clean technologies

Review

Biopolymers, Bioplasticizers and Biolubricants from Waste Cooking Oil: A Systematic Review

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Abstract

Waste cooking oils (WCO) are large-scale residual streams from domestic and industrial food processing. Their improper disposal poses severe environmental risks, yet their integration into the oleochemical sector offers a strategic opportunity for the green transition by substituting fossil-based feedstocks. This systematic review provides a comprehensive assessment of WCO valorization as a sustainable precursor for high-value products, specifically biopolymers, bioplasticizers, and biolubricants. The study followed the PRISMA 2020 guidelines, searching PubMed, Scopus, and MDPI databases (up to September 2025). The search strategy utilized combinations of keywords present in the title. Inclusion criteria focused on peer-reviewed chemical and biotechnological conversion pathways published in English within the last decade. Studies addressing biofuel production, patents, and review were excluded. Screening, data extraction, and qualitative risk of bias assessment, centered on experimental reproducibility and reporting transparency, were performed independently by multiple reviewers. From an initial pool of 2637 records, 87 studies met the eligibility criteria. The analysis reveals that polyhydroxyalkanoates (PHAs) represent the most extensively researched pathway, followed by WCO-derived epoxides and innovative biolubricant formulations. While several studies report high conversion yields under optimized conditions, the transition from bench-scale to industrial implementation remains hindered by the heterogeneous composition of WCO and a lack of standardized pre-treatment protocols. WCO valorization shows transformative potential for the circular economy, offering a dual benefit of waste mitigation and sustainable material synthesis. However, future research must address scalability challenges and feedstock variability. This review identifies emerging trends and provides a roadmap for the industrial adoption of WCO-based processes in the framework of clean technologies.

Keywords: waste cooking oil; waste management; PRISMA methodology; circular economy; biorefinery; value-added products

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1. Introduction

1.1. Circular Economy and Environmental Relevance of Waste Cooking Oil

The concept of the circular economy (CE) has spread in public opinion and among policymakers as a viable strategy to address global challenges, such as biodiversity loss, climate change, depletion of biomass, inorganic raw material (including metals, minerals and fossil fuels) and limitless waste production [1]. Waste management has also been pointed out by European and international institutions such as the United Nations (UN). The European Green Deal [2] explicitly promotes the proper management of several supply chains, emphasizing the need "to design longer lasting products that can be repaired, recycled and re-used". At the same time, the UN Sustainable Development Goals, particularly Goal 12 "Ensure sustainable consumption and production patterns" highlight target 12.5 with the following achievement: "By 2030, substantially reduce waste generation through prevention, reduction, recycling and reuse" [3]. CE aims to replace the classic linear economy, responsible for the irrational use of natural resources and supply chain management, with a new economic model inspired by the "zero waste concept", in which waste streams are considered as a potential new raw material [4]. This framework has been conceived on three principles: avoid or reduce waste and the resulting pollution, extend the duration of use of raw materials, intermediates and final products, and promote the regeneration of the initial environmental conditions [5]. Finally, as reported by Sala et al. [6], waste management issues were addressed extensively using the approach called Life Cycle Thinking (LCT) in order to generate policies and communications in the EU. LCT aims at an increasing integration of sustainability in policy-making, emphasizing the need for a holistic view that focuses on the relationships between products, sectors and projects. This approach aims to minimize negative impacts on different environmental impact categories, at the geographical level and within product life cycle phases. The World Health Organisation claims that one litre of WCO contaminates one thousand litres of water, producing pollution of water and soil, harming aquatic life, plants, and human health in addition to raising the cost of wastewater treatment [7]. Moreover, fat, oil and grease accumulation in sewer systems is an increasing global issue, causing blockages ("fatbergs"), sewer overflows, flooding, and environmental contamination. Despite these impacts, there is no standardized international management approach, although some successful programs exist (e.g., Dublin and Scandinavian countries). Current strategies mainly focus on preventing oil entry into sewers through awareness campaigns, while its valorization remains largely underexploited, highlighting the need for integrated and sustainable management across its entire lifecycle [8].

CE principles promote the recovery and transformation of such hazardous residues to mitigate their environmental and socio-economic impacts [9].

In this regard, cascading biorefinery approaches can be applied to high-value compound recovery, recycling, and production in a circular strategy promoting sustainability, long-term resilience, and job creation, businesses, and technological advancements [10].

1.2. Waste Cooking Oil: Origin, Composition, and Valorization Potential

The recovery and valorization of WCOs have emerged as a strategic industrial practice aligned with the principles of circular economy, waste minimization, and sustainable resource management. Generated as by-products of domestic, commercial, and industrial food-processing activities, WCOs represent one of the most abundant lipid-based residues worldwide and an increasingly important renewable feedstock for bio-based industries [11].

In terms of chemical composition, waste cooking oil is an extremely heterogeneous substrate whose characteristics depend on the origin of the starting oil or fat, the cooking process, and the extent of thermal degradation [12]. WCO is generally composed of different

vegetable oils such as palm, soybean, sunflower, rapeseed, cottonseed, olive, and palm kernel oils [13]. Therefore, the physicochemical properties and fatty acid profile of WCO can vary considerably among different sources. Chemically, oils and fats are mainly composed of triglycerides, consisting of three fatty acid chains esterified to a glycerol backbone. Fatty acids may be classified as saturated fatty acids (SFAs), monounsaturated fatty acids (MUFAs), or polyunsaturated fatty acids (PUFAs), depending on the presence and number of carbon–carbon double bonds [13]. Typically, the fatty acids present in vegetable oils contain carbon chain lengths ranging from C12 to C20. Saturated fatty acids, such as lauric, myristic, palmitic, stearic, and arachidic acids, generally exhibit higher oxidative stability and are solid at room temperature. In contrast, unsaturated fatty acids are liquid at room temperature and display higher chemical reactivity due to the presence of double bonds. Among unsaturated fatty acids, oleic acid (C18:1) is one of the most abundant fatty acids in edible oils, while palmitoleic and myristoleic acids are also commonly detected. Polyunsaturated fatty acids mainly include linoleic acid (C18:2) and linolenic acid (C18:3), which are particularly susceptible to oxidative and thermal degradation during frying processes. The fatty acid composition differs significantly depending on the vegetable oil source. Sunflower oil typically contains 14–43% oleic acid, 45–74% linoleic acid, 5–7% palmitic acid, and 2–6% stearic acid. Soybean oil is generally composed of 17–30% oleic acid, 48–59% linoleic acid, 4–11% linolenic acid, 8–13% palmitic acid, and 2–5% stearic acid. In contrast, palm oil is characterized by a higher proportion of saturated fatty acids, containing approximately 36–44% oleic acid, 9–12% linoleic acid, 39–47% palmitic acid, and 3–6% stearic acid [14].

During cooking at approximately 200 °C, the oil undergoes a series of chemical transformations, including oxidation, hydrolysis, and polymerization, which significantly modify its composition. The physicochemical characteristics of WCO are largely influenced by the origin of the oil, cooking methods (e.g., degree of reuse, operating conditions, and local dietary habits), and waste management practices, including storage time and conditions [15]. Substantial compositional changes occur during prolonged use or when multiple food types are processed simultaneously. In addition to the leaching of compounds from cooked foods (e.g., moisture, carbohydrates, proteins, and lipids), the composition of WCO further evolves during frying due to thermal degradation reactions [16]. These transformations affect the oil's physicochemical properties, such as colour, viscosity, and density, and lead to the formation of toxic by-products, making the oil unsuitable for further consumption. WCO is particularly suitable for the production of biopolymers, bioplasticizers, and biolubricants due to its molecular architecture. Chemically, WCO consists predominantly of triacylglycerols (TAGs), which contain ester functional groups readily accessible for transesterification, hydrolysis, and polymerization reactions fatty acids (FA), triglycerides (TG), Maillard reaction products, and suspended food residues. In addition, the fatty acid chains typically exhibit varying degrees of unsaturation (C=C double bonds), which serve as reactive sites for epoxidation, oxidative cleavage, and radical polymerization. These structural features enable a cascade biorefinery approach in which a single feedstock can be selectively converted into multiple classes of value-added products (Figure 1). For example, epoxidized WCO derivatives are widely used as bioplasticizers, while transesterified or polymerized fatty acid derivatives form the basis of biolubricants and bio-based polyesters.

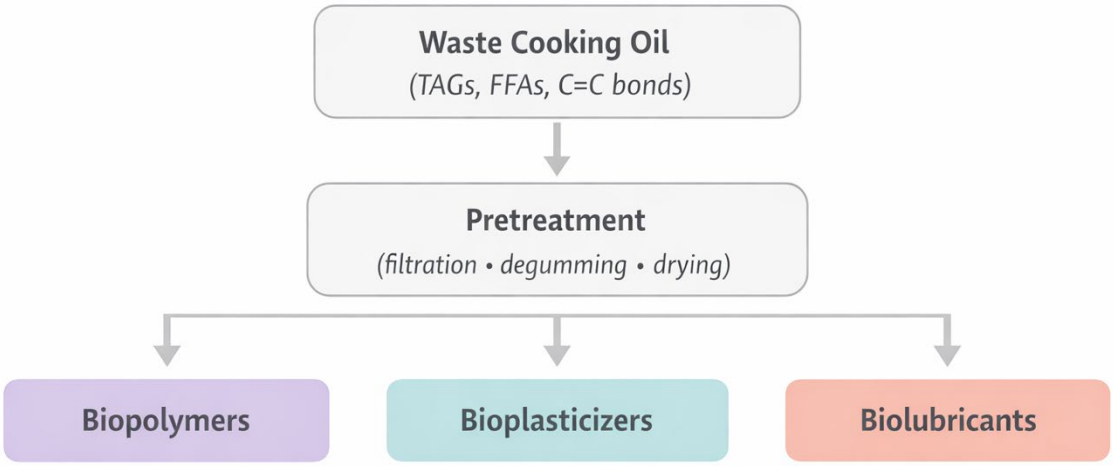

Figure 1. Schematic of the cascade biorefinery concept applied to waste cooking oil (WCO). The intrinsic chemical features of WCO, namely ester groups and unsaturated C=C bonds, enable its conversion into three main categories of value-added products: biopolymers (lavender), bioplasticizers (aqua), and biolubricants (salmon). Pretreatment steps are shown in neutral grey.

1.3. Current Management Strategies, Challenges, and Scope of This Review

The disposal of such contaminated oil as municipal waste has a detrimental environmental impact. The global annual production of WCOs is estimated at approximately 190 million metric tons [17]. The United States and China are the leading producers, accounting for approximately 55% and 25% of the total production considered, respectively. Together, these two countries contribute roughly 80% of the overall annual global production. They are followed by India (5%), Europe (4%), and other countries, which collectively account for the remaining share [18]. The main challenges in WCO management relate to its collection, disposal, and valorization [15].

Global regulatory frameworks governing WCOs' collection exhibit substantial heterogeneity between EU and non-EU countries. In fact, a more harmonized waste classification and requirements are present in EU [19], while more fragmented directives are still creating challenges for the collection of this waste in other countries. In Asian countries, different approaches are carried out. For example, China has a regulatory model for the collection of used cooking oils for the safety and control of foods, following the use of WCO for biofuels and other applications [20]. On the other hand, South Korea has a very developed WCO collection system through licensed operators [21]. Moreover, in EU, recent policies, including the implementation of RED III and stricter import controls, are shifting the sector toward enhanced chain-of-custody verification and sustainability certification [22]. These trends indicate a transition from conventional waste management practices to a highly regulated biofuel feedstock market, where traceability and compliance are critical determinants of scalability and market access [23].

Improper disposal, particularly discharge into sewer systems, poses serious risks to human health, the environment, and aquatic ecosystems.

To ensure its sustainable utilization, comprehensive pretreatment and refining processes are required before WCO can be used as an industrial feedstock (Figure 2).

Figure 2. Role of WCO in a circular bioeconomy perspective.

The choice of pretreatment strategy depends on both the physicochemical profile of the oil and its intended application, either as a drop-in ingredient (e.g., in asphalt, rubber, or lubricants) or as a feedstock for thermal, chemical, or biochemical conversion processes. The market for Waste Cooking Oils (WCO) has been consolidated around direct combustion or first-generation biodiesel production through transesterification [24,25]. However, recent years have seen a significant industrial shift toward the production of Hydrotreated Vegetable Oil (HVO) and Sustainable Aviation Fuel (SAF) [26,27], which currently account for over 90% of the energetic valorization of WCO. While the energy sector remains the dominant outlet, the very latest research trends are moving toward integrated biorefinery models. In these frameworks, WCO are employed as versatile feedstocks for the biotechnological synthesis of high-value bioproducts, representing a strategic frontier that, although still primarily at the R&D stage, promises to maximize the economic and environmental value of this waste stream.

