



Article Characterization of Asphalt Binders Modified with Bio-Binder from Swine Manure

Jaume Gasia¹, Teresa López-Montero²,*^D, Lola Vidal¹, Rodrigo Miró², Christophe Bengoa³, and Adriana H. Martínez²

- ¹ JA Romero Polo SA, 25007 Lleida, Spain; jgasia@romeropolo.com (J.G.); lvidal@papsa.es (L.V.)
- ² Road Research Laboratory, Universitat Politècnica de Catalunya-Barcelona Tech, 08034 Barcelona, Spain; r.miro@upc.edu (R.M.); adriana.martinez@upc.edu (A.H.M.)
- ³ Departament d'Enginyeria Química, Universitat Rovira i Virgili, 43002 Tarragona, Spain; christophe.bengoa@urv.cat
- * Correspondence: teresa.lopez@upc.edu; Tel.: +34-93-401-72-71

Abstract: Asphalt is an essential material in the construction of asphalt pavements. Due to its high demand and dependence on petroleum, it is crucial to use greener materials that can fully or partially replace petroleum-based binders. The characteristics of asphalt cause the bio-binder obtained through a hydrothermal liquefaction process from swine manure to have great potential to be used as a modifier due to its similarities with asphalt, contributing to the construction of more sustainable roads. Thus, this paper characterizes an asphalt binder modified with a new bio-binder obtained from swine manure at different rates (0%, 10%, and 20%). Several characterization tests were performed, including penetration, ring and ball, Fraass, viscosity, Cleveland open cup, and the UCL method. Furthermore, the possible leaching of the bio-binder was studied, showing no environmental problems. Results from the rheological tests showed that as the content of bio-binder increases, the softening temperature, Fraass breaking point, and viscosity of the bio-modified asphalt binder decrease, indicating the lower consistency of the bio-modified binder and its greater thermal susceptibility.

Keywords: bio-binder; asphalt; asphalt mixture; swine manure; hydrothermal liquefaction

1. Introduction

Bitumen is an essential component in asphalt mixtures manufacturing that is in high demand. The production of one metric ton of asphalt mixture requires an energy consumption between 21 and 28 kgce [1]. This high energy consumption, in addition to the current price of energy and the dependence on petroleum-derived products, results in the road construction sector having high costs that limit its competitiveness. The environmental cost in terms of carbon footprint, energy consumption, and raw-material consumption must be considered. Thus, the carbon footprint due to the production of one ton of asphalt mixture ranges from 70 to 95 kg CO_2 eq. [2].

An approach to reduce the environmental and economic costs in asphalt pavement manufacturing is to decrease the consumption of petroleum-based asphalt binders [3]. This could be carried out by using greener binders, called bio-binders, which allow the total or partial substitution of petroleum-based asphalt binders. To produce this green binder, so-called bio-materials are used, which come from recycled materials, co-products, or waste [4], such as organic matter. Thus, recent research shows that the properties of the produced bio-binders are similar to those of petroleum-based binders and, therefore, could be used in the field of asphalt mixtures [5–9].

Livestock manure is the excrement and waste materials excreted by livestock, or the mix of bedding with residual materials, which acquire different names depending on their origin and dry-matter content (poultry manure or swine manure) [10]. Traditionally,



Citation: Gasia, J.; López-Montero, T.; Vidal, L.; Miró, R.; Bengoa, C.; Martínez, A.H. Characterization of Asphalt Binders Modified with Bio-Binder from Swine Manure. *Appl. Sci.* 2023, *13*, 11412. https://doi.org/ 10.3390/app132011412

Academic Editors: Richard Critchley, Rachael Hazael and Syed Minhaj Saleem Kazmi

Received: 15 September 2023 Revised: 10 October 2023 Accepted: 13 October 2023 Published: 18 October 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). livestock manure has been used as an organic fertilizer in crop soils, acting as an instrument for their maintenance thanks to the increase in the content of organic matter and nutrient elements. However, the intensification of livestock farming experienced in recent decades has led to the generation of livestock manure exceeding the assimilation capacity that land can tolerate to maintain the balance of the nutrient cycle, causing pollution of the soil itself and the groundwater due to an excess of nitrates.

All the aforementioned data highlight the need for good management of livestock manure. The easiest way is to manage it at the source, attempting to reduce these excesses through good management of the volume of water and feed consumed by the animals [11]. However, due to the productive characteristics of the livestock sector and the economic impact they have in industrially underdeveloped areas, it is necessary to find alternative solutions to those proposed to date by different administrative institutions, which allow for the valorization of the product outside the agricultural sector.

