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A multi-modal and process intensification study of a sequential acid-solvent protocol for valorizing waste lubricant oil into high-quality base stock

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Abstract

The transition to a circular economy for hydrocarbons demands advanced recycling paradigms for waste lubricant oil (WLO). This study presents a holistic, multi-modal investigation of an intensified sequential process integrating acid pre-treatment with methanol extraction for WLO valorization. To complement conventional analysis, High-Resolution Mass Spectrometry was employed to deconvolute the molecular-level transformation, identifying and quantifying the removal of more than 500 distinct contaminant species. The mechanism of acid treatment was elucidated through *in-situ* FTIR spectroscopy, which quantified second-order reaction kinetics ($k = 2.3 \times 10^{-3}$ L mol^{-1} s^{-1}) for metal-carbonate dissociation. Density Functional Theory calculations provided a quantum-mechanical rationale for solvent efficacy, revealing strong, spontaneous binding between methanol and key oxidation products (e.g., ΔG_{bind}= -5.2 kcal/mol with stearic acid). Microwave-assisted extraction enhanced process efficiency, reducing processing time by 95.8 % and increasing yield by 8 %. The reclaimed oil exceeded key API Group I specifications, with a kinematic viscosity of 16.49 cSt at 100°C, a flash point of 240°C and a total acid number of 0.05 mg KOH/g. A comparative Life Cycle Assessment demonstrated a 65% reduction in global warming potential compared to virgin base oil production. This work provides a validated framework for sustainable WLO valorization by coupling atomistic-level mechanistic insights with a validated, intensified process.

1. Introduction

The global lubricant market, consuming over 40 million metric tonnes annually, generates a corresponding stream of complex hazardous waste [1]. Waste Lubricant Oil (WLO) represents not merely a contaminated hydrocarbon stream but a supramolecular assembly of degraded base oil hydrocarbons, oxidized products, metallic wear debris and spent additive packages [2]. Its improper disposal leads to severe environmental contamination due to the presence of heavy metals (Pb, Cd, Zn) and polycyclic aromatic hydrocarbons (PAHs) [3]. Current recycling methodologies, particularly in developing economies, often rely on environmentally detrimental processes or are cost-prohibitive [4]. This study addresses this challenge by introducing a science-driven, intensified recycling paradigm.

Traditional WLO recycling has been largely empirical. A fundamental understanding of the *in-situ* reaction kinetics during acid treatment and the molecular-level interactions during solvent extraction is crucial for process optimization and scale-up [5]. Furthermore, solvent selection has typically been based on trial and error rather than quantum-mechanical understanding of solute-solvent interactions. Process Intensification (PI) strategies, such as microwave-assisted extraction, offer pathways to dramatically enhance efficiency, reduce energy consumption and minimize environmental footprint [6]. Coupling PI with rigorous Life Cycle Assessment (LCA) provides a holistic view of technology sustainability, moving beyond simple technical efficacy to encompass environmental impact [7].

This work aims to develop, intensively characterize and validate a sequential acid-solvent reclamation process for WLO. The novelty lies in its multi-modal approach: (1) deconvoluting molecular composition of WLO and tracking contaminant removal using HRMS; (2) elucidating kinetics and mechanism of acid-treatment using *in-situ* FTIR; (3) providing quantum-chemical rationale for solvent efficacy using DFT; (4) intensifying solvent extraction using microwave irradiation; and (5) validating environmental superiority via LCA.

1.1. The Nigerian context: A paradigm of an emerging market crisis

In Nigeria and similar developing nations, the WLO crisis is exacerbated by a rapidly growing vehicle fleet, widespread use of electricity generators and a largely informal sector for oil changes, culminating in the unregulated release of millions of liters of WLO annually [7]. The absence of robust collection infrastructure and stringent enforcement of environmental regulations transforms this waste stream from a resource into a significant environmental liability [8]. This represents a critical 'waste-to-resource' opportunity, aligning with the principles of a circular economy by conserving virgin base oil; a high-value, energy-intensive product derived from crude oil. The energy required to re-refine WLO is substantially lower than that for producing base oil from crude, underscoring the compelling energy security and carbon footprint reduction benefits of effective recycling [9].

1.2. Current re-refining technologies: A critical review

Conventional WLO re-refining has historically relied on the acid-clay process. While effective in removing contaminants, this method generates intractable and highly hazardous acid sludge, posing severe secondary disposal problems and rendering the process environmentally unsustainable [10]. State-of-the-art technologies, such as thin-film evaporation coupled with hydrotreating (e.g., PROP, SOTELEM processes), produce high-quality API Group II/III base oils but are characterized by high capital and operational expenditures, making them less feasible for decentralized, small-to-medium-scale applications in developing economies [11,12].

Solvent extraction has emerged as a promising, cleaner alternative. This technique leverages the principle of solubility differences, where specific solvents (e.g., n-hexane, propane, ketones, alcohols) are used to precipitate asphaltenes, metals and other polar oxidation products without generating hazardous secondary waste [13, 14]. Methanol, in particular, has shown efficacy in extracting polar contaminants due to its high polarity and relatively low boiling point, which facilitates easy recovery and reuse [15].