One of the major challenges associated with biotechnological conversion involves limitations in conversion efficiency, product yield, process productivity, and the downstream processing phase. Furthermore, process standardization remains a major challenge owing to the inherent heterogeneity of WCO feedstocks. Their chemical composition is strongly influenced by factors such as the source of the oil, processing conditions, degree of reuse, and presence of impurities, which together hinder the pretreatment process and standardization of the methods. Despite the extensive literature on WCO-derived biodiesel, a consolidated and critical analysis of non-fuel biotechnological valorization pathways remains lacking.

Given this context, a systematic review following PRISMA guidelines was conducted to provide a comprehensive and critical assessment of current research on the transformation of WCO into value-added products such as biopolymers, bioplasticizers, and biolubricants, excluding biofuel production. The objective is to consolidate existing knowledge, identify technological gaps, and outline future research directions that may facilitate industrial implementation in alignment with contemporary waste management and circular economy policies.

2. PRISMA Methodology

This systematic review was conducted in accordance with the PRISMA 2020 guidelines [28] (Supplementary Materials).

2.1. Information Sources and Search Strategy

A comprehensive literature search was performed between 1 and 30 September 2025 in the PubMed, Scopus and MDPI databases to identify relevant studies published. The search was limited to articles published within the last 10 years.

The search strategy was developed using predefined keywords related to waste cooking oil (WCO) and its valorization into value-added products. The following search strings were applied to titles and abstracts:

- PubMed: (“waste cooking oil” OR “used cooking oil” OR WCO) AND (“biopolymer” OR “bioplasticizer” OR “biolubricant”)
- Scopus: TITLE-ABS (“waste cooking oil” OR “used cooking oil” OR WCO) AND (“biopolymer” OR “bioplasticizer” OR “biolubricant”)
- MDPI: (“waste cooking oil” OR “used cooking oil” OR WCO) AND (“biopolymer” OR “bioplasticizer” OR “biolubricant”)

2.2. Eligibility Criteria

Studies that met the following criteria were included:

- Peer-reviewed articles published in English;
- Studies reporting experimental data on the conversion of WCO into biopolymers, bioplasticizers, or biolubricants;
- Studies providing quantitative or qualitative information on process performance (e.g., yields, conversion efficiency, catalyst).

Studies that met the following criteria were excluded:

- Focused exclusively on biofuel production;
- Reviews, conference abstracts, symposium proceedings, or patents;
- Lacked analytical or experimental data relevant to the scope of the review.

The restriction to English-language publications may introduce language bias.

2.3. Study Selection Process

All retrieved records were imported into Mendeley reference management software (v1.19.8), and duplicates were removed.

Four reviewers independently performed the initial screening based on titles and abstracts. Subsequently, two reviewers independently assessed the full-text articles for eligibility. Any discrepancies were resolved through discussion or by consultation with a third reviewer.

The study selection process is summarized in a PRISMA flow diagram (Figure 3).

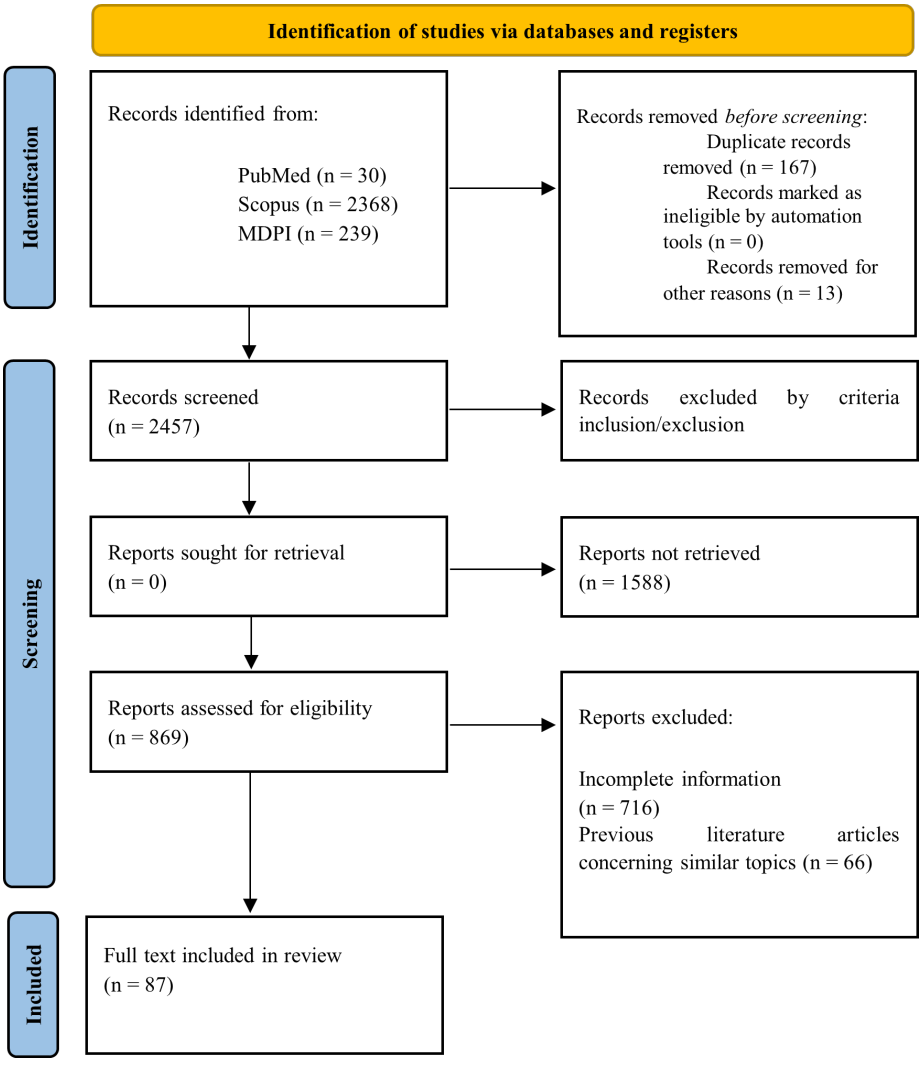

Figure 3. Flowchart for the search and selection of studies considered in the review.

2.4. Data Collection Process and Data Items

Data extraction was performed independently by two reviewers using a standardized data collection framework. The primary outcome sought was the successful chemical or biotechnological conversion of WCO into value-added products. We specifically targeted and categorized outcomes into three main domains: biopolymers, bioplasticizers, and biolubricants. For each included study, we sought all results compatible with these domains, including the chemical characterization of the end-product. Yield values are reported as described in the original studies and may refer to different metrics. Where possible, yields are specified explicitly to avoid ambiguity.

Other variables for which data were sought included: study characteristics (country of origin), process parameters (feedstock type, pretreatment methods, catalyst type, and target compound), and qualitative indicators (main application, process feasibility, and scalability). In cases of missing or unclear information, no assumptions were made unless the data could be unequivocally inferred from the context; otherwise, the data were marked as 'not reported'.

2.5. Risk of Bias Assessment

Due to the heterogeneity of study designs and reported outcomes, a formal risk-of-bias assessment using standardized tools was not feasible. However, the methodological quality of the included studies was qualitatively evaluated based on completeness of experimental data, reproducibility of the methodology, and transparency of reporting.

2.6. Data Synthesis

A meta-analysis was not performed due to substantial heterogeneity in methodologies, outcome measures, and reporting units across the included studies. Therefore, a structured narrative synthesis was adopted to summarize and compare the findings, with studies grouped according to application areas (biopolymers, bioplasticizers, and biolubricants). The primary effect measures presented include product yield expressed as conversion percentage (%), concentration (g/L), or intracellular accumulation (P/X).

2.7. Synthesis of Results

Studies were categorized by conversion pathway (chemical vs. biotechnological) and application area (biopolymers, bioplasticizers, or biolubricants). Data were standardized into a uniform framework that included country, substrate, catalyst, target compound, yields, and process scale; where applicable, specific quality indicators such as Iodine (IV) and Epoxy (EV) values or pretreatment methods were recorded. Results are presented in structured comparative tables. Given the high methodological diversity, a narrative synthesis was adopted. The heterogeneity of results was critically explored through a Technology Readiness Level (TRL) analysis to assess the feasibility and scalability of the reported processes. Furthermore, the robustness and reliability of the synthesized findings were evaluated through a qualitative critical assessment of the included papers, addressing study limitations and reporting quality.

2.8. Certainty of Evidence

The certainty of the evidence was assessed narratively using a GRADE-inspired approach, considering study limitations, consistency of results, and overall quality of reporting.

2.9. Protocol and Data Availability

Although the review protocol was not registered, given its exploratory nature, a structured internal protocol was rigorously followed. This included predefined inclu-

sion and exclusion criteria, systematic data extraction, and transparent reporting, ensuring methodological consistency and reproducibility. No formal protocol was developed; however, the methodology was defined a priori and conducted in accordance with PRISMA 2020 guidelines (Supplementary Materials). As no protocol was established, no amendments were applicable. Data collection forms extracted data from the included studies, and all materials used in this review are provided within the manuscript. No analytic code was generated, as the study did not involve quantitative synthesis. Additional data are available from the authors upon reasonable request.

3. Results

3.1. Geographic Distribution and Temporal Evolution of the Reviewed Papers

The bibliometric and visual analysis of the selected literature reveals a distinct geographical concentration and temporal evolution of global research efforts dedicated to WCO valorization. As shown in the world map (Figure 4), China emerges as the undisputed leader, contributing 17 publications over the last decade, followed by Brazil (10) and Italy (7). The prominence of Asian and South American countries reflects their dual advantage of abundant waste lipid resources and increasing investment in bio-based industrial technologies, whereas European contributions often focus on process innovation and scalability within circular economy frameworks.

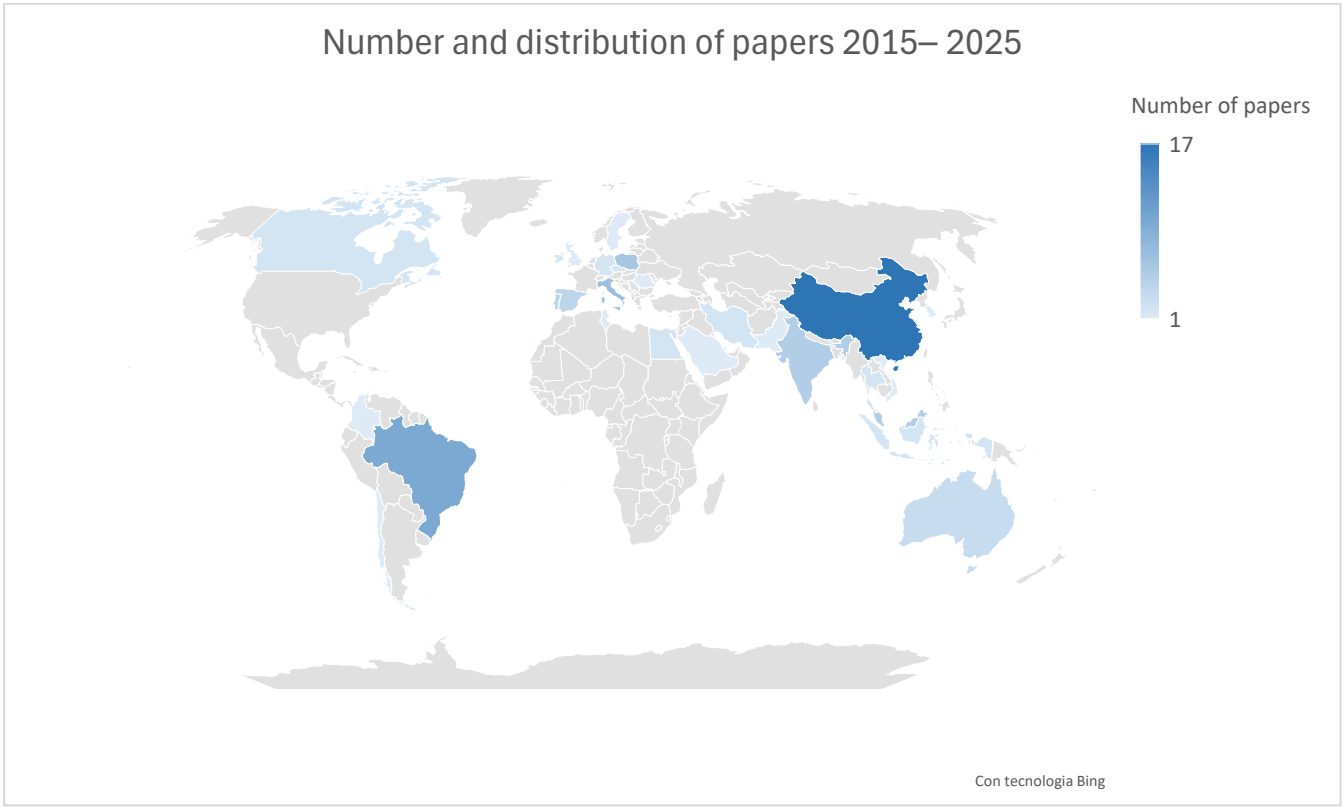

Figure 4. Geographical distribution of the selected paper.