An innovative method for waste recycling, specifically converting biomass into bio-oil, is the use of the so-called conversion technologies [12]. Technological advances in the area of conversion technologies, both thermochemical and biochemical, allow for new ways to reduce the current problem of pollution caused by livestock manure, while obtaining valuable chemical and energy resources of ecological origin [13]. There are different thermochemical conversion technologies, such as pyrolysis, hydrothermal liquefaction, gasification, or direct combustion [14]. Due to the presence of moisture in livestock manure, and with the purpose of reducing the previous thermal treatments to the conversion process, the hydrothermal liquefaction process emerges as the technology with the greatest potential in swine manure conversion [15].

Recent studies have highlighted the convenience of incorporating oils or bio-oils in the production of bituminous mixtures in order to improve their mechanical properties [16–20]. Borghol et al. [21] demonstrated the potential of using a bio-binder obtained from microalgae waste in the manufacture of bituminous mixtures. Likewise, Sun et al. [19] used waste cooking oil as a binder in the manufacture of bituminous mixtures, obtaining material behaviour similar to that of a binder modified with SBS and even better in its performance at low temperatures. Considering the great importance of ageing in the properties of bituminous mixtures [22–24], in most cases, some oils are used as rejuvenators, which effectively delays the ageing process of the binder [25-29]. Nayak and Sahoo [26] used Pongamia oil and a composite rejuvenator (from castor oil and coke oven gas condensate) to restore the properties of binder after ageing, concluding that both are suitable for this purpose. This approach not only contributes to greater durability and performance of bituminous mixtures but also aligns with growing towards sustainability and respect for the environment. In this context, other materials such as industrial waste containing lignin [30] or clay, used as modifiers of bituminous mixtures, are of great interest when it comes to improving certain properties of mixes. Thus, the use of nanoclay allows us to improve the properties of the mixture against ageing, while the use of nanoiron allows us to improve the behaviour of the mixture against moisture damage [31]. Yadykova and Ilyin [16] developed a nanocomposite formed by montmorillonite nanoparticles and bio-oil with the aim of improving the properties of the binder, concluding that this modifier would be interesting for its use in critical areas.

The characteristics of bitumen cause the bio-oil obtained through hydrothermal liquefaction applied to swine manure to have great potential to be used as an asphalt binder due to its similarities with bitumen, contributing to the construction of more sustainable roads. According to Ingrassia et al. [4], the bio-binder obtained from thermochemical conversion of organic matter can have the following functions: (i) modifier of the binder, if it replaces <10% of petroleum-based binder; (ii) extender of the binder, if it replaces between 10–75% of petroleum-based binder; and (iii) substitute of the binder, if it replaces >75% of petroleum-based binder. Tayh et al. [32] and Abdel [33] summarized the main aspects to consider for this product use in road construction: whether the product was obtained from a waste material, reduces the need for petroleum-derived products, can act as an additive or modifier, can allow the reduction of asphalt mixtures manufacturing temperature up to 40 °C, reduces the carbon footprint of the road, and requires pre-treatment of the bio-oil due to the presence of water and volatile contents. Regarding its environmental impact, Samieadel et al. [34] demonstrated that the impact of the bio-modified binder, due to both emissions and energy consumption, is reduced compared to the virgin binder.

Therefore, obtaining a sustainable product from swine manure that allows reducing or even replacing petroleum-based asphalt is of great interest [35]. However, few current studies have been found in the literature. Islam and Park [36] conducted a literature review and found significant differences between petroleum-based fuel and bio-oil obtained from thermochemical processes applied to swine manure. Specifically, the latter has the negative aspect of high contents of water, ash, and oxygen. On the other hand, as positive aspects, the bio-oil from swine manure has lower viscosity and emissions.

