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Waste Cooking Oil as Eco-Friendly Rejuvenator for Reclaimed Asphalt Pavement

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Abstract: Over 50 MioT of Waste Cooking Oil (WCO) was collected worldwide in 2020 from domestic and industrial activities, constituting a potential hazard for both water and land environments, and requiring appropriate disposal management strategies. In line with the principles of circular economy and eco-design, in this paper an innovative methodology for the valorisation of WCO as a rejuvenating agent for bitumen 50/70 coming from Reclaimed Asphalt Pavement (RAP) is reported. In particular, WCO or hydrolysed WCO (HWCO) was modified by transesterification or amidation reactions to achieve various WCO esters and amides. All samples were characterised by nuclear magnetic resonance, melting, and boiling point. Since rejuvenating agents for RAP Cold Mix Asphalt require a melting point $\leq 0\ ^{\circ}C$, only WCO esters could further be tested. Efficiency of WCO esters was assessed by means of the Asphaltenes Dispersant Test and the Heithaus Parameter. In particular, bitumen blends containing 25 wt% of WCO modified with 2-phenylethyl alcohol, showed high dispersing capacity in *n*-heptane even after a week, compared to bitumen alone (1 h). Additionally, the Heithaus Parameter of this bitumen blend was almost three times higher than bitumen alone, further demonstrating beneficial effects deriving from the use of WCO esters as rejuvenating agents.

Keywords: waste cooking oil; reclaimed asphalt pavement; waste valorisation; circular economy

1. Introduction

Waste Cooking Oil (WCO) is a domestic and industrial waste obtained from food cooking [1]. The term WCO generically refers to frying oil used at high temperatures and edible fats mixed with food waste and water, which can no longer be used for cooking [2]. WCO is prevalently obtained from household, commercial, and industrial by-products, and derives mainly from palm, soybean, canola, sunflower, peanut, cottonseed, coconut, olive, and corn oil [3].

Without proper disposal, WCO is highly polluting for both water and land environments, requiring appropriate disposal management [4]. It is important to note that WCO annual production and recovery methods vary consistently, making estimations of WCO yearly collection difficult. For example, according to European Union (EU) estimations, around 8 L WCO/capita/year should be collected, which, considering a total EU population of around 500 million, corresponds to 4 Miot/year of WCO. As a matter of fact, these data are seven times higher than the current collected amount in the EU, clearly evidencing the gap between produced and collected WCO [5]. This considered, in 2020, the amount of WCO collected worldwide was about 50 Miot [2,6–8], of which Europe was responsible for approximately 1 Miot [9]. The United States is the world's leading producer of WCO [10] with 10 Miot/year collected, followed by China, where between 40 and 60% WCO is not disposed of or is illegally reused in kitchens [2]. Despite this, the Chinese government is making efforts to promote the correct disposal and reuse of WCO to produce biodiesel

and has promulgated several regulations, including Regulations on Waste Cooking Oil Management, promoting WCO recovery and recycling [2].

As far as the EU is concerned, starting from the 1970s, with the waste oil directive 75/439/EEC, the European Commission committed to collecting used oil in order to limit environmental damage and promote recovery and recycling technologies and any derived markets. Recently, all EU member states have undersigned the Renewable Energy Directive, in which they committed to enhance the use of WCO for biofuels from 3.5% to 5.5% by 2023 [11].

Italy produces approximately 260.000 t/year of WCO at the industrial level (restaurants, catering), which are collected by CONOE (National Consortium for the collection and treatment of used oil), and used for the production of soaps, additives for lubricating oils, and biodiesel [12]. On the contrary, the proper recovery and disposal of WCO produced at the domestic level is on a voluntary basis; therefore, WCO may be released into the sewer system.

Adequate collection of WCO is not only beneficial for the environment but is also economically advantageous since WCO can be used to obtain biofuels and other high-value chemicals [13,14]. The need to recover and recycle by-products or end-of-life products, reducing primary resource consumption, is becoming increasingly urgent, leading to a change from a linear economy based on a "take-make-discard" model to a circular economy based on green chemistry and eco-design [15–20].

Although WCO is mainly employed at the industrial level for the production of biofuels, due to its similar elemental composition to petroleum, it has also received considerable attention for its potential use as fluxing or rejuvenating agent for aged bitumen [21,22]. According to Uz and Gökalp, the use of WCO rejuvenating agents has beneficial effects on aged bitumen recovered from Reclaimed Asphalt Pavement (RAP) that would otherwise be discarded [21].