The application-based distribution (Figure 5) highlights that half of the reviewed studies (50.6%) address biopolymer production, whereas biolubricants account for 32.2% and bioplasticizers 17.2%. This predominance of polymer-oriented investigations underscores the scientific and industrial relevance of developing sustainable alternatives to conventional plastics through chemical and biotechnological conversion of waste lipids.

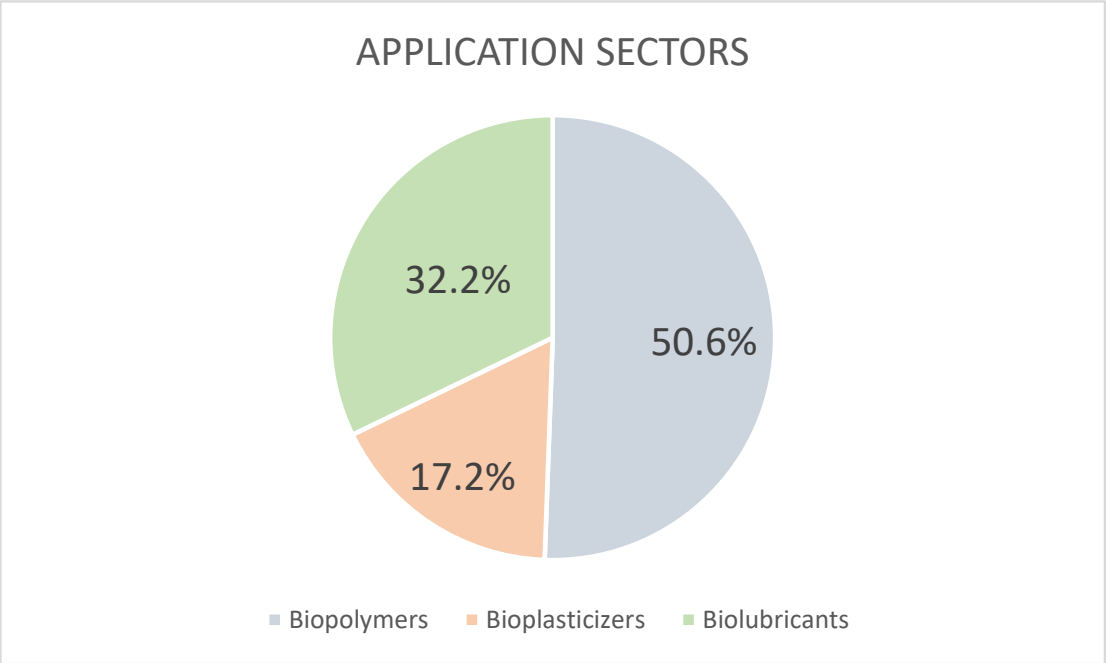

Figure 5. Application-based distribution.

A closer look at research activity trends over time (Figure 6) reveals differentiated dynamics across the three macro-areas. Publications on biopolymers show a consistent and dominant trajectory, with early activity beginning in 2015, followed by pronounced peaks in 2019, 2021, and 2022, corresponding to 6–8 papers per year. This reflects the consolidation of microbial and chemo-enzymatic approaches for polyhydroxyalkanoates (PHA) and related polymers. Bioplasticizer-related research remains comparatively modest, exhibiting low but steady output (1–3 papers per year) without marked peaks, suggesting a more specialized and technologically mature niche. Conversely, studies on biolubricants display a gradual upward trend beginning in 2019, with notable growth in 2021–2022, indicating increasing industrial and environmental interest in high-performance biodegradable lubricants derived from WCOs.

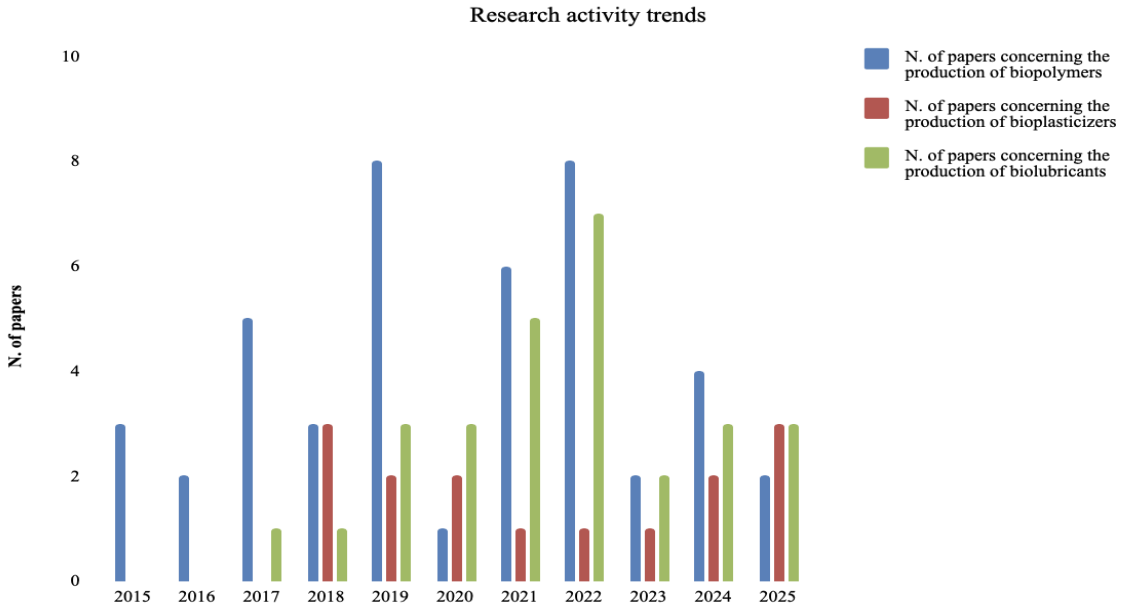

Figure 6. Research activity trends.

Collectively, geographical analysis highlights the global expansion and thematic diversification of research on WCO valorization. The marked increase in publications after 2019 reflects the growing alignment of the scientific community with circular bioeconomy principles, particularly those promoted by the European Green Deal and the UN Sustainable Development Goals.

3.2. Biopolymers

Plastic pollution represents a pervasive and persistent environmental challenge, affecting virtually all ecosystems and raising increasing concerns regarding the impact of macro-, micro-, and nanoplastics [29]. In this context, WCOs, along with other agro-industrial by-products, have emerged as an alternative feedstock for the production of bioplastics through biotechnological routes, particularly for the synthesis of natural-based polyesters such as polyhydroxyalkanoates (PHAs).

Biopolymers are increasingly investigated as environmentally compatible alternatives to conventional plastics, offering the dual advantage of waste valorization and reduced reliance on fossil-based resources. However, their widespread application is still limited by differences in mechanical properties compared to conventional plastics and, in some cases, incomplete biodegradability. These challenges have stimulated extensive research aimed at improving the physicochemical properties and performance of biomaterials [30].

Nevertheless, the transition toward sustainable plastic systems requires not only the development of alternative materials but also a broader reconsideration of waste management strategies, including reduction in single-use plastics, enhanced recycling, and the implementation of safe-by-design approaches [31,32].

To facilitate the interpretation of the analyzed pathways, a schematic overview of biopolymer production routes from WCO is provided in Figure 7.

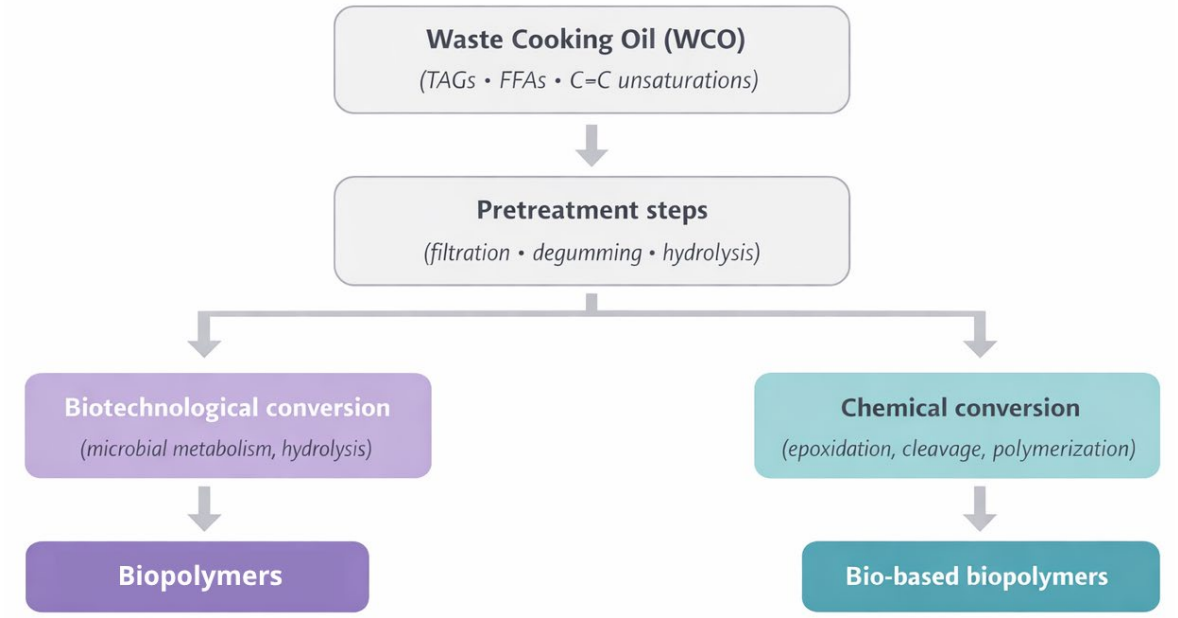

Figure 7. Schematic summarizing the two main routes for biopolymer production from waste cooking oil (WCO).

3.2.1. Analysis of Biotechnological Routes for Biopolymer Production from Waste Cooking Oil: Research Hotspots and Methodological Convergence

Scientific research has long explored enzymatic processes capable of degrading conventional polymers. As reported by Landrigan et al. (2023) [29], the Minderoo-Monaco-Commission on Plastics and Human Health promotes the introduction of a "Global Plastics

Treaty" in order to design and implement an effective working plan at the local, national and regional levels. The Global Plastics Treaty urges a ban on, or strong limitation of, single-use plastics, reducing unnecessary plastic consumption, enhancing recycling policies and promoting safer alternatives to current synthetic plastics. Table 1 summarizes the most recent research concerning the biotechnological conversion of WCO into biopolymers.

Table 1. Biopolymers and monomers research from WCO, a biotechnological approach.