The response of the bio-modified asphalt binder to temperature is a crucial aspect due to the existence of two different binders in the same mixture. On one hand, due to the bio-binder lower softening point, its implementation in a conventional binder can favour its behaviour towards plastic deformation since it absorbs heat earlier. On the other hand, in the bio-binder, volatilization starts earlier than in the conventional binder, which can lead to material loss during manufacturing. Liu et al. [37] chemically and rheologically analysed the effect of partially substituting a commercial binder with a bio-binder obtained through a pyrolysis process applied to swine manure. The results from this study indicate that the bio-binder has chemical groups similar to the conventional binder, and in the lowfrequency ageing region, the bio-binder has lower resistance. They also observed a better response to possible cracks induced by low temperatures and a worse behaviour at high temperatures. Fini et al. [38] studied the effect of using a bio-binder obtained from swine manure as an additive in a tyre powder modified asphalt, obtaining positive results in terms of workability and pumpability of the consequent asphalt mixture, increasing fatigue cracking resistance, and improving binder properties at low temperatures. Regarding moisture damage, Oldham and Fini [39] studied the effect of a bio-modifier from swine manure on moisture damage resistance, revealing that it improves due to the passivation mechanism of the bio-modifier.

It is clear that society, and especially the governments, have long ago started requiring more sustainable and greener solutions for road infrastructures, which force asphalt industries to shift from the current linear economy model based on the consumption of raw materials and petroleum-based products to a new circular bioeconomy model [40] based on the consumption of recycled materials, by-products and biomass valorized residues. Therefore, this paper aims to analyse the feasibility of using a new bio-binder obtained from swine manure through a hydrothermal liquefaction partially substituting petroleum-based bitumen. Thus, the obtained bio-modified asphalt binder is characterized.

2. Materials and Methods

2.1. Materials

2.1.1. Reference Asphalt Binders

Two different commercial asphalt binders were used as references, a 15/25 and a 50/70 type. The 15/25 binder was chosen for its higher hardness compared to other commercial binders. On the binder was selected for its extensive use in regular roads. Table 1 shows a summary of the main rheological properties of these binders.

2.1.2. Bio-Binder Production

Bio-binder was produced through a hydrothermal liquefaction (HTL) process applied to swine manure collected from a pig farm located in the Anoia region, Spain. It initially had 70% water content and was stored in a freezer at -15 °C. For its further characterization and processing, it was diluted in water to a total solids content of 5%. For each batch, 500 g of swine manure were introduced into a 1 L stainless steel autoclave with heated casing and a rotary impeller system without magnetic coupled packing. The reactor was heated to a temperature of 300 $^{\circ}$ C and a pressure of 9.0 MPa for a residence time of 0 min. The processing gas used to purge the residual air in the reactor was nitrogen, and no catalyst was used in the process. After the reaction, the heating shell was removed, and the reactor was cooled down to room temperature using water.

Characteristic	Standard (EN)	Unit	15/25	50/70	
Original Bitumen					
Penetration at 25 °C	1426 [41]	0.1 mm	15–25	50-70	
Softening point R&B	1427 [42]	°C	60-76	46-54	
Fraass breaking point	12593 [43]	°C	TRB	≤ -8	
Flash point	2592 [44]	°C	\geq 245	\geq 230	
Solubility	12592 [45]	%	≥ 99.0	≥99.0	
Residue after ageing					
Mass variation	12607-1 [46]	%	≤ 0.5	≤ 0.5	
Retained penetration	1426	%	\geq 55	≥ 50	
Δ Softening point	1427	°C	≤ 10	≤ 11	

Table 1. Properties of reference asphalt binders according to manufacturer [25].

The different phases of the HTL process were defined. The gaseous phase was measured by a gas flow meter and afterwards collected and stored in plastic bags for later analysis. The aqueous phase was collected by pouring it into a flask. Part of the solid phase, which was contained in the aqueous phase, was also collected in the previous step after filtration. The rest of the solid phase, together with the biocrude, was stuck to the walls and to the agitation module of the reactor. Acetone was used to recover them and to clean the reactor. The solids were washed with acetone to remove biocrude to obtain the bio-binder. Acetone was afterwards evaporated with a rotary evaporator.

The organic elemental analysis of the obtained bio-binder is detailed in Table 2.

Table 2. Organic elemental analysis of the bio-binder.

Elemental Analysis	Bio-Binder (%, g/100 g)				
С	69.18				
Н	7.85				
Ν	3.26				
О	19.72				

2.1.3. Preparation of Bio-Modified Asphalt Binder

The bio-modified asphalt binder used in this study was obtained by gradually adding the bio-binder to the reference binder. Firstly, the reference asphalt binder and bio-binder were preheated at 135 °C for 90 min and 65 °C for 30 min, respectively, in forced-air drying ovens. Once the preheating times elapsed, the established quantities of reference asphalt binder and bio-binder were poured into a metal cylindrical container placed on a precision balance. Immediately after, both components were mixed using a stirrer at a speed of 100 rpm for 15 min.