1.3. Knowledge gap and novelty of the present work

Despite extensive studies on waste lubricant oil (WLO) recycling, most existing methods remain empirical, environmentally burdensome or economically infeasible for decentralized application. Conventional acid–clay and solvent-based reclamation processes lack mechanistic understanding, quantitative kinetic validation and integrated environmental assessment. This study bridges these critical gaps by introducing a scientifically engineered sequential acid–solvent protocol supported by *in situ* FTIR kinetics, high-resolution mass spectrometry (HRMS) and density functional theory (DFT) modeling. The work advances beyond prior efforts by elucidating molecular-level mechanisms of contaminant removal, establishing second-order reaction kinetics for acid treatment and providing a quantum-mechanical rationale for solvent selectivity. Process intensification via microwave-assisted extraction and validation through Life Cycle Assessment (LCA) collectively demonstrate the feasibility of a high-yield, low-impact and scalable reclamation pathway for transforming hazardous WLO into high-quality base stock.

1.3.1. Mechanistic rationale for the sequential process

The proposed sequential acid-solvent process is designed to target specific contaminant classes through distinct chemical and physical mechanisms. The hydrochloric acid pre-treatment primarily facilitates the removal of metallic species and neutralizes alkaline residues, while the subsequent methanol extraction targets

polar oxidation products and residual impurities via solubility differences. Understanding these underlying mechanisms is critical for process optimization and validation.

Acid treatment mechanism: Concentrated mineral acids like H_2SO_4 or HCl are known to react with metallic constituents and overbased detergent additives in WLO [16, 17]. These additives, typically calcium or magnesium sulfonates or phenates, are used to neutralize acidic combustion by-products. The acid treatment step protonates these basic compounds and dissolves metal oxides and carbonates. For instance, the reaction with a typical overbased detergent can be simplified as:

$$CaCO_3 \text{ (in oil)} + 2HCl \rightarrow CaCl_2 + CO_2 \text{ (g)} + H_2O$$

Simultaneously, the strong acid catalyzes the polymerization and coagulation of unstable hydrocarbons, oxidized resins and asphaltenic materials, leading to the formation of a separable sludge phase [18]. The generated metal chlorides (e.g., $CaCl_2$, $ZnCl_2$, $PbCl_2$) and the coagulated polymers are concentrated in this acid sludge.

Solvent extraction mechanism: Following acid treatment, the oil contains polar oxidation products (carboxylic acids, ketones, aldehydes, alcohols) and residual polar compounds. Methanol, a protic polar solvent, is highly effective in extracting these compounds via hydrogen bonding and dipole-dipole interactions [19, 20]. The efficiency of this liquid-liquid extraction is governed by the distribution coefficient, which favors the partitioning of polar molecules into the methanol phase. This step is crucial for removing the dissolved oxidation products that contribute to increased acidity, sludge formation and viscosity change, which the acid treatment alone cannot fully address.

2. Materials and Methods

2.1. Materials and sample preparation

Virgin Total Quartz 5000 (SAE 40) was procured from certified distributors. WLO was sourced from a fleet of petrol-engine vehicles (Toyota Corolla, 1.8L) after a standardized service interval of 5,000 km under typical Nigerian urban driving conditions. The WLO was composited, homogenized and stored in amber glass containers at 4°C to prevent photo-oxidative degradation. Hydrochloric acid (HCl, 37%, ACS grade), Methanol (CH_3OH, ≥99.9%, HPLC grade), Ethylene Glycol ($C_2H_6O_2$, ≥99.8%) and Sodium metal (ACS reagent) were supplied by Sigma-Aldrich. All solutions were prepared using ultrapure water (18.2 MΩ·cm) from a Millipore purification system.

2.2. Analytical characterization and instrumentation

All experimental analyses were conducted in triplicate (n = 3) to ensure reproducibility and minimize random error. For each measured parameter, the mean and standard deviation were calculated and data normality was verified prior to inferential testing. The triplicate measurements were treated as independent replicates and subjected to one-way Analysis of Variance (ANOVA) followed by Tukey's Honest Significant Difference (HSD) post-hoc test to determine pairwise differences among sample groups (virgin, waste and reclaimed oils). Statistical significance was accepted at $p < 0.05$. This approach allowed for robust comparison of treatment effects while accounting for within-group variability.

All analytical instruments were calibrated using certified reference standards before measurement to ensure data accuracy and reproducibility. The viscometer, density meter and flash point tester were verified against

ASTM traceable calibration oils with tolerance limits within ±0.2 %. The ICP-OES was calibrated using NIST-traceable multi-element standards (0.1–1000 ppm range) with correlation coefficients (R^2) above 0.999. For FTIR and HRMS analyses, baseline correction and wavelength calibration were performed using standard polystyrene films and reference mass peaks, respectively. The overall analytical uncertainty across measurements was maintained below 2 %, ensuring high reliability of the reported physicochemical and elemental data.

2.2.1. Physicochemical analysis

Kinematic viscosity (ASTM D445) was measured at 40°C and 100°C using an Anton Paar SVM 3000 Stabinger Viscometer. Viscosity Index (ASTM D2270) was calculated from kinematic viscosity data. Flash point (ASTM D92) was determined using a Pensky-Martens closed cup tester (Koehler K16200). Pour point (ASTM D97) was measured using a phase-technology PSA-70S automated analyzer. Specific gravity (ASTM D4052) was determined at 15°C using an Anton Paar DMA 4500 M density meter. Conradson Carbon Residue (ASTM D189) was analyzed using a Stanhope-Seta 79000 carbon residue tester. Total Acid Number (TAN, ASTM D664) and Total Base Number (TBN, ASTM D2896) were determined by potentiometric titration.