Country	Substrate	Biocatalyst	Target Compound	Yields wt/wt% *	Process Scale	Ref.
Chile	WCO	*P. putida* KT2440	mcl-PHA	38.3	3 L	[33]
China	WCO	Engineering *Cupriavidus necator* H16	PHA	94.9	150 m^3	[34]
China	Mixed substrates 10 gL WCO 2 gL corn starch 4 gL corn steep liquor	*Photobacterium* sp. TLY01	PHB	P/X 53.6	250 mL, 3 L	[35]
China	WCO + MPW	*Bacillus megaterium* UMTKB-1	P(3HB)	11	n.r.	[36]
China	WCO	*Pseudomonas alcaligenes* H3	PHB	P/X = 65.0	5 L	[37]
China	WCO	*E. coli* AA0306	medium-chain α,ω-dicarboxylic acids	calculated P/S 9.8	5 L	[38]
China	WCO (gutter oil)	Engineering *E. coli*	3-HP	3.4 g/L	At flask level	[39]
Czech Republic	WCO	*C. necator* H16	P(3HB)	43 (WCO alone) and 61 (WCO + precipitate)	100 mL, 250 mL	[40]
Czech Republic	WCO + chicken feather hydrolysate	*Cupriavidus necator* H16	3(PHB-co-PHV)	P/X 85	100 mL	[41]
Germany	WCO	*R. eutropha* H16	PHB	P/X = 79.2	250 mL, 5 L	[42]
Germany	WCO	Mixed microbial culture	scl-PHA and mcl-PHA	Maximum PHA accumulation capacity 38.2% cdw	2 L	[43]
Ireland	WCO	*Pseudomonas chlororaphis* 555	mcl-PHA	15	5 L	[44]
Ireland	WCO	*Pseudomonas putida* KT2440	mcl-PHA	P/X 36.4	5 L	[45]
Italy	WCO	Engineered *E. coli* BL21	10-HSA	98	10 mL	[46]
Italy	WCO	Engineered *E. coli* BL21	poly-HSA	80	2 L	[47]
Italy	WCO + glycerol	*P. resinovorans*	mcl-PHA	42.7	100 mL	[48]
Malaysia	WCO	*Cupriavidus necator* transformants harbouring *phaC*$_{BP-M-CPF4}$	poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate] [P(3HB-co-3HHx)]	CDW of 8.5 g/L, PHA content of 75.5 wt% and PHA concentration of 6.4 g/L from 1% (*v*/*v*) WCO	500 mL	[49]
Pakistan	WCO	*Pseudomonas aeruginosa* (KF270353)	PHA, PHB, 3(PHB-co-PHV)	53	250 mL	[50]
Poland	WCO + peptone	*Pseudomonas fluorescens*	PHB	0.68	n.r.	[51]
Portugal	WCO	*Burkholderia thailandensis* E264	PHB	P/S 0.35 P/X 0.60	10 L	[52]
Portugal	WCO	*Cupriavidus necator* DSM 428	PHA	68	50 mL	[53]

Table 1. *Cont.*

Country	Substrate	Biocatalyst	Target Compound	Yields wt/wt% *	Process Scale	Ref.
Portugal	WCO	*Cupriavidus necator* DSM 428	PHB	P/S 0.77 P/X 0.63	2 L	[54]
Spain	fish-canning waste oil	*Mixed microbial cultures*	PHA	82.3	4 L	[55]
Saudi Arabia	WCO	*Neobacillus niacini* *Metabacillus niabensis*	PHA	1.13 g/L 0.85 g/L	10 L	[56]
Republic of Korea	WCO + glucose	*Starmerella bombicola* ATCC 22214	Methyl hydroxy branched fatty acids-derived Bioplastic	315.5 g/L	5 L	[57]
Thailand	WCO	Photosynthetic bacterium *Rhodopseudomonas faecalis* PA2 immobilised in the beads	Removal of cooking oil waste (triglyceride-rich oil)	76.3% with 25% BC beads	lab scale	[58]
Thailand	30 gL WCO Stored 4 we	*Cupriavidus necator* H16	PHA	P/X 27.4	250 mL	[59]
Tunisia	WCO	*Pseudomonas rhizophila* S211	mcl-PHA	1.8 g/L	100 mL	[60]
UK	waste date seed oil extract	*Cupriavidus necator* H16	PHB	P/X 82	500 mL	[61]
Vietnam	WCO WCO soybean oil	*Cupriavidus necator* H16	PHB	P/S 0.76 P/X 78.9 P/S 0.92 P/X 72.5	500 mL, 3 L (for both carbon sources)	[62]

n.r.: not reported; WCO: waste cooking oils; MPW: medical plastic waste; 10-HSA: 10-hydroxysteraic acid; CDW: cell dry weight; Polyhydroxyalkanoate: PHA; 3-hydroxypropionate: 3-HP; poly(3-hydroxybutyrate: PHB; BC: bacterial cellulose. * Yield metrics vary by source study; specific types are noted to prevent ambiguity.

This section presents the results derived from the analysis of the selected studies focusing on the biotechnological conversion of WCO into biopolymers. The discussion emphasizes experimental strategies, process conditions, and performance trends, rather than reiterating detailed data reported in Table 1.

The analyzed literature highlights a strong predominance of microbial bioconversion processes, particularly for the production of PHAs, which represent the most extensively studied class of biopolymers derived from WCO. As shown in Table 1, different microbial strains, including bacteria and yeasts, have been employed, with yields strongly influenced by substrate composition and cultivation conditions.

Strain optimization and metabolic engineering emerge as a primary research focus. High-performing strains such as *Photobacterium* sp. TLY01 and engineered *Pseudomonas* demonstrate significant PHA accumulation, although enzyme-based approaches remain comparatively underexplored despite their potential advantages in terms of selectivity and mild processing conditions.

Feedstock diversification represents a second major trend, with studies increasingly exploring mixed and unconventional substrates, including combinations of WCO with corn-derived residues and other waste oils. This approach enhances process flexibility and contributes to improved economic and environmental sustainability by enabling the valorization of heterogeneous waste streams.

Process intensification strategies constitute a third key research direction, with metabolically engineered strains and optimized fermentation conditions leading to improved yields

and productivity. However, as evidenced in Table 1, the variability in process configurations and reporting metrics (e.g., % dry cell weight vs. g/L) limits direct comparison across studies, highlighting the need for standardized evaluation criteria.

A notable methodological convergence is represented by the widespread adoption of two-stage bioprocesses, involving initial hydrolysis of triglycerides followed by microbial fermentation. While scale-up efforts are increasingly reported, most studies remain confined to laboratory or bench-scale systems, with only limited examples of industrial validation.

Overall, despite promising advancements, key challenges remain, including feedstock variability, lack of standardization, and limited scalability assessments, which hinder the transition from laboratory research to industrial application.

3.2.2. Analysis of Chemical Conversion Routes for Biopolymer Production from Waste Cooking: Research Hotspots and Technological Convergence

Table 2 shows a comprehensive overview of chemical conversion strategies for transforming waste cooking oil (WCO) into biopolymers and polymer precursors.

Table 2. Biopolymers research from WCO. Chemical conversion.

Country	Substrate	Pretreatment	Treatment	Catalyst	Target Compound	Yields wt/wt% *	Process Scale	Ref.
Australia	Elemental sulfur + waste canola cooking oil	no	Rapid microwave-irradiated co-polymerisation	Heat	Polysulfide sorbents (captured Fe^{+})	98.0	1 L	[63]
Australia	WCO	no	Inverse vulcanisation	Sulfur 180 °C	Polysulfide rubber (captured mercury)	≈100 conversion	≥10 kg in a parallel batch reactor	[64]
Brazil	RSO	Yes (two-step purification)	Epoxidations	Autocatalytic reaction	RESO-based epoxy resin	n.r.	500 mL	[65]
Brazil	WCO	Vacuum-filtered oil; no degumming, oil heated to 60–65 °C before reaction	Methyl transesterification of WCO	0.22 g of Na NaOH + 10 mL of CH_3OH	Glycerol-based bioplastics	83.3	30 mL	[66]
China	WCO	no	Epoxidations, ring-opening esterification	n.r.	4D-Printable Photocurable Resin	n.r.	n.r.	[67]
China	WCO	yes	Microwave-assisted co-pyrolysis	HZSM-5	Monocyclic aromatic hydrocarbons	48.0	n.r.	[68]
Colombia	EPS and WCO	Filtration 410 µm	EPS pieces dissolved in excess WCO at 165 °C under atmospheric pressure until complete degassing	n.r.	Recycled EPS-WCO composite	12.1	n.r.	[69]
Indonesia	WCO	Purified with warm water and a small amount of activated-carbon powders	Cationic polymerization of the purified WCO	$BF_3{\cdot}OEt_2$ and microwave	Solid polymer product derived from the polymerized triglycerides	n.r.	n.r	[70]
Malaysia	WCO	Filtration and then heating to 110 °C	Epoxidation–hydroxylation to polyol, then reacted with MDI and LiI to form PU-based solid polymer electrolyte.	$HCOOH/H_2O_2$ system	WCO-based polyurethane solid polymer electrolyte	n.r	Lab scale	[71]
Malaysia	WVO	Epoxidation of unsaturated fatty acids followed by acid-catalysed ring-opening	Hydrogen peroxide (30% *w*/*w*) and orthophosphoric acid (85% *w*/*w*)	Epoxidation and hydroxylation: H_3PO_4 and H_2O_2, 90 °C	Bio-polyols (polyurethane polymer)	n.r	<1 L	[72]

Table 2. *Cont.*

Country	Substrate	Pretreatment	Treatment	Catalyst	Target Compound	Yields wt/wt% *	Process Scale	Ref.
Poland	Used rapeseed palm oil	Simple decantation purification	Epoxidation & Ring-opening	Amberlite IR 120 ion-exchange resin for epoxidation; HBF_4 solution for oxirane ring-opening C	bio-polyols (bio-polyurethane foams)	n.r.	2 dm^3	[73]
Poland	WCO	Filtration of the used oil	Batch annealing in a laboratory furnace at 180–220 °C	H_2SO_4 180–220 °C	Solid "oil blocks" (building-material bricks) obtained after curing	n.r.	n.r.	[74]
Poland	RO, UO, WCO	Simple filtration to remove solids	Two-step process: oil epoxidation with acetic acid/H_2O_2 followed by DEG-mediated ring opening to polyols.	Amberlite IR-120 ion-exchange resin (10% wt of oil) for epoxidation; HBF_4 (0.3% wt of epoxidized oil) for ring opening	Bio-polyols (bio-polyurethane foams)	n.r.	1 L	[75]
Portugal	RO and WCO	Filtration and heating at 110 °C	Biomass ash, dolomite, eggshells, and PET wastes calcined and sulfonated to yield CaO-based solid acid catalysts.	FAD (biomass ash), FAC; Dolomite C; Dolomite CSC; CaO-SiO_2; CaO-S-SiO_2; CA-PET; CA-PET-S	FAMEs	≈96.0	1 L	[76]
Sweden	Rapeseed oil	Oil frozen at −18 °C to limit evaporation; fluidized bed pre-oxidized before feeding	Fluidized-bed steam cracking in a BFB reactor at 650–750 °C	Amberlite 120 (heterogeneous) for epoxidation; HBF_4 for ring-opening	Light olefins (C_2–C_4) and mono-aromatics (BTXS)—the molecular building blocks for plastics	n.r.	laboratory-scale BFB reactor	[77]

n.r.: not reported; WCO: waste cooking oils; RSO: residual soybean oil; RESO: residual epoxidized soybean oil; HZSM-5: proton-exchanged form of the ZSM-5 zeolite; BTXS: benzene, toluene, and xylenes; EPS: Expanded polystyrene; WVO: Waste vegetable oil; RO: Refined palm oil; UO: Unrefined palm oil; FAMEs: fatty acid methyl esters; BFB: bubbling fluidized-bed; DEG: diethylene glycol; HBF_4: tetrafluoroboric acid; HCOOH: Formic acid; NaOH: Sodium Hydroxide; CH_3OH: Methanol; H_3PO_4: Orthophosphoric acid; * Yield metrics vary by source study; specific types are noted to prevent ambiguity.

The epoxidation–ring opening pathway emerges as the most widely adopted approach, enabling the production of hydroxylated polyols suitable for polyurethane synthesis. As shown in Table 2, this method is commonly based on in situ generation of peracids (e.g., formic acid/H_2O_2 systems), followed by acid-catalyzed ring opening reactions. The widespread use of this approach reflects its technological maturity and versatility.

Heterogeneous catalysis represents a second major research trend, with increasing efforts to replace homogeneous catalysts with solid acid systems. This shift facilitates catalyst recovery and reuse, contributing to improved process sustainability and economic feasibility.

Process intensification, particularly through microwave-assisted reactions, constitutes a third key development. Several studies report significant reductions in reaction times while maintaining high selectivity (average >95%), as highlighted in Table 2, demonstrating the potential of this approach for industrial-scale applications.

Feedstock diversification is also evident across chemical routes, encompassing a wide range of lipid-based and polymeric waste streams. This flexibility underscores the robustness of chemical conversion processes, which often require minimal pretreatment compared to biotechnological approaches.

A clear methodological convergence can be observed in the adoption of solvent-free or low-solvent systems, combined with recyclable catalysts, aligning with green chemistry principles.