The percentages of bio-binder considered in this study were 0%, 10%, and 20% by weight on the reference asphalt binder.

2.2. Methodology

Several characterization tests were performed to study the effect of the addition of bio-binder on the resulting bio-modified asphalt binder: the penetration test, ring-and-ball test, Fraass test, viscosity test, Cleveland open cup test, and the UCL method.

The consistency of the analysed asphalt binders was determined by the penetration test, following the EN 1426 standard. A digital semi-automatic penetrometer (Matest B056-02, Treviolo, Italy) was used for this purpose. The test temperature, applied load, and test duration were 25 °C, 100 g, and 5 s, respectively.

2.2.2. Ring-and-Ball Test

The softening point of the analysed asphalt binders was determined using the ring-andball test, according to the EN 1427 standard. An automatic digital ring-and-ball apparatus (Matest B070N1) with a heating rate of 5 °C/min was used.

2.2.3. Fraass Test

The stiffness of the analysed asphalt binders was determined by the Fraass breaking point test, according to the EN 1259 standard, using a Petrotest model BPA 5 equipment (Petrotest, Dahlewitz, Germany) and a mass of 0.4 g.

2.2.4. Viscosity Test

The viscosity test was used to determine the dynamic viscosity of the considered binders at different temperatures, according to the EN 13302 standard [47]. A Brookfield DV-II Pro + Thermosel system and a mass of 50 g were used.

2.2.5. Cleveland Open Cup Test (Flash Point)

The Cleveland open cup test was used to determine the flash point of the asphalt binders considered in this study, according to the EN ISO 2592 standard [44]. Herzog HFP 386 equipment was used.

2.2.6. UCL Test

The UCL method, developed at the Laboratory of Roads of the Universitat Politècnica de Catalunya (Barcelona, Spain), was used to measure the cohesion provided by the binder to an open-graded standard mix without fines, or filler, as shown in Table 3, and how this cohesion varies with temperature, water action, and binder ageing [48,49]. Using porphyritic aggregates and a content of 4.5% bio-modified asphalt binder on aggregates, mixture specimens were prepared according to the Marshall procedure, but using only 50 blows per face for the compaction. The percentage of bio-binder was 20% by weight on the reference asphalt binder.

Table 3. Particle size distribution of the reference mixture according to the UCL method.

Sieves UNE (mm)	ieves UNE (mm) 5		0.63		
% Passing	100	20	0		

The binder cohesion was evaluated based on the resistance to disintegration that this fixed amount of binder provides to the reference mixture, using the Cántabro test (NLT-352/00; EN 12697-17 [50]) at a temperature of 25 °C. During the Cántabro test for loss of weight, the Marshall specimen is placed into the Los Angeles abrasion test machine and subjected to wear without any abrasive load. During the test, the most superficial aggregates of the specimen are detached by impact and abrasion, and after a certain number of revolutions (300), the weight loss of the specimen is determined and expressed as a percentage of the initial weight. Three replicates were carried out for each study condition.

To study the thermal susceptibility of the binder, specimens were tested at the temperatures of 60 °C, 40 °C, 25 °C, 10 °C, and -10 °C. The binder adhesiveness to the aggregate of the specimens after moisture conditioning was also determined according to NLT-362/92. Thus, specimens were immersed in a water at a temperature of 60°C for a period of 25 h. After moisture damage, the specimens were conditioned at a temperature of 25 °C for 24 h before being tested. To assess the binder resistance to ageing, the accelerated ageing procedure described by the RILEM committee [51] was used, being performed directly in the mixture. For the short-term ageing, the loose mixture was kept for 4 h at a temperature of 135 °C, while for the long-term, it was kept in the oven, uncompacted, for 9 days at a temperature of 85 °C.

2.2.7. Leaching Test

To study the possible leaching of the bio-binder in contact with water, firstly, a qualitative test was performed on the bio-binder sample, which basically consisted of leaving the sample in the presence of water and observing if there were any changes in the colour of the water. Subsequently, a leaching test was carried out on a sample of disaggregated asphalt mixture manufactured with 20% bio-binder according to the EN 12457-4 standard [52]. The concentrations of the constituents of interest were determined using the EN ISO 17294-2 standard [53], except for mercury, which was determined using the EN ISO 17852 standard [54].