The presence of variable quantities of free fatty acids (FFAs) is responsible for increasing acidity content in WCO which influences its performances. Specifically, when WCO is employed for the production of bitumen blends, acidity content negatively influences the interaction between WCO and bitumen [20,21]. Reducing the FFAs in WCO by pretreatment techniques such as esterification or refining processes can promote the overall performance of WCO-modified bitumen. Although the use of WCO as additive for bitumen modification has been previously reported in the literature [23,24], only a few studies report the possibility to achieve higher performances, using chemically modified WCO by transesterification [25,26]. In particular, Oldham and coworkers recently reported that a reduction in WCO acidity content by transesterification with methanol significantly improved its efficiency for the production of bitumen blends employed as rejuvenators for RAP, improving asphalt recycling [26]. Similar results were also reported by Wan Azahar and coworkers with WCO prepared by alkali-promoted esterification in the presence of methanol [27].

Within this panorama, the aim of this work is to study a wide range of chemical modifications of WCO by transesterification or amidation reactions with aliphatic and aromatic alcohols or amines, having alkyl chains of variable length (Figure 1) [28].

All products prepared were characterised by ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) and their determined melting and boiling points. Preliminary data to determine the efficacy of WCO modified by transesterification and amidation as rejuvenating agents for aged bitumen were found by using the Asphaltene Dispersant Test and the measurement of Heithaus Parameter.
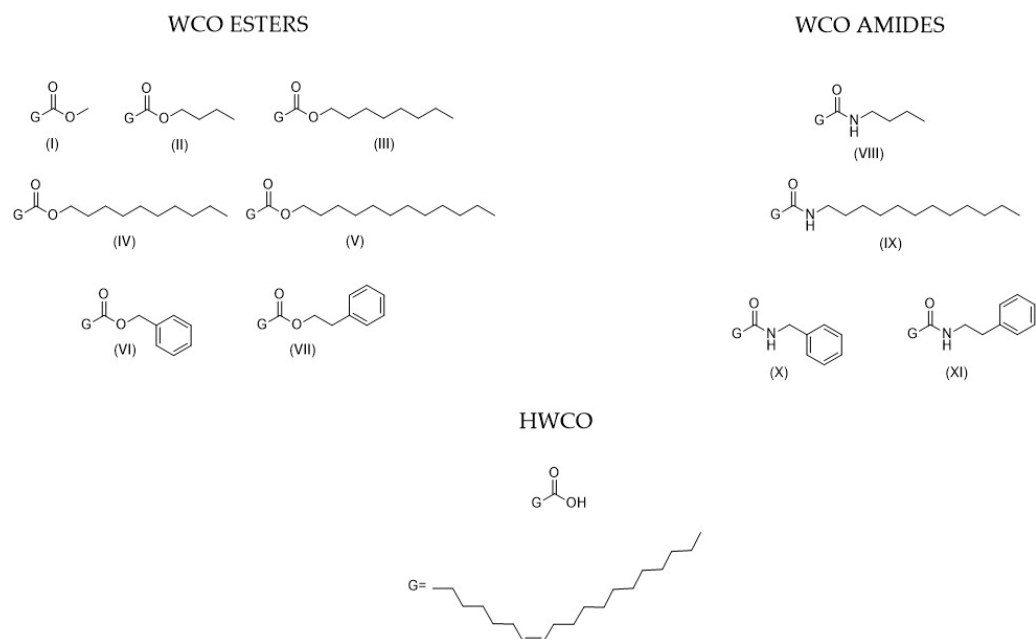
Figure 1. Esters and amides obtained from chemical modification of WCO and HWCO (Hydrolysed WCO).