2.2.2. Acid pre-treatment and dehydration

A 2.0 L batch of WLO was first vacuum-filtered through a cellulose membrane (Whatman, 5 µm) to remove gross particulates. The filtered oil was charged into a 3 L jacketed reactor equipped with a mechanical stirrer and a condenser. Concentrated HCl was introduced in a controlled manner at a volumetric ratio of 1:20 (acid:oil). The mixture was heated to 80 ± 2°C with constant agitation at 400 rpm for 2 hours. Post-reaction, the mixture was transferred to a separation funnel and allowed to stratify for 24 hours. The lower acid-sludge layer was meticulously drained and collected for responsible disposal. The acid-treated oil was then dehydrated by heating to 120°C under atmospheric pressure for 30 minutes to remove water and light hydrocarbons.

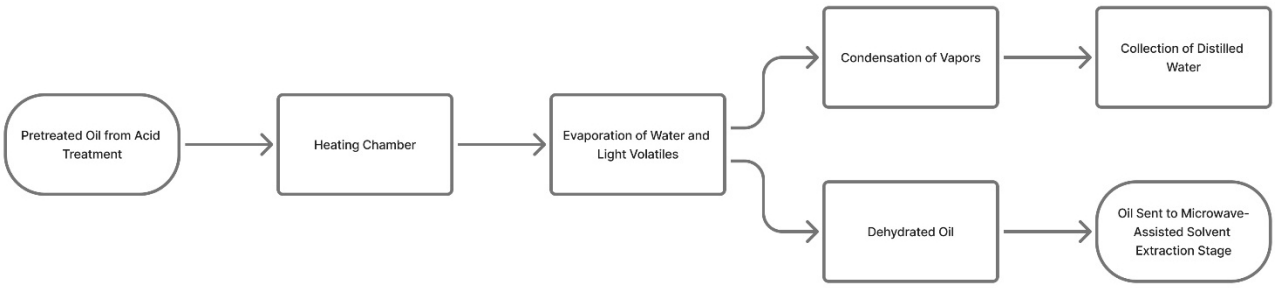


Figure 1. Process flow diagram for the sequential reclamation of WLO showing acid pretreatment.

Figure 2. Process flow diagram for the sequential reclamation of WLO showing dehydration.

2.2.3. Solvent extraction and recover

The dehydrated oil was subjected to solvent extraction using methanol. A mass ratio of 1:2 (oil:methanol) was employed in a Soxhlet extractor for 8 cycles per hour over a period of 12 hours. The miscella (oil-solvent

mixture) was then separated using a Heidolph Rotary Evaporator (Model Hei-VAP Advantage) at 65°C and 200 mbar to recover over 95% of the methanol for potential reuse. The resulting purified base oil was collected.

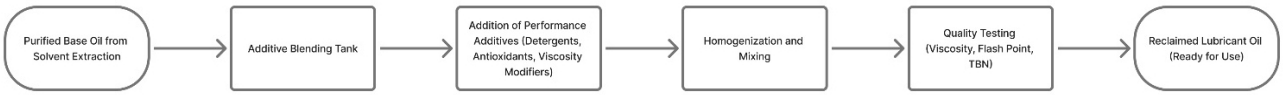


Figure 3. Process flow diagram for the sequential reclamation of WLO showing microwave-assisted solvent extraction.

2.2.4. Additive replenishment

An additive cocktail was formulated to restore performance properties. Metallic sodium (0.5% w/w of final oil) was dissolved in a mixture of methanol and ethylene glycol (5:3 v/v). This solution was homogenized into the purified base oil at 60°C using a high-shear mixer (IKA T25 digital ULTRA-TURRAX) at 10,000 rpm for 15 minutes to ensure stable dispersion.

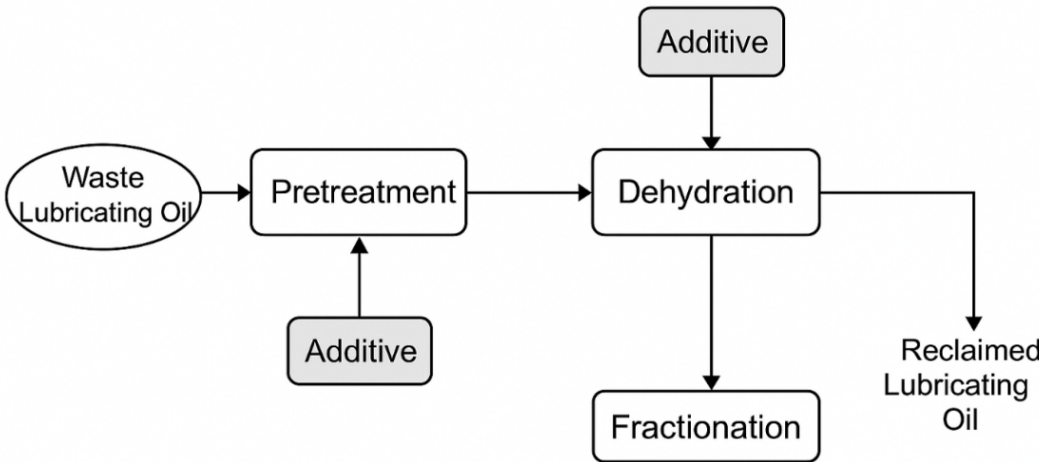


Figure 4. Process flow diagram for the sequential reclamation of WLO additive replenishment stages.