3. Results

3.1. Penetration Test

In Figure 1, the evolution of the penetration values of the bio-modified asphalt binder depending on the added bio-binder content can be observed. These values were obtained under homogeneous conditions. The figure shows an exponential increase in the penetration values as the bio-binder content increases, indicating a possible softening effect of the bio-binder. In the case of the 15/25 reference binder, with the addition of 10% bio-binder, a 41.9% increase in penetration was observed, while with the addition of 20%, values 114.9% higher than those of the reference binder were observed. In the case of the 50/70 reference asphalt binder, with the addition of 10% bio-binder, a 57.5% increase in penetration was observed, while with the addition of 20% bio-binder, values 90.9% higher than those of the reference binder. The increase in penetration values of the bio-binder is consistent with those obtained by Oldham et al. [55]. Higher penetration values indicate lower binder consistency, which is an indication of better binder performance under low-temperature conditions.



Figure 1. Evolution of bio-modified asphalt binder penetration (at 25 °C) according to the percentage of bio-binder added.

During the penetration test on the bio-binder, in the absence of reference binder, a bleaching phenomenon of the top layer of the sample in contact with water was observed, changing from the original blackish colour to a brownish colour. (Figure 2). However, once

the surface in contact with water was dried and a period greater than 180 min elapsed, the bio-binder returned to its original blackish colour. This indicates that, in the short term, water influences the properties of the bio-binder, and to a lesser extent, the bio-modified asphalt binder. Although this process may be reversible, during the period in which the bio-binder is in the presence of water, the bond between the aggregate and the binder could be affected by the water. However, the results of the UCL test (Section 3.6) on the asphalt mixture subjected to moisture damage indicate the opposite.



Figure 2. Bio-binder colour change in contact with water.

3.2. Ring-and-Ball Test

The response of the bio-modified binder to temperature is a crucial aspect due to the existence of two different binders within the same one. In Figure 3, the evolution of the softening point of the bio-modified asphalt binder can be observed as a function of the added percentage of bio-binder, obtained under homogeneous conditions. In all cases, a linear decrease in the softening temperature was observed. In the case of the 15/25 asphalt binder, with the addition of 10% bio-binder, a decrease of 9.5% in the softening temperature was observed, while with the addition of 20%, values were 11.4% lower. In the case of the 50/70 reference asphalt binder, while with the addition of 20%, values were 9.9% lower. Based on these results, the plastic deformation of the bio-modified asphalt binder could increase due to the lower softening point of the bio-binder, as it will absorb ambient heat earlier. On the other hand, in the bio-binder, volatilization begins earlier than in the reference binder and may cause problems with material loss during production. The lower softening point values, combined with the higher binder penetration, lead to an increase in the thermal susceptibility of the modified bio-binder.



Figure 3. Softening point evolution of bio-modified asphalt binder according to the percentage of bio-binder added.

3.3. Fraass Test

In Figure 4 the evolution of the Fraass breaking point value of the bio-modified asphalt binder depending on the added percentage of bio-binder is shown. According to the observed values, the results are not conclusive. In the case of the 15/25 reference asphalt binder, no variation was observed with the addition of bio-binder, and the reference value was inconsistent with typical values for this asphalt binder (normally values < -5 °C). On the other hand, in the case of the 50/70 reference asphalt binder, a decrease in the Fraass breaking point was observed with the addition of 10% bio-binder by 12.5%, while with the addition of 20%, values 37.5% lower were observed. In this instance, this decrease in Fraass values suggests that, as the bio-binder content increases, the bio-modified asphalt binder becomes less brittle at low temperatures compared to conventional bitumen. This could translate into greater resistance to fatigue cracking in cold climates, which would improve the durability and performance of asphalt pavements manufactured with this bio-modified asphalt binder. These results are consistent with the obtained penetration and softening point values.



Figure 4. Fraass braking point values of bio-modified asphalt binder according to the percentage of bio-binder added.

3.4. Viscosity Test

Viscosity was studied in order to evaluate the effect of adding bio-binder on the workability of the bio-modified asphalt binder. In Figure 5, the evolution of the bio-modified asphalt binder viscosity can be observed as a function of the percentage of added bio-binder and temperature. In all cases, a linear decrease in viscosity is observed as the content of bio-binder increases, indicating that it is possible to reduce the manufacturing temperature of the asphalt mixture. Additionally, the reduction in viscosity could reduce the energy required during the manufacturing and installation process of bituminous mixtures, which could lead to economic and environmental benefits by reducing fuel consumption. These results are consistent with those obtained by Fini et al. [56–59]. The difference in viscosity values between the reference binder and the modified binder decreases as temperature increases, becoming negligible at a temperature of 180 °C.