2. Materials and Methods

2.1. General Remarks

All commercially available reagents, solvents and chemicals were provided by Sigma Aldrich (Milan, Italy) and used as received. WCO was delivered by Elite Ambiente (Grisignano di Zocco, VI, Italy). Aged bitumen was extracted from RAP, a kind gift from IFAF Spa (Noventa di Piave, Italy). ^{1}H and ^{13}C NMR spectra of the products were registered on a Bruker Ultra Shield 400 spectrometer operating at 400.0 and 101.0 MHz, respectively, and are reported in the Supplementary Materials. Nuclear Magnetic Resonance (NMR) spectroscopy is an analytical technique used to determine the content and purity of a sample as well as its molecular structure. A picture of a Bruker Ultra Shield 400 NMR spectrometer is reported in Figure 2 (left) Melting points were measured with a Stuart Scientific SMP3 (Figure 2 center). Samples were loaded into a sealed capillary tube, which was then placed in the apparatus. The sample was then heated with an oil bath and, as temperature increases, the sample is observed to determine when the phase change from solid to liquid occurs.
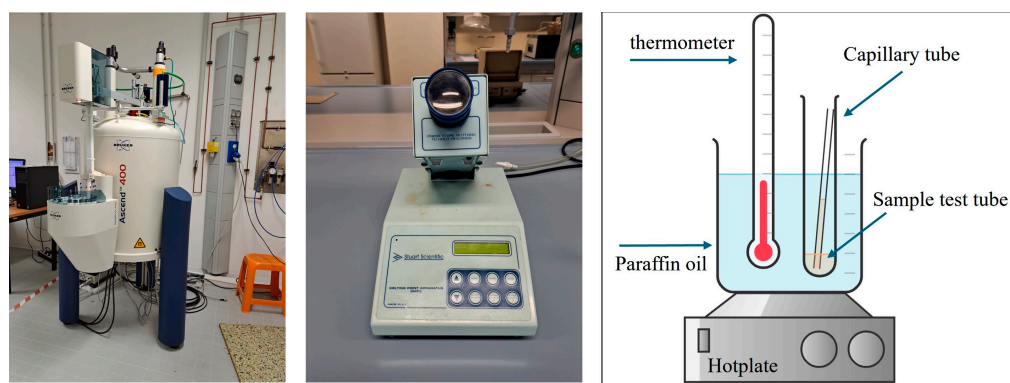

Figure 2. Pictures of a Bruker Ultra Shield 400 NMR spectrometer (**left**), a Stuart Scientific SMP3 melting point apparatus (**center**) and apparatus set up for boiling point determination (**right**).

Boiling points were measured according to the Capillary Method [29]. Samples were placed in a capillary, sealed at one end, and opened at the other. The capillary was placed in a liquid with the open side facing downwards and heated. As the temperature increases, the air in the capillary escapes and is replaced by the vapor of the liquid and vapor pressure in the capillary increases. Once it exceeds the atmospheric pressure, the vapor escapes the capillary in a stream of bubbles. When the heat is removed, the liquid cools, and the vapor pressure in the capillary decreases. When the vapor pressure reaches the atmospheric pressure, the liquid begins to fill the capillary. The temperature at which this occurs is the boiling point. The apparatus set up for boiling point by capillary method is reported in Figure 2 right.

2.2. Cooking Oil Purification and Chemical Modification

Prior to chemical reactions WCO was purified as follows: to a 1 L bottom round flask, equipped with a magnetic stirrer, 500 g of WCO, 30 g of activated charcoal DARCO®, 100 mesh particle size, powder (6 wt%), and 130 mL dichloromethane (CH_2Cl_2) (35 wt%) were added and stirred for 3 h at room temperature. Then, WCO was filtered on paper to remove solid cooking residues and activated charcoal, and dichloromethane was evaporated [30]. Purified WCO, recovered in the form of an amber-coloured liquid, was characterized by ^1H NMR, and ^{13}C NMR (see Supplementary Materials).

2.2.1. Transesterification of WCO

Seven different esters were prepared by transesterification of WCO with seven different alcohols, specifically methyl, *n*-butyl, octyl, decanoyl, dodecyl, benzyl, and phenylethyl alcohol (Scheme 1). The general synthesis procedure is as follows: to a 250 mL round bottom flask, equipped with a magnetic stirrer, 5 g of purified WCO and 20 wt% of the selected alcohol were added and stirred for 5 min at room temperature. Then, 0.87 g (16.2 mmol) of sodium methoxide was added and the temperature was raised to that of the alcohol boiling point for 2 h for (**I**), 4 h for (**II**), 48 h for (**III**), and (**IV**) and 24 h for (**V**), (**VI**), and (**VII**) [31]. The crude products were poured in dichloromethane and washed with brine, then the organic phase was dried over anhydrous magnesium sulphate. After filtration and solvent evaporation under reduced pressure, the products were obtained in yields between 60 and 98%, depending on the alcohol employed (see Table 1). Purified products were characterised by ^1H NMR and ^{13}C NMR in $CDCl_3$ (see Supplementary Materials). Melting and boiling points were measured and are reported in Table 1.