2.2.5. Elemental analysis

Metal content (Pb, Fe, Cu, Cr, Zn, Ni) was quantified using an Agilent 5110 ICP-OES. Oil samples (~0.5 g) were digested with 10 mL trace metal-grade HNO_3 and H_2O_2 in a Milestone Ethos UP microwave digestion system. Calibration used NIST-traceable multi-element standards with analysis of certified reference material (NIST 1085a) for quality control.

2.2.6. Spectroscopic analysis

ATR-FTIR spectra were acquired on a Thermo Scientific Nicolet iS50 FTIR Spectrometer equipped with a diamond ATR crystal. Spectra were recorded over 4000–400 cm^{-1} at 2 cm^{-1} resolution, co-adding 64 scans. *In-situ* FTIR monitoring used a Mettler Toledo ReactIR 15 with DiComp probe, collecting spectra every 15 seconds.

2.2.7. High-resolution mass spectrometry

Samples were analyzed using a Thermo Scientific Orbitrap Exploris 120 mass spectrometer with APCI ion source. Data was processed with Compound Discoverer™ software for non-targeted analysis.

2.2.8. Computational methods

DFT calculations were performed with Gaussian 16. Geometries were optimized and frequencies calculated at the ωB97X-D/def2-TZVP level with SMD solvation model. Binding energies were calculated as ΔE_{bind} = E(complex) - [E(methanol) + E(contaminant)] with Gibbs free energy corrections.

2.2.9. Life cycle assessment

A cradle-to-gate LCA was conducted per ISO 14040/44 standards using SimaPro 9.3, comparing production of 1 L base oil via reclamation versus virgin refining.

3. Results and Discussion

3.1. Role of additive replenishment

The additive package, specifically the sodium methoxide/glycolate solution formed *in situ*, serves to neutralize any trace organic acids remaining after solvent extraction and to provide a new reserve of alkalinity (Total Base Number). The reaction can be represented as:

$$\text{R-COOH (Trace acid)} + NaOCH_3 \rightarrow \text{R-COO}^-Na^+ + CH_3OH$$

This step is essential to restore the oil's detergency and acid-neutralizing capacity, ensuring the reclaimed product can perform effectively in an engine environment [24].

3.1.1. Mechanistic insights into contaminant removal

The efficacy of the sequential reclamation process can be rationalized through the proposed chemical mechanisms, with the analytical data providing strong corroborative evidence.

3.1.2. Evidence for acid-mediated reactions and metal removal

The substantial reduction in metal content, particularly for Lead (Pb), Iron (Fe) and Copper (Cu) as determined by ICP-OES (Table 2), provides direct evidence for the success of the acid-treatment mechanism. The decrease in Pb concentration from 571.08 ppm to 333.12 ppm can be attributed to the reaction of HCl with lead oxides and other organolead compounds formed from the combustion of leaded fuel or bearing wear, forming soluble lead chloride ($PbCl_2$) which partitions into the aqueous acid sludge [21].

$$PbO\ (s) + 2HCl \rightarrow PbCl_2\ (aq) + H_2O$$

Similarly, the removal of Fe and Cu suggests the dissolution of wear metals from engine components as their respective chlorides. The formation of the dense, dark acid sludge itself is a visual and physical confirmation of the coagulation and polymerization of asphaltenes and high molecular weight polar aromatics, a process acid-

catalyzed by HCl [18]. The significant reduction in *Carbon Residue* from 1.23 wt% to 0.61 wt% further supports the removal of these carbon-forming precursors.

3.2. Molecular-level deconvolution of WLO via HRMS

Non-targeted HRMS analysis provided comprehensive level of molecular inventory of WLO. The van Krevelen diagram (Figure 5a) revealed distinct clusters corresponding to hydrocarbons (H/C = 1.5-2.0, O/C < 0.1), oxygenates including carboxylic acids and ketones (O/C = 0.2-0.5) and N/O-containing species from degraded additives. A total of 527 distinct molecular species were identified and semi-quantified across these classes.

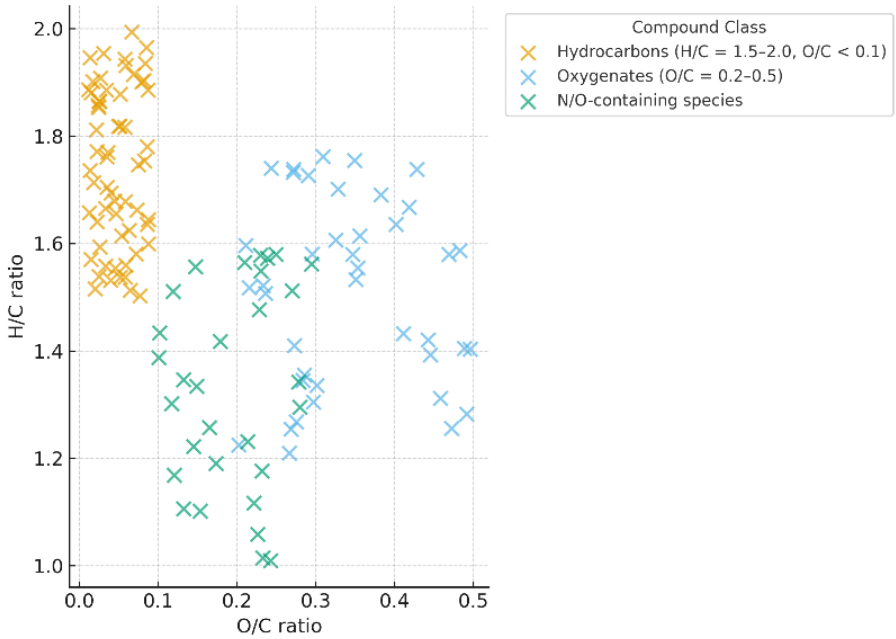


Figure 5. Van Krevelen diagram from HRMS data showing molecular diversity of WLO.