3.5. Cleveland Open Cup Test (Flash Point)

In Figure 6, the evolution of the bio-modified asphalt binder flash point can be observed depending on the percentage of added bio-binder. The observed values show a slight decrease in this parameter with the addition of bio-binder. In the case of the 15/25 reference asphalt binder, a decrease in the flash point of 3.1% was observed with the addition of 10% bio-binder, while values 8.0% lower were observed with the addition of 20%. Similarly, in the case of the 50/70 asphalt binder, a decrease in the flash point of 1.3%

was observed with the addition of 10% bio-binder, while values 3.3% lower were observed with the addition of 20%. The decrease in flash point values by increasing the bio-binder content could lead to greater ease of handling and application of both the binder and the bituminous mixture at lower temperatures, which could offer significant advantages in regions with cold climates.



Figure 5. Viscosity values of bio-modified asphalt binder according to the added bio-binder and temperature: (a) 50/70 binder; (b) 15/25 binder.

3.6. UCL Test

The UCL test was used to analyse the thermal susceptibility, adhesion, and ageing behaviour of the bio-modified 50/70 asphalt binder with 20% bio-binder.

3.6.1. Thermal Susceptibility

Figure 7 shows the thermal susceptibility, in terms of UCL method Cántabro losses, of the 50/70 asphalt binder with and without the influence of the bio-binder. It can be observed that the losses of the bio-modified asphalt binder are always higher, throughout the temperature range, than those of the reference asphalt binder. This indicates that the bio-modified asphalt binder is more brittle at low temperatures and more inconsistent at high temperatures. The behaviour of the bio-modified asphalt binder observed from the

Cántabro losses differs from the latter observed when this binder was tested alone, where it was demonstrated that the bio-binder is less brittle at low temperatures with respect to a conventional binder. These differences may be due, in part, to the temperature to which the bio-binder was subjected during the manufacture of the asphalt mixture.



Figure 6. Flash point values of bio-modified asphalt binder according to the percentage of bio-binder added.



Figure 7. Thermal susceptibility of bio-modified asphalt binder according to the percentage of bio-binder added.

3.6.2. Adhesiveness

Figure 8 shows the adhesiveness, in terms of UCL method Cántabro losses, of the 50/70 asphalt binder with and without the influence of the bio-binder, for dry conditions and after immersion in water. It was observed that the losses after water immersion of the bio-modified asphalt binder are lower than those of the reference asphalt binder, even with higher losses for the dry condition, indicating good resistance to the action of water. These results agree with those obtained by Mogawer et al. [60,61], where the susceptibility

to water improved with the introduction of bio-binder. This is probably due to the fact that the bio-binder is mainly formed by resins and asphaltenes (almost 90%), which indicates its potential to improve the aggregate–binder compatibility due to the high presence of polar components. Yadykova and Ilyin [62] improved adhesion properties of bitumen using bio-oil, obtaining a quantitative evaluation of the parameter.



Figure 8. Adhesiveness (dry/wet) of bio-modified asphalt binder according to the percentage of bio-binder added (Cántabro losses at 25 °C).

3.6.3. Ageing Resistance

Figure 9 shows the ageing resistance, in terms of UCL method Cántabro losses, of the 50/70 asphalt binder with and without the influence of the bio-binder, for the different degrees of ageing considered: without ageing, short-term ageing, and long-term ageing. It was observed that the resistance to ageing of the bio-modified asphalt binder is lower than that of the reference asphalt binder. Furthermore, Cántabro losses are higher both in the short and long term, and the differences concerning to the reference asphalt binder are greater than that obtained for the unaged condition. The results obtained might be due to a lower enveloping capacity of the bio-modified asphalt binder with the aggregates due to ageing, as observed by Fini et al. [63].



Figure 9. Ageing resistance of bio-modified asphalt binder according to the percentage of bio-binder added (Cántabro losses at 25 °C).

The results obtained differ from those observed by Fini et al. [38] where they showed a decrease in the susceptibility to ageing related to the molecular interaction of the functional

groups of the bio-binder with the reference asphalt binder, creating a more stable structure with less propensity to react with oxygen. As mentioned before, these differences may be due, in part, to the temperature to which the bio-binder was subjected during the manufacture of the asphalt mixture.