Overall, chemical conversion routes offer advantages in terms of reaction speed, scalability, and process robustness; however, they may involve harsher operating conditions

compared to biotechnological approaches, highlighting a trade-off between efficiency and environmental sustainability.

3.3. Bioplasticizers

Plasticizers are widely used additives in polymer technology to enhance flexibility, reduce glass transition temperature (Tg), and improve processability in a broad range of materials, including poly(vinyl chloride) (PVC), cellulose derivatives, and various biodegradable polymers. Their incorporation is essential to tailor mechanical properties and facilitate polymer processing.

Globally, approximately 6–7 million tons of plasticizers are consumed annually, the vast majority of which are derived from fossil-based feedstocks [78]. This strong dependence on non-renewable resources raises significant sustainability concerns, further reinforced by the linear production–disposal model associated with petrochemical plasticizers.

In addition to sustainability issues, conventional phthalate plasticizers—widely used due to their effectiveness and low cost—have been associated with potential risks to human health, including endocrine disruption and reproductive toxicity. These effects are mainly linked to their tendency to migrate from polymer matrices into the surrounding environment [79]. Consequently, increasing regulatory restrictions have been implemented, particularly in sensitive applications such as children's toys, medical devices, food packaging, automotive interiors, and indoor materials [80].

In response to these combined sustainability and safety concerns, increasing attention has been directed toward the development of bio-based plasticizers derived from renewable and waste feedstocks. Among these, WCOs represent a particularly attractive resource, as they enable both the replacement of fossil-derived inputs and the valorization of a widely available waste stream within a circular economy framework.

Table 3 summarizes recent studies on the use of WCO as a feedstock for plasticizer production, providing an overview of the main chemical strategies, target compounds, and process performances reported in the literature.

Table 3. Bioplasticizers research from WCO, chemical conversion.

Country	Substrate	Catalyst	Target Compound	Yields wt/wt% *	Iodine (IV) and Epoxy Value (EV) of the Products	Process Scale	Ref.
Brazil	USCO	CRL, benzyl alcohol in solvent-free systems, H_2O_2 and formic acid	BE and EBE from USCO	conversion of double bonds into epoxy groups at approximately 42.4	BE: IV of 95.1 ± 3.8 mg I_2 per 100 g of ester EBE: IV 54.7 ± 2.7 mg I_2 per 100 g of ester	350 mL	[81]
Brazil	WCSO	citric acid and H_2O_2	ESO	Double bond conversion 92.5 Relative conversion 55.7	IV—6.7% (g I_2/100 g)	n.r.	[82]
China	WCO	CH_3COOH; H_2O_2, (epoxidation) AA; MAA (ring-opening esterification)	EWOMA EWOA	n.r.	IV WCO: 83 EV E-WCO: 4.37	1000 g	[67]
China	WCO, malic acid	CH_3OH, H_2SO_4 (FAME) HCOOH, H_2O_2 (EFAME) TBAC (FAME-MAE) acetic anhydride (AC-FAME-MAE)	AC-FAME-MAE	71.07	EV_{EFAME}—4.4%	500 mL	[83]

Table 3. *Cont.*

Country	Substrate	Catalyst	Target Compound	Yields wt/wt% *	Iodine (IV) and Epoxy Value (EV) of the Products	Process Scale	Ref.
China	WCO	NaOH or H_2O_2	GE-WCO EGE-WCO	n.r.	IV_{GE-WCO}—89.80 (g I_2/100 g) EV_{GE-WCO}—0.21 (mol/100 g) $IV_{EGE-WCO}$—3.52 (g I_2/100 g) $EV_{EGE-WCO}$—0.41 (mol/100 g)	500 mL	[84]
China	WCO	KOH-CH_3OH (FAME) H_2SO_4 (EFAME) TBAC (ring opening reactions of EFAME)	ring-opening EFAME	EFAME with terephthalic acid—66.2 EFAME with adipic acid—58.3 EFAME with benzoic acid—76.8	IV_{FAME}—910 (g/kg) IV_{EFAME}—4.1 (g/100 g) EV_{EFAME}—4.2%	500 mL	[85]
China	WFO	maleic anhydride, hydroquinone and acetic acid p-toluenesulfonic acid or benzyltriethyl ammonium chloride	WFOPA WFOPA-n	85.9 (WFOPA) 95–98 (WFOPA-n)	n.r.	500 mL	[86]
China	WCO, citric acid	Peroxophosphotungstate, TBAC	AC-FAME-CAE	n.r.	EV—0.08%	500 mL	[80]
China	WCOMEs	potassium carbonate H_2O_2, formic acid	WCOEtHEs Ep-WCOEtHEs	92	$IV_{Ep-WCOEtHEs}$—0.68 (g I_2/100 g)	250 mL, 1000 mL	[87]
Indonesia	EWCO	glacial acetic acid, H_2O_2, H_2SO_4	BC-based biocomposites reinforced with bamboo MFC and plasticized with EWCO	n.r.	n.r.	n.r.	[88]
Italy	WCO	CaO transesterification (conventional); microwave-assisted CaO transesterification; epoxidation (30% H_2O_2 + HCOOH)	Guerbet esters and epoxidized esters	>95 after 24 h >95 after 1 h >95 after 6 h	n.r.	10 mL, 250 mL, 500 mL	[89]
Malaysia	EWCO	88% of formic acid, HCOOH, 30% of H_2O_2	PLA/EWCO blends	n.r.	n.r.	250 mL, 500 mL	[90]
Poland	rapeseed oil, sunflower oil, linseed oil, castor oil, and UCO	n.r.	Unmodified vegetable oils	n.r.	IV (g I_2/100 g) rapeseed oil: 110.6 IV (g I_2/100 g) sunflower oil: 124.1 IV (g I_2/100 g) linseed oil: 173.2 IV (g I_2/100 g) castor oil: 85.5 IV (g I_2/100 g) UCO: 98	n.r.	[91]

CRL: Candida rugosa lipase; n.r.: not reported; WCO: waste cooking oils; EWCO: epoxidized waste cooking oil; WCSO: waste cooking soybean oil; WFO: waste frying oil; WCOMEs: waste cooking oil methyl esters; GE-WCO: glycidyl esterized waste cooking oil; EGE-WCO: epoxidized glycidyl ester of waste cooking oil; TBAC: tetrabutylammonium chloride; AC-FAME-CAE: acetylated-fatty acid methyl ester-citric acid ester; AC-FAME-MAE: acetylated-fatty acid methyl ester-malic acid ester; MFC: microfibrillated cellulose; ESO: epoxidized soybean oil; WFOPA: waste frying oil-derived polyacid; WFOPA-n: WFO-derived ethoxylated esters; WCOEtHEs: waste cooking oil 2-ethylhexyl esters; Ep-WCOEtHEs: epoxidated waste cooking oil 2-ethylhexyl esters; EWOMA: epoxy waste oil methacrylate; EWOA: epoxy waste oil acrylate; AA: acrilic acid; MAA: methacrilic acid; USCO: used soybean cooking oil; BE: benzyl-based esters; EBE: epoxidized benzyl-based esters; UCO: used cooking oil. * Yield metrics vary by source study; specific types are noted to prevent ambiguity.

From a technological perspective, chemical conversion represents the most widely adopted strategy for the valorization of WCO into bioplasticizers. This predominance is

mainly related to the fact that plasticizers are typically low-molecular-weight compounds whose functional properties—such as plasticizing efficiency, compatibility, and thermal stability—strongly depend on well-defined chemical structures, which are more readily obtained through conventional chemical synthesis.

Furthermore, established chemical routes allow precise control over functionalization, reaction yields, and product purity, which are critical parameters for meeting industrial and regulatory requirements. In contrast, biotechnological approaches remain less developed, mainly due to limitations related to metabolic pathway availability, product recovery, and downstream processing, as well as the difficulty of achieving the structural specificity required for effective plasticization.

Analysis of Chemical Pathways

The comparative analysis of the studies summarized in Table 3 highlights several converging trends in the valorization of WCO to produce bioplasticizers. A primary observation concerns the predominance of chemical processes, particularly epoxidation, transesterification, and ring-opening reactions. These pathways represent the most established routes for generating functionalized esters suitable as PVC plasticizers, largely due to their high selectivity, operational simplicity, and compatibility with heterogeneous feedstocks such as WCO.

Among these, epoxidation emerges as the most recurrent transformation step, reflecting its strong industrial relevance. Reported double-bond conversion efficiencies range from moderate (~40%) to very high values (>90%), although final epoxy values (EV) vary significantly depending on catalyst type, reaction conditions, and purification strategies.

A second common feature is the widespread use of classical acid–peroxide systems (e.g., formic acid/H_2O_2 or acetic acid/H_2O_2) and phase-transfer catalysts (e.g., TBAC) to promote epoxidation and subsequent ring-opening reactions. While these systems are cost-effective and broadly applicable, their extensive use also indicates a continued reliance on conventional chemistries rather than fully green or alternative catalytic approaches.

Another critical aspect emerging from Table 3 is the limited availability of consistent yield and scalability data. Most studies are conducted at laboratory scale, typically within volumes ranging from 250 mL to 1 L, while only a few contributions report larger-scale implementations.

This heterogeneity complicates direct comparisons between studies and highlights a gap between laboratory feasibility and industrial applicability. Conventional processes such as transesterification and epoxidation appear closest to scale-up readiness, whereas more advanced functionalization strategies—such as glycidyl esters, epoxy-acrylate derivatives, and EFAME-based plasticizers—remain at earlier stages of technological maturity. From a performance perspective, reported yields above 70–90% indicate promising conversion efficiencies. However, inconsistencies in reporting metrics (e.g., wt%, g/L, or mol-based EV) limit cross-study comparability and hinder the development of standardized benchmarks.

A further relevant pattern concerns the geographical distribution of research efforts. China clearly dominates in terms of the number of published studies, covering a wide spectrum of approaches ranging from conventional epoxidation reactions to advanced polymerizable derivatives and polyacid systems. This leadership likely reflects both the large availability of WCO feedstocks and targeted investments in sustainable materials and polymer chemistry. Other countries, including Brazil, Italy, Malaysia, Tunisia, Indonesia, and Poland, tend to focus on specific technological innovations, such as microwave-assisted catalysis, bio-based esterification strategies, or microbial polymer production.

From a structural standpoint, iodine value (IV) generally decreases across epoxidized and further functionalized products, confirming the progressive saturation and modifica-

tion of unsaturated fatty acid chains. At the same time, epoxy values (EV) remain highly dependent on process conditions and are sometimes relatively low, suggesting incomplete epoxidation or partial ring-opening reactions—both of which can significantly affect the final plasticizer performance.

Overall, Table 3 demonstrates that WCO constitutes a chemically versatile feedstock capable of supporting a wide range of plasticizer structures, including epoxidized oils, functional esters, glycidyl derivatives, and polymerizable acrylates. However, the intrinsic variability in WCO composition, combined with inconsistencies in reporting purification methods, stability, and compatibility with polymer matrices such as PVC, indicates that further standardization of analytical methods and performance metrics is required.

Future research should therefore focus on the development of greener catalytic systems, improved process integration, and more robust scale-up strategies to enable the transition from laboratory-scale demonstrations to industrial implementation.

3.4. Biolubricants

Biolubricants derived from renewable resources represent a sustainable alternative to conventional mineral oils, whose large-scale production and limited biodegradability contribute significantly to environmental contamination. It is estimated that a substantial fraction of lubricants is released into the environment without adequate treatment, leading to severe impacts on water and soil systems.

Biolubricants, typically formulated as fatty acid esters, exhibit advantageous physicochemical properties, including high viscosity indices, excellent lubricity, low volatility, and biodegradability. These characteristics are largely attributed to the presence of polar ester functional groups, which enhance surface adsorption and reduce wear. However, unmodified vegetable oils, including WCO, often suffer from oxidative instability and poor low-temperature behavior due to the presence of unsaturated fatty acids [92]. To overcome these limitations, several chemical and enzymatic modification strategies have been developed, including transesterification with polyols, epoxidation, and esterification with branched alcohols. These approaches improve oxidative stability, viscosity, and cold-flow properties, making WCO-derived products suitable for demanding industrial applications. Enzymatic catalysis, particularly using immobilized lipases, has emerged as a promising alternative to conventional chemical processes. These systems operate under milder conditions, offering high selectivity, reduced by-product formation, and improved sustainability, especially when applied to waste-derived feedstocks. Both chemical and enzymatic pathways enable efficient conversion of WCO into high-performance biolubricants. Optimization strategies based on Response Surface Methodology (RSM) have demonstrated conversion efficiencies exceeding 90–97%, depending on the system and product formulation [93]. Despite these promising results, several challenges remain, including feedstock variability, long-term oxidative stability, compatibility with additives, and economic feasibility. Current research efforts are therefore focused on integrated biorefinery approaches, advanced catalyst design, and improved control of feedstock quality [94].