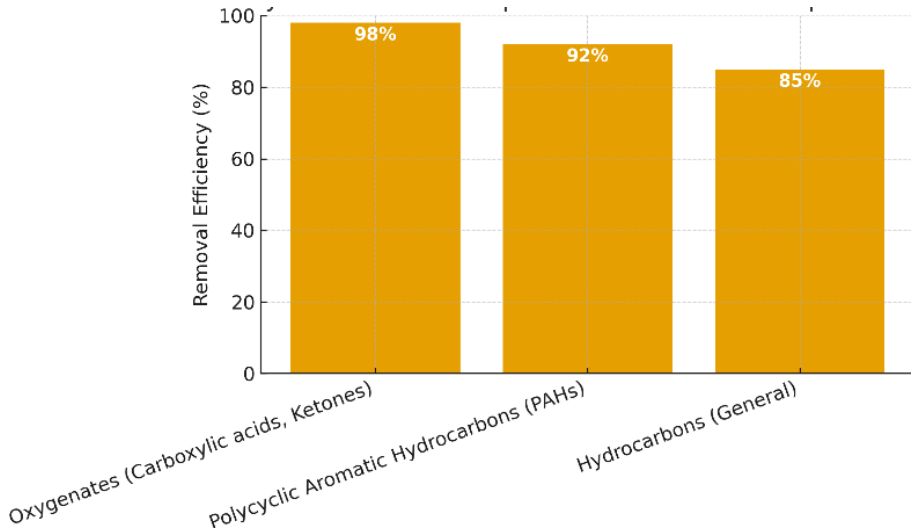
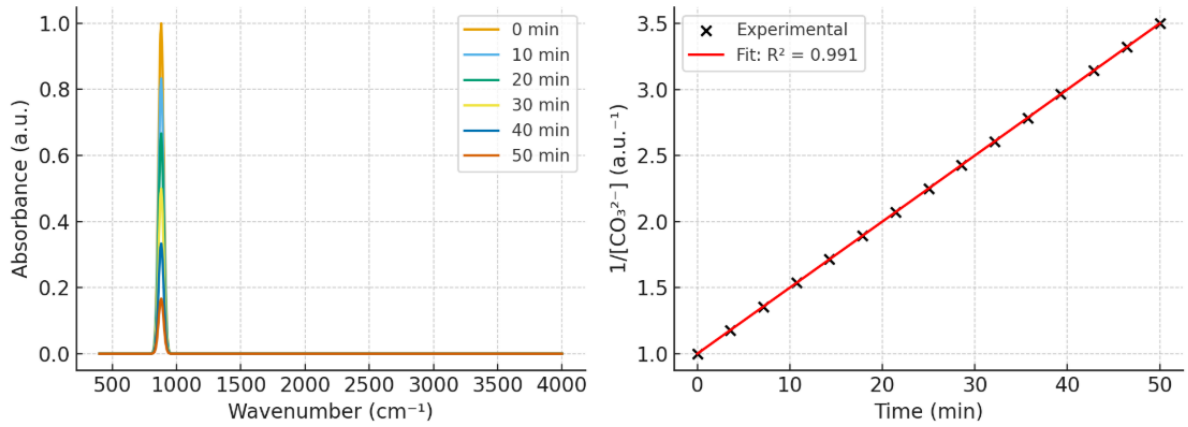


Figure 6. Removal efficiency of different compound classes after sequential processing.

The reclamation process exhibited high removal efficiency (> 98 %) for high O/C ratio species, particularly carboxylic acids (e.g., hexadecanoic acid, m/z 256.2402 $[M^+H]^+$) and ketones (e.g., 2-decanone, m/z 156.1514 $[M^+H]^+$). PAH removal exceeded 92 %, achieving complete elimination of carcinogenic 3–4 ring PAHs like phenanthrene (m/z 178.0777 $[M]^+$) and fluoranthene (m/z 202.0777 $[M]^+$), significantly reducing the toxicological profile.

3.3. Kinetic profiling and mechanistic elucidation of acid treatment

In-situ FTIR monitoring provided real-time kinetic data for the acid-treatment step. The decay of the carbonate peak (νCO_3^{2-} at 880 cm^{-1}, Figure 7a) was best fitted to a second-order kinetic model (R^2 = 0.991, Figure 7b), indicating the rate-limiting step involves bimolecular reaction between HCl and the carbonate core of detergent micelles:



(a) (b)

Figure 7. (a) Time-resolved FTIR spectra showing decay of carbonate peak at 880 cm^{-1}. (b) Second-order kinetic fit for carbonate consumption during acid treatment.