Table 1. Reaction conditions and yields for the synthesis of WCO esters and amides and boiling/melting points.

	Product	Optimum Reaction Condition	Yield (%)	b.p. (°C)	m.p. (°C)
		Esters [a]			
CH_3OH	**I**	65 °C, 2 h	72	>200	0.6
n-C_4H_5OH	**II**	118 °C, 4 h	50	>200	0.6
$C_8H_{17}OH$	**III**	188 °C, 48 h	58	>200	0.4
$C_{10}H_{21}OH$	**IV**	235 °C, 24 h	34	>200	0.4
$C_{12}H_{25}OH$	**V**	250 °C, 24 h	34	>200	0.3
$PhCH_2OH$	**VI**	205 °C, 24 h	36	>200	0.2
$PhCH_2CH_2OH$	**VII**	225 °C, 24 h	34	>200	0.2
		Amides [b]			
n-$C_4H_5NH_2$	**VIII**		69	>200	48
$C_{12}H_{25}NH_2$	**IX**	110 °C, 48 h	44	>200	73
$PhCH_2NH_2$	**X**		92	>200	90
$PhCH_2CH_2NH_2$	**XI**		54	>200	92

[a] Reaction Conditions: Solvent: neat; alcohol to WCO weight ratio: 1/5; Catalyst: NaOMe. [b] Reaction Conditions: Solvent: Toluene; toluene to HWCO weight ratio 7/1; amine to HWCO weight ratio: 1/5.
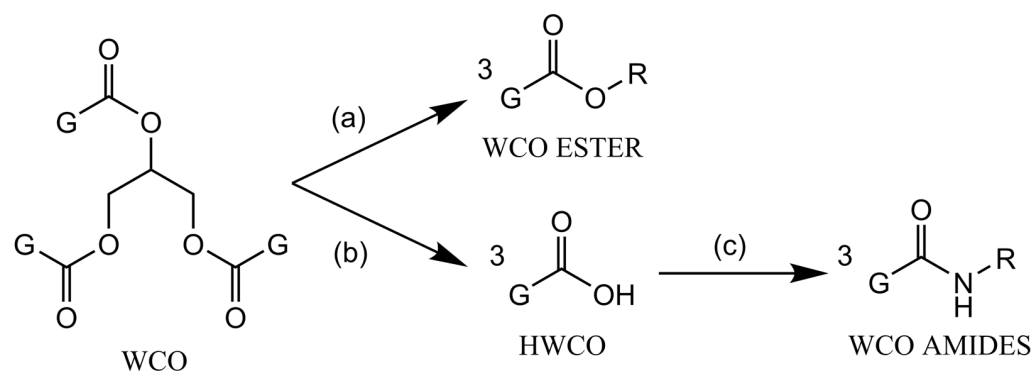
Scheme 1. Synthetic strategies for the preparation of WCO esters and amides. (**a**) ROH, NaOMe, neat, reflux; (**b**) NaOH 4.5 M, 60 °C, 8 h/HCl 5 M; (**c**) RNH$_2$ in toluene, 110 °C, 48 h, Dean–Stark apparatus.

2.2.2. Purified WCO Hydrolysis

For amidation reactions, WCO was first hydrolysed to obtain the free fatty acid structure (HWCO) and then amidated with different types of amines: *n*-butyl, dodecyl, benzyl, and phenylethyl amine (Scheme 1). The general synthesis procedure is as follows: to a 100 mL round bottom flask, equipped with a magnetic stirrer, 20 g of purified WCO and 3.6 g of a 4.5 molar concentration water solution of sodium hydroxide (NaOH 4.5 M) were added and stirred for 8 h at 60 °C. Then, hydrochloric acid (HCl) 5 M was added until pH 2–3 was reached. Then, the aqueous mixture was washed with diethyl ether, the organic fraction collected and dried over anhydrous magnesium sulphate. After filtration and solvent removal under reduced pressure, a white solid product was obtained in a 67% yield.