Overall, biolubricants derived from WCO represent a strategic opportunity within the framework of green chemistry and circular economy, enabling the valorization of waste lipids into high-value industrial products.

3.4.1. Hotspots and Converging Trends in Enzymatic Hydrolysis–Esterification of Waste Cooking Oils

Figure 8 represents a schematic streamline for the biocatalytic conversion of WCO into biolubricants.

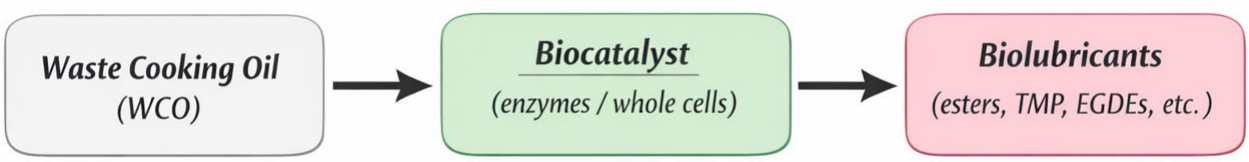

Figure 8. Schematic representation of the biocatalytic conversion of WCO into biolubricants via enzymatic/whole-cell catalysis.

Analysis of experimental data in Table 4 reveals distinct research hotspots in the enzymatic valorization of waste cooking oils into biolubricants.

Table 4. Biotechnological conversion of biolubricants.

Country	Substrate	Pretreatment	Biocatalyst	Target Compound	Yields wt/wt% *	Process Scale	Ref.
Brazil	RSBO, USCO	Hydrolysis	CRL; TLL on SiO_2 variants; Lipozyme TL IM (ctrl)	Decyl esters	81.3–87.6	n.r.	[81]
Brazil	WCO, RSBO	Vacuum filtered	Eversa-mCLEA; liquid Eversa	Fatty acid isoamyl esters	Eversa-mCLEA:90; Liquid Eversa: 34	n.r.	[95]
Brazil	USCO	Hydrolysis	Eversa® Transform 2.0 on PSty-DVB beads	EGDEs	≈100	n.r.	[96]
Brazil	RSO, USCO	Enzymatic hydrolysis	Immobilized Eversa® Transform 2.0	TMPTEs	≈97	100 mL	[97]
Brazil	PFAD	no	CRL (Lipomod™ 34MDP)	PFAD-TMP & PFAD-NPG	PFAD-TMP: 94; PFAD-NPG: 87	n.r.	[98]
China	WCO	Enzymatic hydrolysis + urea complexation (UFA enrichment)	*Candida* sp. 99e125; Novozym 435; [HMIm][PF6]	Octylated branched biolubricant	81	2 L; 250 mL	[99]

n.r.: not reported; CRL: Candida rugosa lipase; EGDEs: ethylene-glycol di-esters; mCLEA: magnetic cross-linked enzyme aggregate; NPG: neopentyl glycol; PFAD: palm fatty-acid distillate; PSty-DVB: polystyrene-divinylbenzene; RSBO: refined soybean oil; RSO: residual soybean oil; SiO_2: silicon dioxide; TLL: Thermomyces lanuginosus lipase; TMP: trimethylolpropane; TMPTEs: trimethylolpropane triesters; UFA: unsaturated fatty acids; USCO: used soybean cooking oil; [HMIm][PF6]: 1-hexyl-3-methylimidazolium hexafluorophosphate; WCO: waste cooking oil. * Yield metrics vary by source study; specific types are noted to prevent ambiguity.

This subsection presents the main trends emerging from the enzymatic conversion of WCO into biolubricants, as summarized in Table 4. Hydrolysis–esterification pathways. The predominant strategy involves a two-step process consisting of enzymatic hydrolysis of triacylglycerols into free fatty acids, followed by esterification with short- or branched-chain alcohols. As shown in Table 4, *Candida rugosa* lipase is frequently employed in the hydrolysis step, while immobilized lipases such as *Thermomyces lanuginosus*, Lipozyme TL IM, and Eversa® Transform 2.0 are widely used for esterification, immobilization and catalyst stability.

Immobilization techniques, including octyl-functionalized supports and magnetic cross-linked enzyme aggregates, play a crucial role in enhancing enzyme stability and reusability. These systems often retain up to ~90% activity over multiple cycles, significantly improving process sustainability and economic feasibility. Process intensification and green conditions. A clear trend toward solvent-free systems and mild reaction conditions is observed across the dataset. Under optimized conditions, hydrolysis efficiencies close to 98% and esterification yields exceeding 80–90% are commonly reported, demonstrating

the effectiveness of enzymatic approaches. Feedstock flexibility. The analyzed studies demonstrate a high degree of feedstock adaptability, successfully processing WCO from different sources as well as alternative lipid residues without significant loss of performance.

Overall, the convergence toward reusable enzymes, solvent-free conditions, and flexible feedstock utilization highlights a mature and sustainability-oriented research landscape, with strong potential for industrial implementation.

3.4.2. Hotspots and Converging Trends in Chemical Waste Cooking Oil Valorization Pathways

Inspection of the experimental dataset compiled in Table 5 reveals diversified strategies for upgrading waste cooking oils and related lipid residues into biolubricants, frequently combined with biodiesel or biochemical intermediates. A schematic of the streamline is present in Figure 9.

Table 5. Chemical conversion of biolubricants.

Country	Substrate	Pretreatment/ Treatment	Catalyst	Target Compound	Yields wt/wt% *	Feasibility/Scalability	Ref.
Australia	WCOME	Acid esterification	MeONa, 1% (*w*/*w*)	TWCOE biolubricant	96	500 mL	[100]
Brazil	RFA (deodorization stage)	Direct esterification	PTSA, 5 wt%	BIOLUB	96	250 mL	[101]
Canada	WCO + oleic/stearic acids	Hydrolysis → ketonizatio → Firedel-Crafts hydrodeoxygenation	Fe_3O_4; Cu/ZSM-5-MgO; Ni/SiO_2-Al_2O_3	BLs	~40	100 mL	[102]
Canada	EWCO, WCO-FAME	Hydroxylation → hexanoylation	H_2SO_4 (1.5 wt%) or IR-120; Amberlyst-15	Hydroxylated & hexanoylated esters	99	n.r.	[103]
China	WCO	Two-step esterification/transesterification → molecular distillation	HT/K_2CO_3	TFATE	93.9	250 mL	[104]
Egypt	Animal fats + WCO blend	Washing, heating, filtering; esterification	CaO (1.2 wt%)	EGDEs	91.56	Aspen Plus simulation; 250 mL	[105]
Egypt	Sunflower, soybean, Jatropha, WCO	Transesterification	CaO, 1.2% (*w*/*w*)	EGDEs	n.r.	n.r.	[106]
India	WCO	Adsorption on charcoal → epoxidation → ring-opening	NaOH (1% *w*/*w*); H_2SO_4 (2% *w*/*w*); H_2O_2 (1.5 mol/FAME); p-TSA (5% *w*/*w*)	Ring-opened epoxidized WCOME	97	500 mL	[107]
India	WCO	Filtration → transesterification → esterification	PTSA, 10 wt%	Ethyl-hexyl esters (WCO-BL)	n.r.	250 mL	[108]
India	Soybean WCO + curcumin	Curcumin extraction → polymerization	No catalyst	BL from curcumin-doped WCO + MGAs + mineral base oil	n.r.	250 mL	[109]
India	Soybean WCO	Curcumin extraction → Blending	No catalyst	BL blends (10–30% *v*/*v* of curcumin-extracted WCO in mineral base oil)	n.r.	n.r.	[110]
India	WCO, WCOME	Transesterification → epoxidation	KOH (1 wt%); H_2SO_4 (1.5 wt%); H_2O_2 (30% *v*/*v*)	EWCO, EWCOME	Methyl ester: 95; oxirane: 60.75	500 mL	[111]
Iran	SWCO	Fatty Acid Extraction (Metcalf method) → epoxydation	CH_3COOH	SWCO tri-ester	82.9	250 mL	[112]
Iran	WCO	Filtration & preheating	K_2CO_3	TFATE	83.33	VPC reactor (0.06 m ID × 0.55 m);	[113]
Italy	Methyl oleate & unsaturated FA esters	Drying resins; dissolution in acetic acid/toluene	Dowex 50WX2	Dihydroxylated FA esters	72	50 mL	[89]

Table 5. *Cont.*

Country	Substrate	Pretreatment/ Treatment	Catalyst	Target Compound	Yields wt/wt% *	Feasibility/Scalability	Ref.
Italy	Purified domestic WCO	Straining, water washing, filtration, deacidification → microwave transesterification → epoxidation	CaO (25 mol%); $HCOOH + H_2O_2$	Guerbet esters; Epoxidized esters	95	10 mL, 250 mL, 500 mL	[89]
Italy	SWCO	Water degumming	No catalyst	Regenerated oil	n.r.	50 L	[114]
Malaysia	WCO, RSO	Transesterification with methanol → esterification	p-TSA, 2% (wt/wt)	TMP ester	WCO: 71 RSO: 14	n.r.	[115]
Romania	SWCO, palm WCO	Sieving, filtration → saponification	LiOH or slaked lime; C18	Lubricating grease	n.r.	n.r.	[116]
Spain	WCO	Filtration; heating	MeONa (0.5% first step; 1% second step)	BL	90.2	250 mL	[117]
Spain	WCO	Filtered, dried	MeONa	WCO-TMP ester	98	n.r.	[93]
Spain	SWCO, palm WCO	Filtration, vacuum drying → short-path distillation	n.r.	BL base stocks or additives	n.r.	n.r.	[118]

n.r.: not reported; BLs: biolubricants; MeONa: sodium methoxide; CH_3COOH: Acetic Acid; EGDEs: ethyleneglycol di-esters; EWCO: epoxidized waste cooking oil; EWCOME: Epoxidized Waste Cooking Oil Methyl Esters; FAME: fatty acid methyl ester; HT/K_2CO_3: hydrotalcite loaded with potassium carbonate; ID: inner diameter; IR-120: Amberlite IR-120 ion-exchange resin; K_2CO_3: potassium carbonate; KOH: potassium hydroxide; LiOH: lithium hydroxide; MGA: methacrylate-grafted additive; NaOH: sodium hydroxide; PTSA/p-TSA: p-toluenesulfonic acid; RFA: refined fatty acids; RSO: rapeseed oil; SWCO: Sunflower Waste Cooking Oil; TFATE: trimethylolpropane fatty acid triester; TMP: trimethylolpropane; TWCOE: Trimethylolpropane Waste Cooking Oil Ester; VPC: vertical pulsed column; WCO: waste cooking oil; WCOME: Waste-cooking-oil methyl ester; WCO-FAME: waste cooking oil fatty acid methyl esters; FA: fatty acids; Fe_3O_4: iron(II,III) oxide; Cu/ZSM-5-MgO: copper/ZSM-5 zeolite-magnesium oxide; Ni/SiO_2-Al_2O_3: nickel/silica-alumina; Amberlyst-15: sulfonic acid resin catalyst; HCOOH: formic acid; H_2O_2: hydrogen peroxide; Dowex 50WX2: ion exchange resin; H_2SO_4: sulfuric acid; C18: stearic acid; CaO: calcium oxide; WCO-BL: waste cooking oil biolubricant. * Yield metrics vary by source study; specific types are noted to prevent ambiguity.

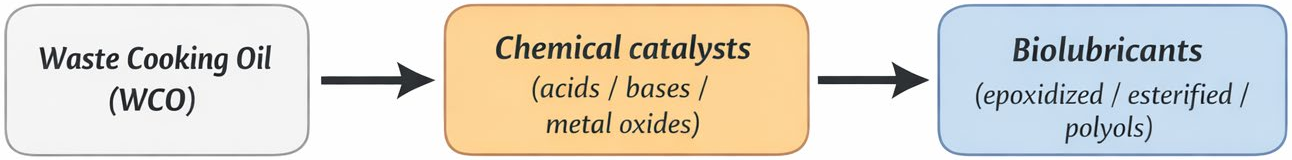

Figure 9. Schematic representation of the chemical conversion of WCO into biolubricants via acid/base/metal-catalyzed processes.