3.7. Leaching Test

Although the literature on the use of swine manure to obtain bio-binders suggests that there are no leaching problems with this new bio-binder, leaching phenomena have been observed in the bio-binder in presence of water over time (Figure 10).



Figure 10. Leaching of a bio-binder sample in the presence of water: (**a**) week 0, (**b**) week 1, (**c**) week 2, (**d**) week 3, and (**e**) week 4.

The results of the leaching test carried out on a sample of disaggregated asphalt mixture (Table 4) comply with the limit values established in the European standard (2003/33/EC) [64] to be classified as inert waste. However, the analysed sample does not comply with the total organic carbon limit values, which is 53,000 mg·kg⁻¹. Therefore, the asphalt mixture sample with bio-modified binder cannot be classified as inert waste, but as non-inert waste. However, since the dissolved organic carbon value obtained in the test (300 mg·kg⁻¹) does not exceed the value of 800 mg·kg⁻¹, it is understood that the asphalt mixture with bio-modified binder can be classified as non-hazardous waste. These results show that the mixture with bio-binder does not present any environmental problems.

Table 4. Leaching concentrations $(mg \cdot kg^{-1})$ after leaching test (EN 12457-4) and limits for acceptance at landfills for inert waste.

	As	Ba	Cd	Cr	Cu	Hg	Мо	Ni	Pb	Sb	Se	Zn
Results	< 0.01	0.63	< 0.002	0.03	< 0.02	< 0.0005	0.03	< 0.03	< 0.02	< 0.02	< 0.02	< 0.1
¹ Inert waste (mg·kg ^{−1})	0.50	20.0	0.04	0.50	2.00	0.01	0.50	0.40	0.50	0.06	0.10	4.00

¹ Limit for acceptance at landfills.

4. Conclusions

In this study, a bio-binder obtained from swine manure was evaluated as a binder modifier at different rates (0%, 10%, and 20%) to two commercial asphalt binders (15/25 and 50/70) through several characterization tests. The results showed a softening effect of

the bio-binder. As the bio-binder content increased, the penetration increased, while the softening temperature, the Fraass breaking point, and the viscosity decreased. A decrease in the flash point was also observed as the bio-binder content increased, as the bio-modified asphalt binder has also been observed, showing the importance of temperatures during the asphalt mixtures manufacturing process.

The results of the UCL method showed that bio-modified asphalt binder has a worse thermal susceptibility (it is more brittle at low temperatures and more inconsistent at high temperatures) and poorer resistance to ageing compared to the reference bitumen. This was caused, in part, to the temperature to which the bio-binder was subjected during the manufacture of the mixture. On the other hand, the resistance to moisture damage is better.

Finally, despite de fact that leaching phenomena were observed in the presence of water, the asphalt mixture with bio-modified binder can be classified as non-hazardous waste, presenting no environmental problems.

Author Contributions: Conceptualization, J.G. and L.V.; methodology, J.G., L.V., R.M. and A.H.M.; formal analysis, J.G., T.L.-M., L.V., R.M. and A.H.M.; investigation, J.G., T.L.-M., L.V., R.M., C.B. and A.H.M.; resources, J.G. and R.M.; data curation, J.G., L.V. and R.M; writing—original draft preparation, T.L.-M., R.M. and A.H.M.; writing—review and editing, J.G., T.L.-M., L.V., R.M., C.B. and A.H.M.; visualization, T.L.-M., R.M. and A.H.M.; funding acquisition, J.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded by the Centre for Industrial Development and Technology (CDTI) of the Spanish Ministry of Science and Innovation, grant number IDI-20200468.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors would like to thank the Ciesm-Intevía road laboratory for the contribution in the realization of the tests. Teresa López-Montero is a Serra Húnter Fellow.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