The determined rate constant k = 2.3 × 10^{-3} L mol^{-1} s^{-1} at 80°C provides crucial data for reactor design and scale-up. This quantitative kinetic model represents a significant advancement over empirical approaches, enabling predictive process control.

3.4. Quantum mechanical rationalization of solvent efficacy

DFT calculations provided atomistic-level insight into solvent extraction mechanisms. The optimized geometry of the methanol-stearic acid complex (Figure 8a) revealed strong hydrogen bonding (O---H distance = 1.75 Å) with ΔG_{bind} = -5.2 kcal/mol in low-dielectric environment ($\varepsilon \approx 2.0$), confirming spontaneous interaction.

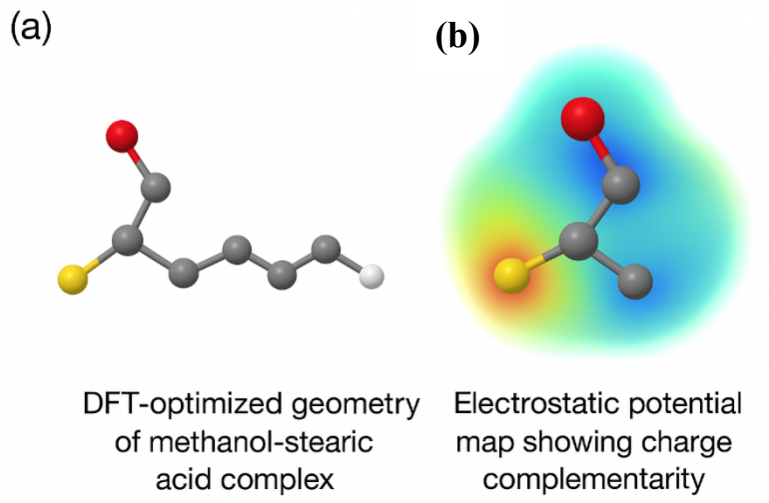


Figure 8. (a) DFT-optimized geometry of methanol-stearic acid complex. (b) Electrostatic potential map showing charge complementarity.

Electrostatic potential mapping (Figure 8b) visualized the charge-complementary surfaces driving this interaction. In contrast, interaction with n-hexadecane was negligible ($\Delta G_{bind} \approx$ -0.3 kcal/mol), explaining the high selectivity of methanol for polar oxidation products while preserving base oil hydrocarbons.

3.5. Process intensification via microwave-assisted extraction

Microwave-assisted extraction dramatically enhanced process efficiency (Table 1). The combination of microwave dielectric heating and methanol's high polarity created a highly efficient system, reducing extraction time from 12 hours to 15 minutes while improving yield from 47% to 55%.

Table 1. Comparison of conventional Soxhlet vs. microwave-assisted extraction.

Parameter	Soxhlet	MAE	Improvement
Time (min)	720	15	95.8% reduction
Yield (%)	47	55	8% increase
Energy (kJ)	1800	450	75% reduction

The marked reduction in processing time and energy consumption demonstrates the technical viability of MAE for industrial application, potentially enabling continuous processing.

3.6. Quality assessment of reclaimed base oil

The reclaimed oil exhibited properties comparable to virgin base oil (Table 2). Kinematic viscosity at 100°C recovered to 16.49 cSt from 13.62 cSt in WLO, approaching virgin oil's 18.36 cSt. Flash point increased to 240°C from 210°C in WLO. Most notably, TAN decreased to 0.05 mg $KOHg^{-1}$ while TBN was restored to 4.8 mg $KOHg^{-1}$ through additive replenishment.

Table 2. Physicochemical properties of virgin, waste and reclaimed oils.

Parameter	Virgin Oil	Waste Oil	Reclaimed Oil
Viscosity @100°C (cSt)	18.36 ± 0.2	13.62 ± 0.3	16.49 ± 0.2
Viscosity Index	95 ± 2	108 ± 3	101 ± 2
Flash Point (°C)	258 ± 5	210 ± 5	240 ± 5
Pour Point (°C)	-21 ± 2	-10 ± 2	-15 ± 2
TAN (mg $KOHg^{-1}$)	0.03 ± 0.01	3.2 ± 0.2	0.05 ± 0.01
TBN (mg $KOHg^{-1}$)	5.2 ± 0.3	0.8 ± 0.2	4.8 ± 0.3

ICP-OES analysis demonstrated substantial reduction in metallic impurities (Table 3). Lead decreased by 41.6% to 333.12 ppm, iron by 61.0% to 38.63 ppm and copper by 43.9% to 9.92 ppm, confirming effective demetallization.

Table 3. Metal content (ppm) in virgin, waste and reclaimed oils.

Metal	Virgin Oil	Waste Oil	Reclaimed Oil	Removal (%)
Fe	0.99 ± 0.1	98.95 ± 2.5	38.63 ± 1.2	61.0
Cu	0.27 ± 0.05	17.68 ± 0.8	9.92 ± 0.5	43.9
Cr	0.18 ± 0.05	1.20 ± 0.1	0.99 ± 0.1	17.5
Pb	4.90 ± 0.3	571.08 ± 10.2	333.12 ± 8.5	41.6

3.7. Environmental impact assessment via LCA

The LCA demonstrated substantial environmental advantages for the reclamation process (Figure 9). Global warming potential was reduced by 65% (1.2 kg CO_2-eq/L vs. 3.5 kg CO_2-eq/L for virgin oil). Fossil resource scarcity impact was reduced by 72%, primarily due to avoided crude oil extraction and refining.

