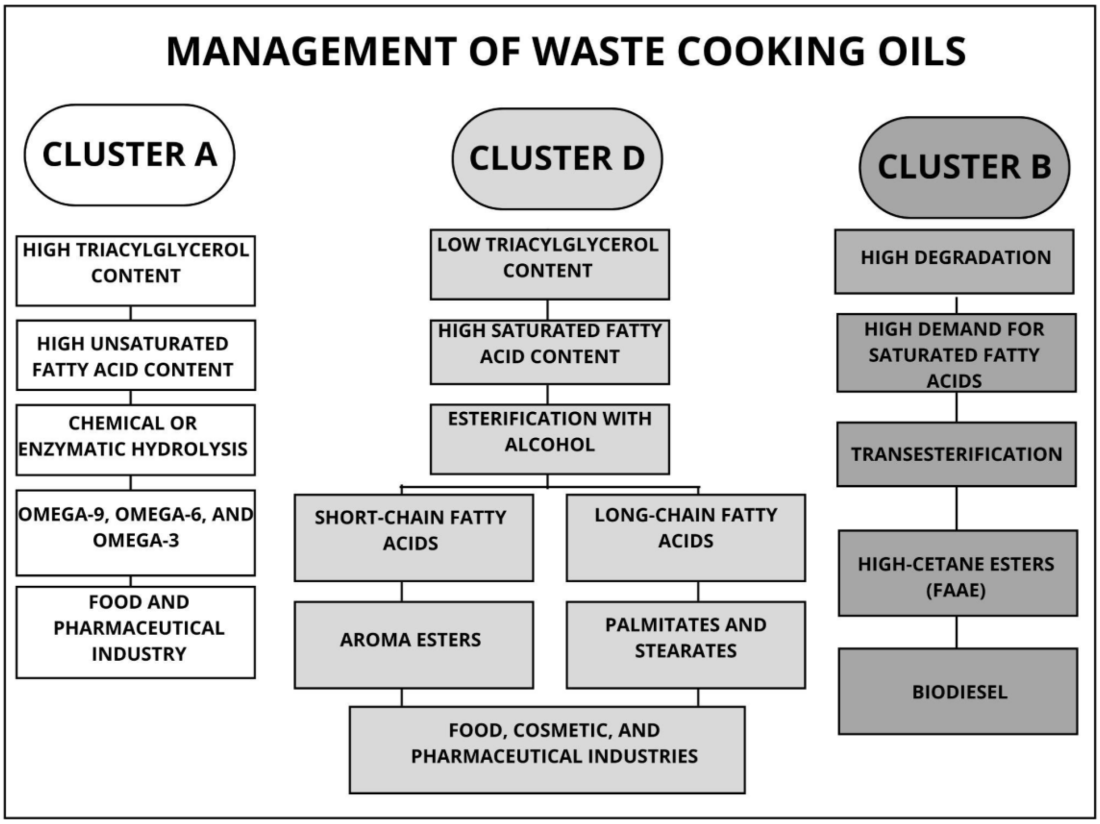

FIGURE 3. STRATEGIC FLOWCHART FOR WASTE OIL MANAGEMENT BASED ON CLUSTER ANALYSIS. THE DIAGRAM ILLUSTRATES THE SEGREGATION OF SAMPLES INTO DIFFERENT VALUE-ADDED CHAINS—BIOTECHNOLOGICAL, CHEMICAL, OR ENERGY SECTORS, ACCORDING TO THEIR PHYSICOCHEMICAL QUALITY AND DEGRADATION LEVELS. CLUSTER COMPOSITION: CLUSTER A (SAMPLES 1, 4, 5, 7, 9, AND 10); CLUSTER D (SAMPLES 2, 3, AND 6); AND CLUSTER B (SAMPLE 8).

4. CONCLUSION

This study demonstrated the significant heterogeneity of waste oils, utilizing Cluster Analysis to segment samples into distinct degradation groups and overcoming the limitations of treating this residue as a uniform material. This approach successfully validated the use of physicochemical profiling to define targeted management strategies.

The applied methodologies are characterized by their low cost and rapid execution, facilitating their adoption as initial screening protocols in collection centers. To further enhance this characterization, future studies should incorporate advanced techniques such as Gas Chromatography (GC) and FTIR, which are essential for validating industrial scalability and refining the proposed valorization strategies.

In conclusion, implementing a selective collection system based on physicochemical profiling proved technically feasible. Proper segregation transforms an environmental liability into a valuable raw material, thereby strengthening the circular economy and enhancing waste management efficiency.

O descarte inadequado de óleo de cozinha residual (OCR) impõe desafios ambientais, exigindo estratégias de reutilização alinhadas à economia circular. Este estudo objetivou realizar a caracterização físico-química de OCR residencial e comercial para propor rotas de gerenciamento baseadas nos níveis de degradação. As determinações (densidade, acidez, peróxido e iodo) foram realizadas em triplicata. Os resultados revelaram alta heterogeneidade e severa degradação, com acidez variando de 1,15 a 5,82 mg KOH/g e peróxidos atingindo 111,92 meq O_2/kg. Notavelmente, a densidade aumentou em relação ao óleo virgem (0,95 g/mL), chegando a 1,17 g/mL. A correlação de Pearson indicou associação significativa entre degradação hidrolítica e oxidativa ($r = 0{,}8349$; $p = 0{,}0014$). A Análise de Cluster (método *Gap Statistic*) categorizou as amostras em quatro grupos. Com base nisso, propuseram-se rotas de valorização: Cluster A (menor degradação) para aplicações biotecnológicas (hidrólise enzimática); Cluster D (intermediária) para produção química de ésteres; e Cluster B (restaurante/alta degradação) para fins energéticos (biodiesel). Tais achados demonstram que o perfil físico-químico viabiliza o direcionamento do OCR para cadeias de valor apropriadas, transformando um poluente ambiental em recurso sustentável.

PALAVRAS-CHAVE: VALORIZAÇÃO DE RESÍDUOS; OXIDAÇÃO LIPÍDICA; TRANSESTERIFICAÇÃO; HIDRÓLISE; QUIMIOMETRIA.

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