This subsection summarizes the main chemical conversion pathways for the valorization of WCO into biolubricants, as reported in Table 5.

Multi-product valorization strategies are a key research trend that involves the integration of biolubricant production with biodiesel synthesis, enabling efficient use of feedstocks and improving overall process economics. Techniques such as short-path distillation and multi-stage transesterification allow separation of lighter biodiesel fractions from heavier components suitable for lubricant applications.

The development of heterogeneous catalytic systems, including K_2CO_3–hydrotalcite, CaO, Amberlyst-15, and Fe_3O_4-based catalysts, represents a major technological advancement. These systems enable catalyst recovery, reuse, and improved process sustainability compared to traditional homogeneous catalysis. Furthermore, several studies report the use of intensified conditions, such as microwave-assisted reactions and reduced-pressure systems, to decrease reaction times and energy consumption while maintaining high yields (>90%).

Chemical routes demonstrate high tolerance toward feedstock variability, processing a wide range of lipid residues, including animal fats, palm derivatives, and mixed waste oils, often requiring only minimal pretreatment.

Overall, chemical conversion pathways are characterized by high efficiency, scalability, and process robustness, making them particularly suitable for industrial applications.

A comparison between enzymatic and chemical routes highlights a trade-off between sustainability and process efficiency. Enzymatic catalysis operates under milder conditions and offers higher selectivity with reduced by-product formation, although it is often associated with higher costs and longer reaction times. In contrast, chemical processes enable faster conversion and easier scalability but typically require harsher conditions and may have a greater environmental impact.

3.5. Comparative Yield Distribution Across WCO Valorisation Pathways

As reported in Figure 10, in order to provide a more comprehensive and visually intuitive assessment of the technological landscape, the compiled results are summarized in a comparative distribution plot. This figure integrates yield data reported across the different WCO valorisation pathways analyzed.

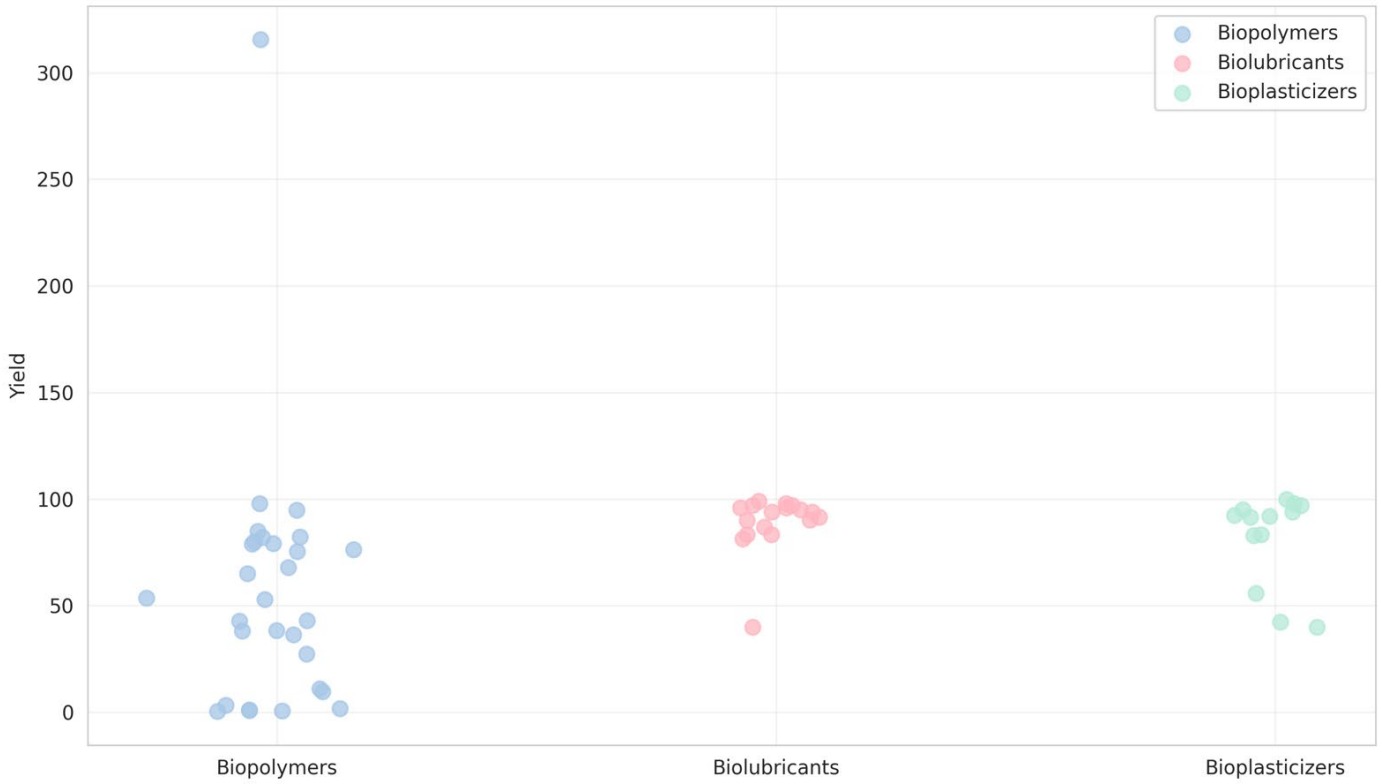

Figure 10. Comparative distribution of reported yields for WCO valorization pathways.

The visualization highlights a pronounced heterogeneity in reported yields for biopolymer production, reflecting the strong dependence on microbial strain selection, metabolic engineering strategies, and substrate composition. In contrast, biolubricant production pathways exhibit generally higher and more clustered yields, suggesting a higher degree of process optimization and technological maturity. Bioplasticizers approaches show intermediate behaviour, often characterized by high efficiency but reduced biological specificity.

4. Feasibility and Scalability Data: An Analysis Through Technology Readiness Levels (TRLs)

4.1. TRL Evaluation

The concept of *Technology Readiness Levels* (TRLs), as defined by Héder (2017) [119], provides a systematic framework for assessing the maturity of a technology. This classifica-

tion ranges from TRL 1, representing basic research, to TRL 9, indicating technologies ready for full commercial deployment. One of the main challenges in innovation lies in bridging the gap between laboratory research and large-scale application. The TRL framework supports this transition by identifying the current stage of technological development and guiding research priorities accordingly. In particular, it enables institutions and funding agencies to strategically allocate resources toward promising innovations and prototype development. In operational terms, TRLs 1 through 4 correspond to laboratory-scale development, where fundamental principles are observed and validated. Levels 5 to 7 refer to pilot-scale stages, in which the technology is integrated and tested in relevant environments. Finally, TRL 8 and 9 describe the demonstration and commercialization phases, where prototypes are finalized, validated, and introduced into the market. By linking research activities to the TRL structure, it becomes possible to align basic and applied research more effectively, facilitating scalability and promoting the development of competitive, market-ready technologies.

4.2. TRL Trends Concerning the Selected Articles

Based on the feasibility and scalability data reported in Tables 1–5, the technologies reviewed are generally feasible at laboratory scale, with most remaining at or below TRL 4. The trends observed in all tables highlight a low tendency to scale up processes, thus identifying a gap between basic and applied research. Only one study, by Jiang et al. (2025) [34], reported the scale-up of WCO conversion to PHA in a 150 m^3 reactor, demonstrating industrial-scale feasibility. This process, based on *Cupriavidus necator* H16, achieved remarkably high yields, with up to 100% substrate conversion, highlighting the potential for commercial PHA production from residual feedstocks such as WCO. In addition, Life Cycle Assessment (LCA) and Techno-Economic Analysis (TEA) could substantially enhance the understanding of the environmental and economic feasibility of these processes, thereby supporting and encouraging experimental scale-up.

The global shift toward a circular bioeconomy has accelerated the development of sustainable alternatives to traditional petroleum-derived chemicals, specifically in the fields of bioplastics, biolubricants, and bioplasticizers. To ensure these innovations are both ecologically sound and commercially viable, it is essential to apply a rigorous evaluation framework that combines Life Cycle Assessment and Technoeconomic Analysis. However, a significant challenge remains in the fact that current experimental data are still limited and predominantly based on small-scale laboratory processes. This scarcity of large-scale data makes the application of Life Cycle Assessment more complex, as researchers must extrapolate the environmental footprint of these bio-products from controlled, small-scale environments to potential industrial scenarios. Similarly, the Technoeconomic Analysis must account for the high degree of uncertainty involved in evaluating production costs and industrial scalability when the available metrics are confined to early-stage development. Despite these limitations, the synergy between these two methodologies is vital to bridge the gap between the laboratory and the market. By carefully modeling available data, we can better predict how bioplastics, biolubricants, and bioplasticizers will perform at scale, ensuring that the transition to bio-based materials is supported by both environmental integrity and economic sustainability.

To provide a clearer overview of the technological maturity of the reviewed studies, a TRL-based classification was performed (Figure 11).

Most studies are concentrated between TRL 3 and TRL 5, corresponding to proof-of-concept and laboratory-scale validation.

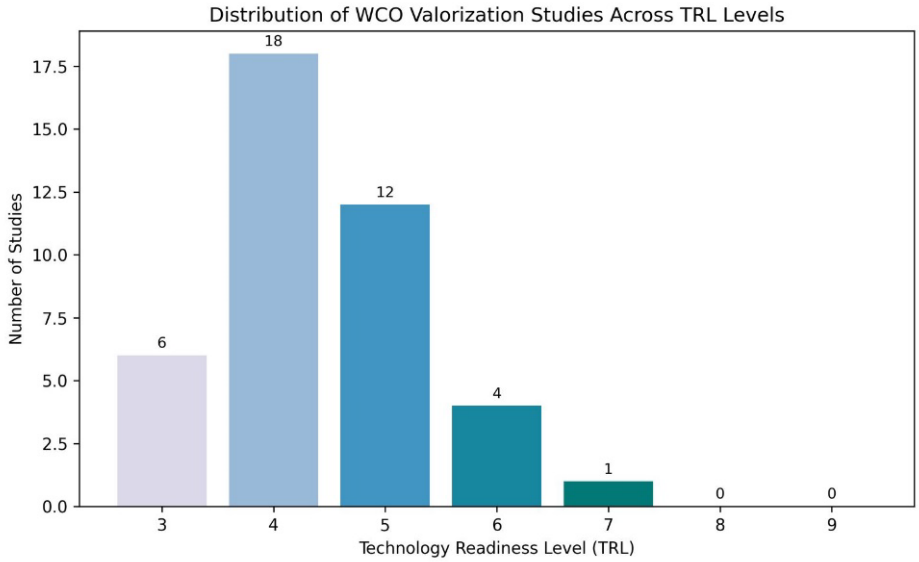

Figure 11. Flowchart illustrating the distribution of the reviewed studies across Technology Readiness Levels (TRLs), from proof of concept (TRL 3) to industrial maturity (TRL 8–9). Node colors follow a pastel hierarchical palette, highlighting the progressive increase in technological maturity. The number of studies identified at each level is reported above the corresponding column.

Only a limited number of works reach pilot scale (TRL 6), while a single study demonstrates industrial-scale validation (TRL 7), highlighting the significant gap between laboratory research and large-scale implementation.

No studies were identified at TRL 8–9, confirming that WCO valorization technologies, although promising, are still far from full industrial deployment.

4.3. Focus on Scalability

The lack of focus on scalability, which is evident in the field of biopolymers, bioplasticisers and biolubricants, is partly justified by the complexity of the processes involved and the technical specifications that value-added products must meet. A similar situation is found in the context of bioactive compounds for the food, cosmetics and additives sectors [11].

Conversely, in other sectors of waste valorization, very high TRLs have been achieved and consolidated, particularly in the bioenergy production sector such as biodiesel and biomethane. Finally, concerning the transition from laboratory-scale synthesis to industrial implementation, it is observed that volumetric productivity remains a significantly underestimated parameter in the current literature. Although not comprehensive, this metric is pivotal in quantifying the Technology Readiness Level (TRL) and the overall developmental maturity of the discussed processes. Achieving semi-industrial or industrial production scales necessitates a rigorous definition of the technical and regulatory frameworks required to stabilize the manufacturing pipeline. Furthermore, the consolidation of the production process must be integrated with a comprehensive techno-economic analysis (TEA) to ensure long-term financial viability and market competitiveness.

Overall, the available evidence highlights the need to prioritize scalability, with particular emphasis on increasing production volumes and addressing the technical challenges associated with pilot and industrial scale applications.