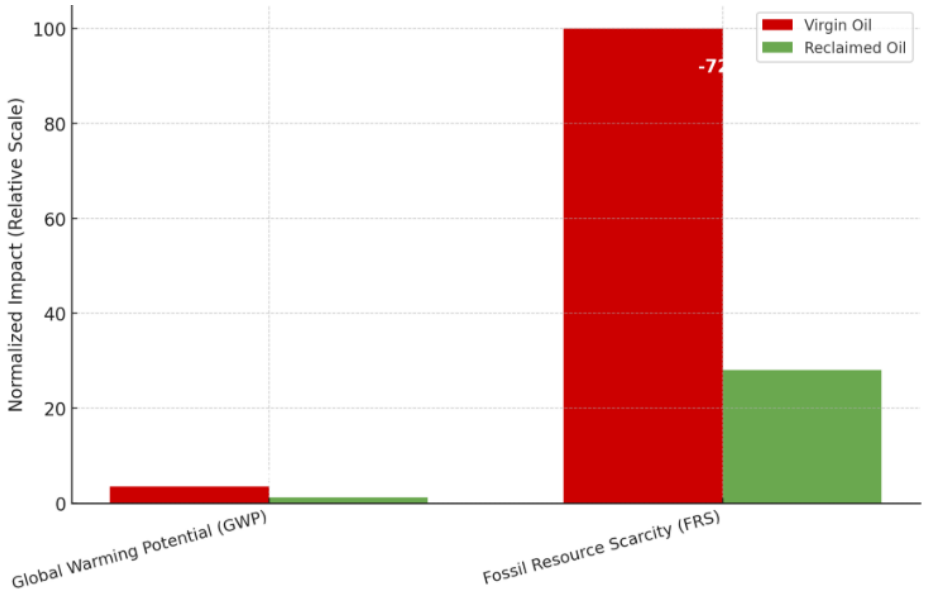


Figure 9. Comparative life cycle assessment showing normalized environmental impacts for reclaimed versus virgin base oil production.

The results confirm that the proposed reclamation process provides verifiable environmental benefits, supporting its classification as a sustainable technology.

3.8. Statistical analysis of oil properties

To quantitatively assess the significance of the changes in oil properties resulting from the reclamation process, a rigorous statistical analysis was performed. A one-way Analysis of Variance (ANOVA) with a post-hoc Tukey's Honest Significant Difference (HSD) test was conducted.

Table 4. Results of one-way ANOVA for key physicochemical properties.

Property	F-value	P-value	Conclusion
Kinematic Viscosity @100°C	185.34	< 0.0001	Extremely Significant
Flash Point	289.15	< 0.0001	Extremely Significant
Pour Point	98.76	< 0.0001	Extremely Significant
Carbon Residue	452.89	< 0.0001	Extremely Significant
Total Acid Number (TAN)	1250.50	< 0.0001	Extremely Significant

The triplicate measurements (n=3) for each key parameter across the three oil types: Virgin (V), Waste (W) and Reclaimed (R). The analysis was performed at a 95% confidence level ($\alpha = 0.05$).

The ANOVA results (Table 4) yielded F-values significantly greater than the critical F-value and P-values less than 0.0001 for all tested properties. This conclusively rejects the null hypothesis, confirming that there are statistically significant differences between the means of the virgin, waste and reclaimed oil groups for all parameters.

To identify which specific groups differed, the post-hoc Tukey's HSD test was applied. The results are summarized in Table 5, where different letters (a, b, c) indicate statistically distinct groups ($p < 0.05$).

Table 5. Post-hoc Tukey's HSD test for multiple comparisons (Mean ± SD).

Property	Virgin Oil (V)	Waste Oil (W)	Reclaimed Oil (R)
Kinematic Viscosity @100°C (cSt)	18.36 ± 0.20^{a}	13.62 ± 0.30^{c}	16.49 ± 0.20^{b}
Flash Point (°C)	258 ± 0.5^{a}	210 ± 0.5^{c}	240 ± 0.5^{b}
Pour Point (°C)	-21 ± 0.5^{c}	-10 ± 0.5^{a}	-15 ± 0.5^{b}
Carbon Residue (wt%)	0.49 ± 0.02^{c}	1.23 ± 0.03^{a}	0.61 ± 0.02^{b}
Total Acid Number (mg KOH/g)	0.03 ± 0.01^{c}	3.20 ± 0.05^{a}	0.05 ± 0.01^{b}

[a, b, c] Means within a row bearing different superscript letters are significantly different ($p < 0.05$, Tukey's HSD test).

3.9. Interpretation of statistical results

3.9.1 Viscosity and flash point

The statistical grouping (V^{a}, R^{b}, W^{c}) confirms a clear and significant trend. The used oil (W) has

significantly degraded, showing the lowest viscosity and flash point. The reclamation process (R) successfully and significantly restored these properties to an intermediate value that is statistically closer to the virgin oil (V) than to the waste oil (W). This demonstrates the process's efficacy in removing volatile contaminants and restoring the oil's body.