2.2.3. Amidation Reactions

Amidation reactions were carried out employing a Dean–Stark Apparatus (Figure 3). A Dean–Stark apparatus is used in combination with a reflux condenser and a distillation flask for the separation of water from other solvents presents (for example toluene). A Dean–Stark apparatus allows continuous removal of the water produced during esterification reactions carried out at reflux temperature, promoting the formation of products [32].
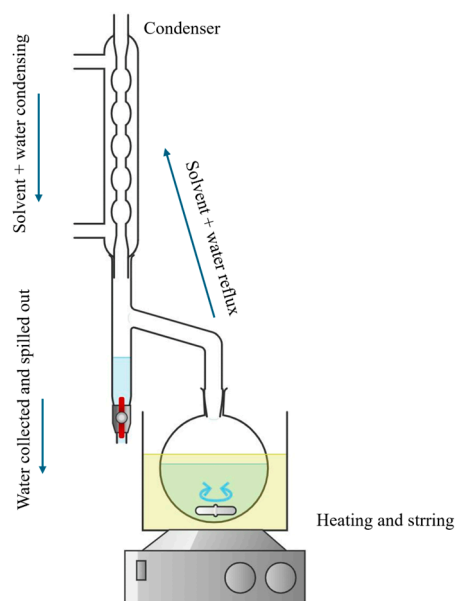

Figure 3. Dean–Stark set up for the transesterification of purified WCO.

The procedure employed was the same both for aliphatic and aromatic amines (Scheme 1). To a 50 mL round bottom flask, equipped with a magnetic stirrer and Dean–Stark apparatus, 2.5 g of hydrolysed WCO was dissolved in 50 mL of toluene. Then, 20 wt% of the selected amine were added and stirred at reflux for 48 h. Toluene was evaporated and the crude solid product poured into dichloromethane, washed three times with NaOH 1 M, and two times with distilled water. The organic fraction was then dried over anhydrous magnesium sulphate. After filtration and solvent removal under reduced pressure, a solid product was obtained in yields between 45 and 92% depending on the type of amine employed (see Table 1). Purified products were characterised by ^{1}H NMR and ^{13}C NMR in CDCl$_3$ (see Supplementary Materials). Melting and boiling points were measured and are reported in Table 1.

2.2.4. Asphaltene Dispersant Test (ADT)

WCO esters were added with a weight ratio of 25 wt% by the weight of aged bitumen 50/70 [33]. RAP employed in this work was derived from asphalt prepared with bitumen 50/70, paved, and reclaimed by IFAF S.p.a. Aged bitumen was recovered from RAP by Soxhlet extraction at 40 °C for 4 h with dichloromethane. According to the literature [34,35], all aged bitumen blends were stirred at 500 rpm with a magnetic stirrer to homogenise the components; consequently, 0.6 mL of the mixture was dissolved in 19.4 mL of *n*-heptane. A sample of crude bitumen was used as reference. All specimens were introduced into graduated centrifuge tubes and left standing for a specific period of time, also called aging time (1 h, 24 h and 1 week). The rejuvenating effect of WCO esters was determined by comparing the translucency of the glass and the amount of sediment at different aging times with respect to the reference bitumen.

2.2.5. Heithaus Parameter Measurement

This method was developed by Heithaus [36,37] to predict the stability of aged bitumen and heavy crude oils. A selected amount of bitumen is dissolved in different volumes of toluene and *n*-heptane is added until flocculation occurs. Flocculation point is monitored by deposing few drops of the titrated solution on filter paper; if a dark precipitate inside the drop on the filter paper is observed, the flocculation point is achieved. Once the volume of *n*-heptane needed for flocculation is known (V_t, mL), the concentration of bitumen in the total volume (C, g/mL) and flocculation ratio (FR) can be calculated according to Equation (1):

$$C = \frac{W_A}{V_s + V_t} \text{ , } FR = \frac{V_s}{V_s + V_t} \tag{1}$$

where W_A (g) corresponds to the mass of the aged bitumen weighted, and V_S (mL) corresponds to the volume of toluene introduced into the solution. C and FR data are plotted, and C_{min} and FR_{max} are determined (see Supplementary Materials). C_{min} is the onset of asphaltene precipitation (OAP, mL/g) corresponding to the minimum volume of *n*-heptane causing bitumen precipitation in the absence of toluene [36,38]. FR_{max} corresponds to the ratio of solvent to titrant at which bitumen is soluble in all concentrations. Thus, P_α, P_0, and P are measured, according to Equations (2)–(4):