5. A Qualitative Critical Assessment of the Papers Reviewed

The articles included in this review were examined through a qualitative analytical framework addressing several key dimensions, including the clarity of the research

objectives, the completeness and reproducibility of the methodological descriptions, the nature of the biotechnological and chemical strategies employed, the robustness of chemical characterization, and the extent to which yield data and scalability considerations were reported.

Overall, the selected studies present clearly defined objectives and provide sufficiently detailed methodological descriptions, allowing the experimental approaches to be understood and, in principle, reproduced. The chemical characterization of the obtained products is also typically described with adequate analytical support.

With regard to the biotechnological strategies adopted, the information provided in the articles allows the catalytic systems to be identified and contextualized. However, as reported in Table 1, only a limited number of studies describe the use of engineered strains or enzyme immobilization techniques, indicating a prevailing reliance on wild-type strains and non-immobilized systems. Greater heterogeneity emerges in relation to yield reporting and scalability considerations. In several cases, yield data are presented in a preliminary or non-uniform manner, and information concerning process scale-up is limited or absent. This suggests that part of the literature is primarily focused on demonstrating the technical feasibility of specific chemical or biotechnological transformations, rather than on providing comprehensive data to support industrial implementation.

To provide a qualitative overview of the reviewed literature, a heatmap summarizing the degree of methodological completeness across different study categories was developed (Figure 12).

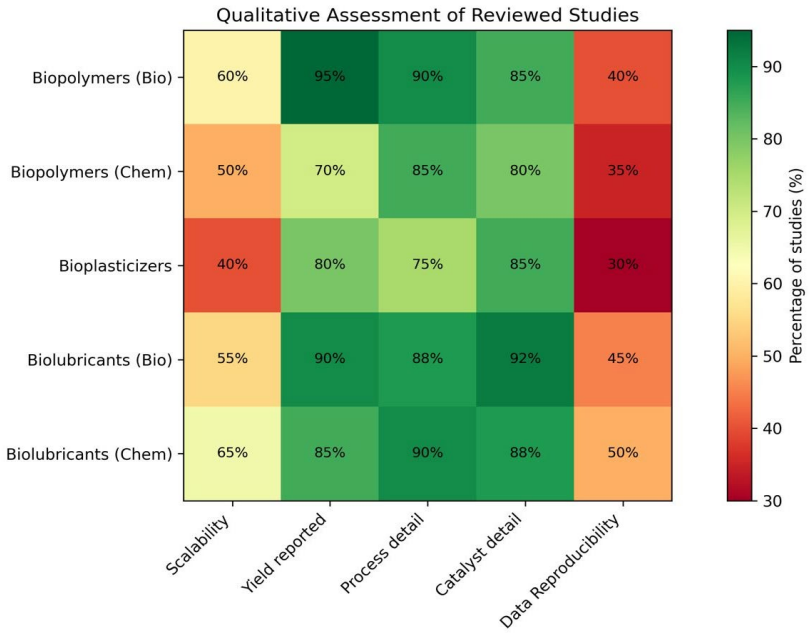

Figure 12. Heatmap summarizing the qualitative assessment of the reviewed studies across five methodological criteria (scalability, yield reported, process detail, catalyst detail, reproducibility). Higher percentages indicate stronger reporting consistency within each research area.

The analysis reveals that yield and process details are consistently reported across most studies (>80%), whereas scalability and data reproducibility indicators remain significantly underreported (<50% in most cases). The data reproducibility section delineates the methodological variability across the selected studies.

This highlights a critical gap between experimental optimization and industrial applicability, reinforcing the need for standardized reporting frameworks and scale-up validation. In this evaluation of analytical data, the analysis of data obtained by GC-MS was considered the predominant analytical support.

Such variability may be contextualized within the specific timeframe of the literature under review. Throughout the decade encompassed by the selected studies, many of the investigated transformations constituted pioneering methodologies for the valorization of waste cooking oils (WCOs). Consequently, a significant portion of these contributions reflects nascent research efforts centered on fundamental process exploration and proof-of-concept validation. This focus inherently accounts for the relatively marginal emphasis placed on critical industrial parameters, such as yield optimization and scalability metrics.

The qualitative considerations discussed above are consistent with the trends highlighted in Chapter 4. Future research would benefit from a stronger focus on standardized yield reporting and on the generation of scalability data to facilitate the transition from laboratory-scale investigations to industrially relevant applications.

6. Research Needs and Future Trends

Beyond academia, the growing interest in WCO valorization is also driven by environmental awareness among governments, industries, and consumers. Policy measures promoting circular economic strategies, together with increased public concern regarding environmental impacts, have significantly contributed to this trend. In parallel, rising consumer awareness of the environmental benefits associated with sustainable WCO valorization processes has strengthened market demand and improved the social acceptability of WCO-derived products.

With regard to biopolymers, the data discussed in this work show that biotechnological transformations and chemical conversion routes represent parallel research paths, both characterized by promising preliminary results. Biopolymer production from WCO is also the most extensively explored application, accounting for approximately 53% of the examined studies. However, when performance metrics are examined, some differences emerge. Yield values are reported using non-uniform definitions (mass yield, carbon yield, polymer content), and volumetric productivity is rarely provided. An important exception is the recent work by Jiang et al., 2025 [34], which used engineered *Cupriavidus necator* H16 for PHA production, reporting 94.9% polymer content and a 150 m^3 production scale. This represents one of the few cases in which a large industrially relevant scale is reported. In contrast, most other studies remain confined to laboratory systems, limiting cross-comparison and techno-economic interpretation. For chemical routes to biopolymer production, yields approaching 100% are reported in several studies; however, these values are generally obtained at bench scale. The lack of consistent reporting of volumetric productivity (g/L·h), and full mass balance closure makes it difficult to assess real industrial competitiveness despite the high conversion efficiencies.

Bioplasticizers, accounting for 31% of the analyzed studies, are produced exclusively through chemical transformation pathways. Yields up to 98% have been reported in Tan, 2019 [86] in 500 mL reactors, and Table 3 indicates a maximum reported working scale of 1000 g. Although these data demonstrate technical feasibility and high reaction efficiency, the persistence of small-scale batch systems suggests that scale-up and process intensification remain critical research needs.

A similar difference is observed for biolubricants. Biotechnological approaches are limited to only six studies (five conducted in Brazil and one in China), clearly indicating an early-stage research field. Reactor scale is often not specified; where reported, volumes remain limited to 2 L [99] and 100 mL [97]. These data confirm that TRY parameters (Titers, Rates, Yields) and scale-up considerations are still insufficiently explored for enzymatic and microbial routes.

In contrast, chemical routes for biolubricant production are more widely represented (22 studies), with reported yields generally around 90%. Nevertheless, scale information is

frequently absent or limited to laboratory volumes. An interesting example is the Italian study by Mannu et al. (2019) [114], describing a 50 L water degumming process without a catalyst for regenerated oil production; however, conversion yield is not explicitly reported. This recurring lack of integrated TRY data highlights the need for more standardized performance reporting.

In the research of technological maturity, already discussed in the previous section, it becomes evident that high yield alone cannot be considered a sufficient indicator of industrial readiness. The systematic integration of quantitative performance metrics (Titer, Rate, Yield), together with explicit scale declaration and operating conditions, is essential to bridge the gap between laboratory feasibility and industrial deployment. Furthermore, regulatory constraints and potential contaminant monitoring must be clarified to prevent bottlenecks during market translation. Proper techno-economic analysis (TEA), supported by robust and standardized process data, will be necessary for research targeting higher TRLs.

Future research efforts should prioritize quantitative and scalable process validation over incremental improvements in yield under laboratory conditions. The following research directions are identified as priorities: (a) standardized TRY reporting, including explicit definition of yield basis (mass, molar, or carbon), titer (g/L), volumetric productivity (g/L·h), and mass balance closure to enable cross-study comparability; (b) scale progression beyond bench systems, through pilot-scale validation and process intensification strategies; (c) integration of TRY data with TEA and LCA frameworks, ensuring that performance metrics support industrial modeling and investment assessment; (d) systematic evaluation of regulatory constraints and contaminant monitoring, particularly for polymeric materials and additives intended for consumer applications; and (e) deeper incorporation of green chemistry principles in chemical transformations, targeting reductions in catalyst loading, solvent use, and energy demand. Figure 13 represents a scheme of the proposed future trends.

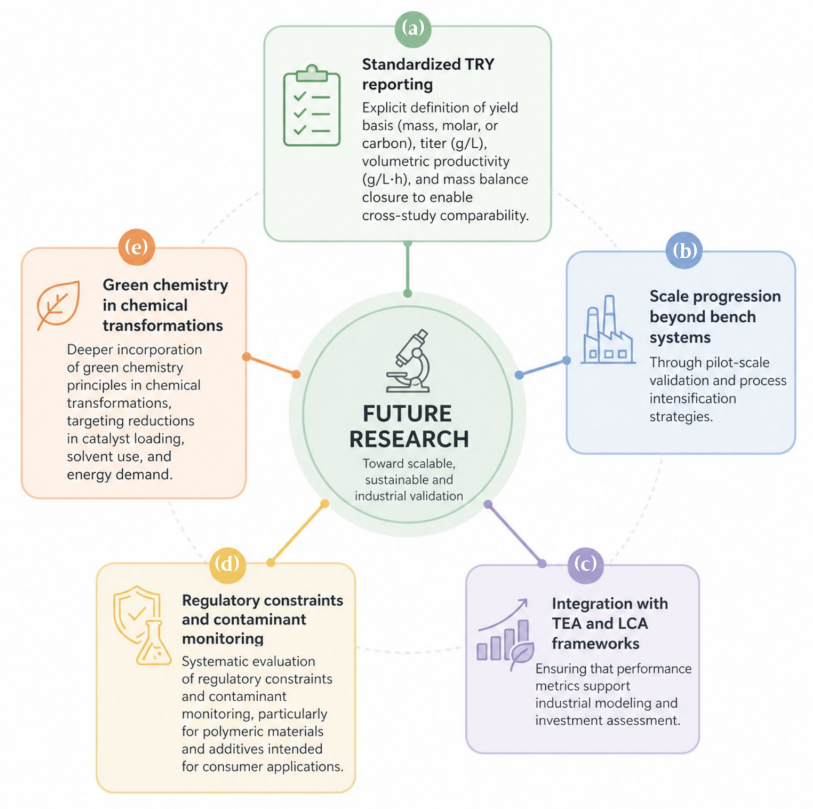

Figure 13. Future trends.

Advancing WCO valorization toward industrial consolidation will require a shift from proof-of-concept demonstrations to quantitatively benchmarked, reproducible, and scalable processes. Establishing harmonized performance metrics and explicitly linking laboratory data to industrial design criteria represents the critical step for the maturation of this.

7. Conclusions

Waste cooking oils represent an interesting and sustainable feedstock for the production of biopolymers, bioplasticizers, and biolubricants. The range of applications is extensive and reflects an emerging trend in the valorization of WCOs as green alternatives to fossil-based processes. Considering the critical analysis of the selected studies, used vegetable oils (WCO) can actually be valid substitutes, especially in the commercial PHA production sector, while they seem to be potential resources for the future in the other industrial fields covered. This increasing interest is supported by the substantial growth of scientific literature over the past decade. From the initial screening, approximately 2457 works were identified. Although many of these studies did not meet the eligibility criteria for inclusion in the present paper, a large proportion nonetheless addressed WCOs either partially or indirectly, highlighting the broad and multidisciplinary attention to these feedstocks. In conclusion, while this review provides a comprehensive synthesis of the current literature, certain methodological limitations must be acknowledged to contextualize the findings. This review, using a systematic and targeted approach to TRL analysis, fills the gaps left by previous reviews. The systematic selection process resulted in the exclusion of a substantial corpus of documents based on the predefined inclusion and exclusion criteria, which may have constrained the breadth of the analysis. Furthermore, the presence of publication bias—specifically the systematic tendency to under-report negative or non-significant experimental outcomes—remains a critical variable. This is compounded by the inherent heterogeneity of the experimental methodologies encountered, which complicates a direct comparative assessment of performance metrics. Given the rapid evolution of the bio-based chemical sector, it is recommended that this review be updated within a five-year horizon. Such an iterative approach will be essential to refine the current conclusions and to monitor the technological advancements in the conversion of waste cooking oil (WCO) into high-value biopolymers, bioplasticizers, and biolubricants.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/cleantechnol8030090/s1: Table S1: PRISMA 2020 for Abstracts Checklist; Table S2: PRISMA 2020 checklist.

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