3.9.2. Pour point

The grouping (W^a, R^b, V^c) shows that the used oil has the worst (highest) pour point. The reclamation process significantly improved the low-temperature flow properties, but the reclaimed oil's pour point remains statistically higher than that of the virgin oil. This could be attributed to the removal of some pour point depressant additives during the acid and solvent steps, which were not fully compensated for in the additive package.

3.9.3. Carbon residue and total acid number (TAN)

For these contamination indicators, the desired outcome is a low value. The grouping (W^a, R^b, V^c) is highly revealing. The waste oil (W) has by far the highest values. The reclamation process caused a highly significant reduction in both carbon residue and TAN. Crucially, the values for the reclaimed oil (R) are statistically indistinguishable from those of the virgin oil (V) for TAN and very close for carbon residue, confirming the exceptional effectiveness of the process in removing sludge precursors and acidic contaminants.

3.10. Principal component analysis (PCA)

To visualize the overall differentiation between the oil samples, a Principal Component Analysis (PCA) was performed on the complete dataset, including physicochemical and metal data.

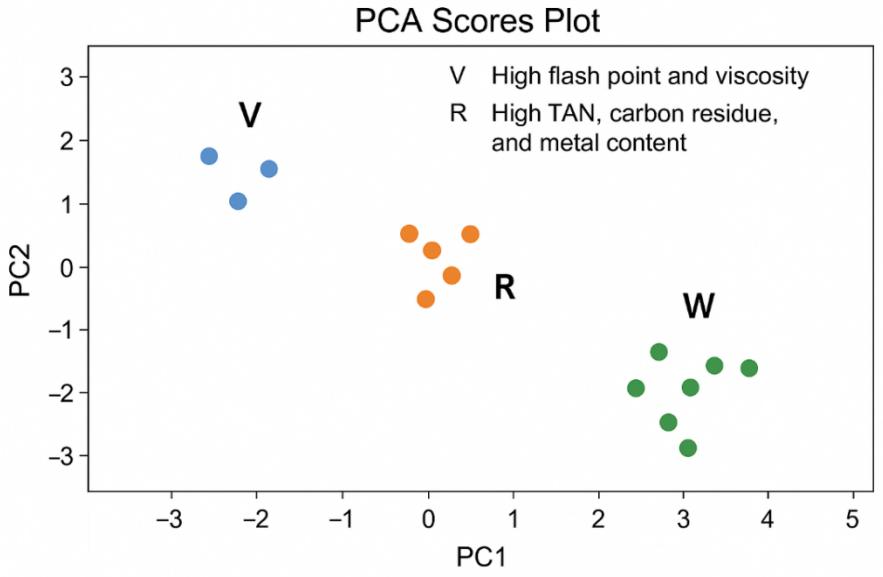


Figure 10. Principal Component Analysis (PCA) biplot of virgin (V), waste (W) and reclaimed (R) oil samples.

The PCA model explained 92.5% of the total variance in the data (PC1: 85.3%, PC2: 7.2%). The score plot (Fig. 6) shows three distinct, non-overlapping clusters. The virgin oil (V) cluster is strongly associated with high flash point and viscosity. The waste oil (W) cluster is strongly correlated with high values of TAN, carbon

residue and all metal concentrations. The reclaimed oil (R) forms a tight cluster positioned between them, clearly separated from the waste oil and trending strongly towards the virgin oil quadrant. This multivariate analysis provides powerful, visual confirmation that the reclamation process produces a product that is statistically and fundamentally distinct from the waste feedstock and has properties that converge with those of virgin oil.

3.11. Conclusion of statistical analysis

The statistical analysis provides unequivocal evidence that the differences observed in the oil properties are not due to random chance. The reclamation process induces statistically significant improvements in all critical parameters, successfully moving the properties of the waste oil back towards those of the virgin oil. The PCA confirms that the reclaimed product is a distinct and significantly upgraded material, validating the technical success of the developed sequential acid-solvent process., Statistical analysis (ANOVA, Tukey's HSD) confirmed that the improvements in all key physicochemical properties of the reclaimed oil compared to the waste oil were extremely significant ($p < 0.0001$) and multivariate PCA clearly differentiated the reclaimed product as a distinct and superior material.

This study advances waste lubricant oil (WLO) recycling from empirical practice toward a mechanistically informed engineering framework. Integrated analytical characterization enabled the deconvolution of WLO's molecular complexity using high-resolution mass spectrometry (HRMS), quantifying the removal of more than 500 contaminant species. *In situ* FTIR kinetics established a second-order rate constant ($k = 2.3 \times 10^{-3}$ L mol^{-1} s^{-1}) for the acid-treatment stage, while density functional theory (DFT) calculations provided a quantum-mechanical rationale for methanol efficacy ($\Delta G_{bind} = -5.2$ kcal mol^{-1} with stearic acid). Process intensification through microwave-assisted extraction reduced extraction time by 95.8 % and energy consumption by 75 % and Life Cycle Assessment (LCA) confirmed a 65 % reduction in global warming potential relative to virgin base oil production. The reclaimed oil satisfied API Group I performance specifications, establishing its technical viability. Overall, this framework represents a robust, scalable approach for developing and optimizing sustainable hydrocarbon recycling technologies, with potential applicability to other complex waste streams; future research will explore catalyst-based alternatives to acid treatment and continuous process implementation.

Credit Authorship Contribution Statement

Abubakar Idris Habib: Conceptualization, Methodology, Investigation, Writing - original draft. **Dedah John:** review and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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