$$P_a = 1 - FR_{max}, \tag{2}$$

$$P_0 = FR_{max} \cdot \left[\frac{1}{C_{min}} + 1 \right], \tag{3}$$

$$P = \frac{P_0}{1 - P_a} \tag{4}$$

P_α and P_0 correspond to asphaltenes and maltenes solubility, respectively, and allow us to calculate P, the Heithaus Parameter. If P > 1, the bitumen is stable and does not flocculate, while if P < 1, bitumen is not stable and flocculates. For the measurement, 1 g of aged bitumen (with or without 25 wt% of WCO ester) was dissolved in 1.00 mL, 1.25 mL,

1.50 mL, and 2.00 mL of toluene and titrated with *n*-heptane until the flocculation point of the asphaltenes was reached. Tests were performed in triplicate. Calculations are reported in the Supplementary Materials.

3. Results and Discussion

Oil mixtures received from Elite Ambiente derive from industrial or household operations and contain different commercially available vegetable oils. Due to the variability in WCO, no analytical characterization of the mixture was carried out to determine the composition of the specific batch under analysis, and all the data reported in this paper refer to tests carried out with the same sample of WCO [39–45]. Pictures of WCO, HWCO, and chemically modified WCO are reported in Figure 4.
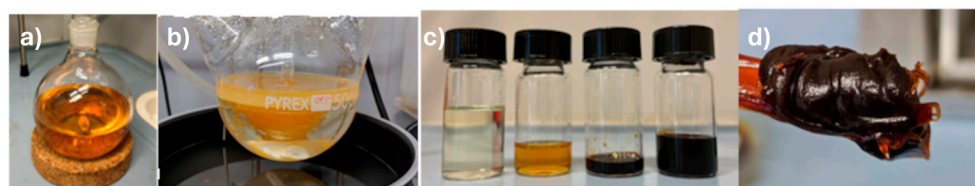

Figure 4. Pictures of purified WCO (**a**), WCOH (**b**), methyl, butyl, octyl, and dodecyl WCO esters (**c**) and butyl amide (**d**).

3.1. WCO Chemical Modification

Purified WCO was chemically modified according to the two different strategies reported in Scheme 1. The first one foresees direct transesterification of purified WCO to obtain different esters, the latter instead requires two steps, i.e., hydrolysis of WCO (HWCO) carried out with a Dean–Stark apparatus (see Section 2) followed by amidation to obtain different amides.

WCO hydrolysis was carried out in the presence of an aqueous solution of NaOH 4.5 M at 60 °C [46], and after work up HWCO was recovered with 70% yield.

Esters were prepared by the transesterification reaction, mixing WCO with an alcohol at reflux temperature for several hours (see Table 1) [46]. For WCO esters, the highest yields were obtained from the reaction of WCO with methanol due to its reduced steric hindrance and high nucleophilicity, while decanol, benzyl alcohol, and phenylethyl alcohol were partially recovered unreacted even if reaction times were prolonged up to 24 h (see Table 1).

Amides, instead, were prepared by reacting HWCO with an amine in toluene at reflux, for 48 h. In agreement with the literature highest yields in WCO amides were achieved in the presence of benzylamine or phenethylamine (see Table 1), because of their higher nucleophilicity compared to other amines tested [47,48]. As mentioned above, in this work for all WCO additives, melting and boiling points were measured and are reported in Table 1. From these data, it emerges that all additives have similar boiling points (>200 °C), while melting points differ significantly between esters and amides. In fact, WCO esters all have melting points around 0 °C, while WCO amides have higher m.p., ranging between 48 °C and 92 °C (see Table 1).

These higher temperatures are probably to be ascribed to the hydrogen bonds that are established between the protons and the nitrogen electron pairs in the amides [34]. Since it is widely known from the literature that solid additives cannot be used for Cold Mix Asphalt preparation, WCO amides were not further investigated for this application. Amides could be suitable for Warm Mix Asphalt and Hot Mix Asphalt, and thus future studies will focus on this application.

On the contrary, thanks to their low melting point, WCO esters appeared to be interesting candidates as additives for Cold Mix Asphalt preparation, and so tests for this specific application were performed.

Based on their different applications, asphalts can be classified into Hot Mix Asphalt (HMA), Warm Mix Asphalt (WMA), and Cold Mix Asphalt (CMA) [49,50]. Considering costs and environmental sustainability [51], CMA is considered to be highly efficient since it requires lower processing temperatures (between 0 °C and 40 °C) and easily available equipment. Since prevention, recycling and reuse is highly encouraged to face the existing environmental issues of waste generation [52], CMA appears to be particularly interesting since it allows recycling of reclaimed asphalt pavement (RAP). RAP is obtained from the removal of aged road pavement and thus its reuse generates both environmental and economic advantages [53,54]. Babashamsi et al. highlighted that by incorporating between 30 wt% and 50 wt% RAP into CMA, savings of up to USD 58,000/km may be achieved [55]. Asphalt mixtures consist of two valuable non-renewable resources [56], both subject to aging processes: aggregates and bitumen. Aggregates are inert rock materials which reduce the amount of bitumen required in the asphalt preparation and can have different grain sizes such as sand and crushed stone [57]. Bitumen is a viscous fluid in which aggregates of polar macromolecules (asphaltenes) are dispersed in a more apolar continuous phase (maltenes). This fraction is composed of aromatics, resins, and saturates which, during asphalt processing, undergo different chemical modifications [58–60]. In fact, when bitumen is mixed with aggregates [49,61,62] to produce asphalt for pavement constructions, it starts to age and loses its original physical mechanical characteristics. Polymerization and oxidation [63] reactions are among the main causes for maltenes reduction, which results in aggregation into larger macromolecules [58,64]. This process stiffens the material, making it more brittle [58].

Rejuvenating additives may help to solve this problem, promoting recycling and reuse of aged bitumen contained into RAP. These additives are mostly amphiphilic molecules composed of a non-polar tail and a highly aromatic polar head [24]. Their amphiphilic nature contributes to reduce bitumen aging since their polar head interacts with asphaltene aggregates de-agglomerating them, while their non-polar tail enriches the maltenes fraction [34,61], replenishing the volatiles and renewing the chemical–physical characteristics of bitumen [24,65].

Within this panorama, all WCO ester additives synthesised in this paper are potentially rejuvenating agents for aged bitumen, possessing both polar head and a non-polar tail (WCO) together with a low melting point. Preliminary evaluations on the use of WCO esters was carried out with additives (**II**), (**VI**) and (**VII**) to verify their potential rejuvenating properties by the Asphaltenes Dispersant Test [34] and the measurement of the Heithaus Parameter [36].

3.2. Asphaltene Dispersant Test (ADT)

To evaluate the rejuvenating efficacy of additives (**II**), (**VI**), and (**VII**), the precipitation of the asphaltenes fraction present in aged bitumen was observed after one hour, one day, and one week (see Figure 5), and compared to the reference. According to the Asphaltene dispersant test, a rejuvenating agent reduces flocculation phenomena and improves the dispersion of aged bitumen in *n*-heptane [34]. As shown in Figure 5, after just 1 h, asphaltenes present in aged bitumen alone begin to precipitate, occupying a volume of 0.5 mL into the reference tube. On the contrary, after 1 h, bitumen samples containing 25 wt% of ester (**II**), (**VI**) and (**VII**) occupy a higher volume (about 1 mL), indicating an improved dispersion efficiency. After one day, no variation was observed in tubes containing the reference sample and aged bitumen blend with additive (**VII**), while asphaltenes occupied a lower volume in tubes containing additives (**II**) and (**VI**) (approximately 0.7 mL).

After one week, no significant variations were observed in the reference tube, while the volume occupied by the precipitated asphaltenes was further reduced to 0.5 mL in tubes containing additives (**II**) and (**VI**). Interestingly, in samples containing additive (**VII**), asphaltenes occupied a volume of 0.7 mL, suggesting an improved dispersing capacity of this additive even after a week. It may be supposed that due to its aromatic nature, additive (**VII**) reintegrates the maltene fraction in the aged bitumen, with a potential

rejuvenating effect. Additionally, properties shown by (**VII**) could be ascribed to the fact that, compared to (**VI**), the ester moiety is further away from the aromatic ring and, therefore, less encumbered [34]. Further tests were thus carried out only on best performing additive (**VII**).
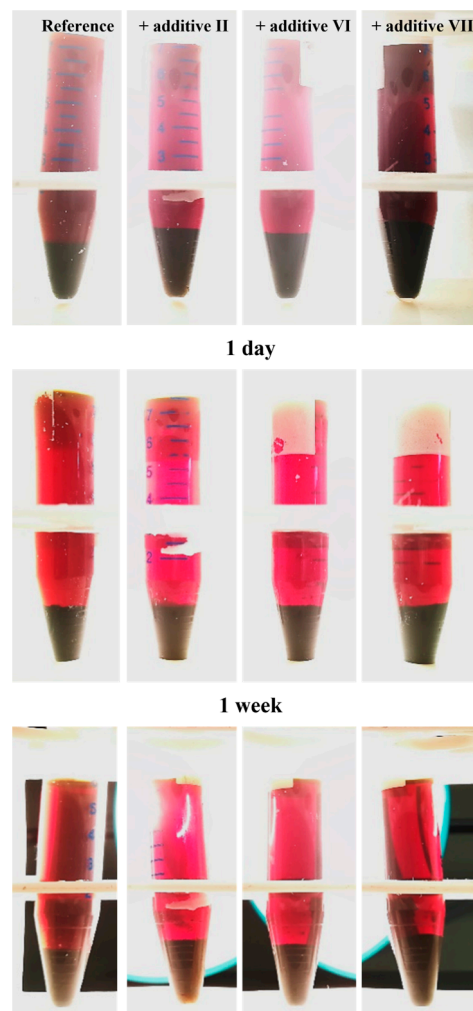

Figure 5. Deposition of asphaltenes observed after 1 h, 1 day, and 1 week in *n*-heptane; from left to right: aged bitumen (reference), aged bitumen enriched with 25 wt% of additive (**II**), aged bitumen enriched with 25 wt% of additive (**VI**), and aged bitumen enriched with 25 wt% of additive (**VII**).

3.3. Calculation of the Heithaus Parameter

The Heithaus parameter (P) provides information on the stability of aged bitumen and of the aged bitumen blends enriched with an additive, giving indications on whether the mixture is in equilibrium or tends to flocculate. To measure P, two different sets of experiments were carried out and compared: the first one was performed on a sample of crude aged bitumen, and the second one on a sample of aged bitumen enriched with 25 wt% of additive (**VII**) by weight of bitumen. The Heithaus Parameter (P) is measured by Equations (1) and (2), together with linear correlation, as described in the experimental section. If P > 1, the bitumen is stable and does not flocculate, while if P < 1, bitumen is not stable and flocculates. From these experiments, it was possible to determine that the Heithaus Parameter for aged bitumen is of 1.48, while when additive (**VII**) was present, the Heithaus parameter increased to 2.73 (see Supplementary Materials). This value is almost double compared to that of the aged bitumen alone, indicating that additive (**VII**) is a rejuvenating agent, improving aged bitumen stability.

4. Conclusions

In conclusion, in this paper, an innovative methodology for the modification of WCO was reported together with its use as rejuvenating agent for asphalt pavement. In particular, a set of different alcohols and amines were used to modify WCO or hydrolysed WCO (HWCO) by transesterification or amidation reaction. All WCO and HWCO derivatives were characterised by ^{1}H and ^{13}C NMR. Melting and boiling temperatures of WCO derivatives were used to select potentials of rejuvenating agents to be used for RAP recycling for Cold Mix Asphalt production. Since only compounds with m.p. $\leq 0\,^{\circ}$C may be used for the scope, only WCO esters (**II**, **VI,** and **VII**) were further tested by the Asphaltenes Dispersant Test [34] and the Heithaus Parameter [35], to verify their efficiency as rejuvenating agents. From these experiments, it emerged that additive (**VII**) highly improved the dispersing capacity of bitumen in *n*-heptane even after a week, compared to the reference sample (1 h). Additionally, the Heithaus Parameter of bitumen blends containing 25 wt% of WCO modified with 2-phenylethyl alcohol (**VII**) was almost three times higher than bitumen alone, further confirming that (**VII**) has good potential efficiency as a rejuvenating agent. These results are very encouraging and indicate that WCO may be transformed into a valuable starting material for the production of bio-based rejuvenating agents for asphalt pavement production. Further studies will be carried out on asphalt pavement prepared with aged bitumen blends reported in this work in order to assess the influence on surface texture and noise emissions [66]. Additionally, further tests are ongoing to achieve information on the efficiency of WCO amides for Hot Mix Asphalt modification.

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