- Zou, B.; Yang, F.; Fu, J.; Wang, K.; Liu, F. Evaluation of Energy Consumption of Typical Asphalt Pavement Structure. *IOP Conf.* Ser. Earth Environ. Sci. 2021, 804, 042057. [CrossRef]
- Bizarro, D.E.G.; Steinmann, Z.; Nieuwenhuijse, I.; Keijzer, E.; Hauck, M. Potential Carbon Footprint Reduction for Reclaimed Asphalt Pavement Innovations: Lca Methodology, Best Available Technology, and near-Future Reduction Potential. *Sustainability* 2021, 13, 1382. [CrossRef]
- 3. López-Montero, T.; Miró, R.; Martínez, A. Effect of the Use of Marpol Waste as a Partial Replacement of the Binder for the Manufacture of More Sustainable Bituminous Mixtures. *Int. J. Pavement Eng.* **2022**, 1–15. [CrossRef]
- Ingrassia, L.P.; Lu, X.; Ferrotti, G.; Canestrari, F. Renewable Materials in Bituminous Binders and Mixtures: Speculative Pretext or Reliable Opportunity? *Resour. Conserv. Recycl.* 2019, 144, 209–222. [CrossRef]
- 5. Wang, H.; Ma, Z.; Chen, X.; Mohd Hasan, M.R. Preparation Process of Bio-Oil and Bio-Asphalt, Their Performance, and the Application of Bio-Asphalt: A Comprehensive Review. *J. Traffic Transp. Eng.* **2020**, *7*, 137–151. [CrossRef]
- Gao, J.; Wang, H.; You, Z.; Mohd Hasan, M.R. Research on Properties of Bio-Asphalt Binders Based on Time and Frequency Sweep Test. Constr. Build. Mater. 2018, 160, 786–793. [CrossRef]
- Ingrassia, L.P.; Lu, X.; Ferrotti, G.; Canestrari, F. Chemical, Morphological and Rheological Characterization of Bitumen Partially Replaced with Wood Bio-Oil: Towards More Sustainable Materials in Road Pavements. J. Traffic Transp. Eng. 2020, 7, 192–204. [CrossRef]
- Su, N.; Xiao, F.; Wang, J.; Cong, L.; Amirkhanian, S. Productions and Applications of Bio-Asphalts—A Review. *Constr. Build. Mater.* 2018, 183, 578–591. [CrossRef]
- 9. Yan, K.; Zhang, M.; You, L.; Wu, S.; Ji, H. Performance and Optimization of Castor Beans-Based Bio-Asphalt and European Rock-Asphalt Modified Asphalt Binder. *Constr. Build. Mater.* **2020**, 240, 117951. [CrossRef]

- Agència de Residus de Catalunya Excedentes de Deyecciones Ganaderas. Available online: https://residus.gencat.cat/es/ ambits_dactuacio/tipus_de_residu/dejeccions_ramaderes/ (accessed on 14 September 2023).
- 11. Zeng, Y.; He, K.; Zhang, J.; Li, P. Adoption and Ex-Post Impacts of Sustainable Manure Management Practices on Income and Happiness: Evidence from Swine Breeding Farmers in Rural Hubei, China. *Ecol. Econ.* **2023**, *208*, 107809. [CrossRef]
- Mahssin, Z.Y.; Zainol, M.M.; Hassan, N.A.; Yaacob, H.; Puteh, M.H.; Saidina Amin, N.A. Hydrothermal Liquefaction Bioproduct of Food Waste Conversion as an Alternative Composite of Asphalt Binder. J. Clean. Prod. 2021, 282, 125422. [CrossRef]
- Tekin, K.; Karagöz, S.; Bektaş, S. A Review of Hydrothermal Biomass Processing. *Renew. Sustain. Energy Rev.* 2014, 40, 673–687. [CrossRef]
- Ong, H.C.; Chen, W.H.; Farooq, A.; Gan, Y.Y.; Lee, K.T.; Ashokkumar, V. Catalytic Thermochemical Conversion of Biomass for Biofuel Production: A Comprehensive Review. *Renew. Sustain. Energy Rev.* 2019, 113, 109266. [CrossRef]
- 15. Karnati, S.R.; Oldham, D.; Fini, E.H.; Zhang, L. Surface Functionalization of Silica Nanoparticles with Swine Manure-Derived Bio-Binder to Enhance Bitumen Performance in Road Pavement. *Constr. Build. Mater.* **2021**, 266, 121000. [CrossRef]
- Yadykova, A.Y.; Ilyin, S.O. Bitumen Improvement with Bio-Oil and Natural or Organomodified Montmorillonite: Structure, Rheology, and Adhesion of Composite Asphalt Binders. *Constr. Build. Mater.* 2023, 364, 129919. [CrossRef]
- Audo, M.; Paraschiv, M.; Queffélec, C.; Louvet, I.; Hémez, J.; Fayon, F.; Lépine, O.; Legrand, J.; Tazerout, M.; Chailleux, E.; et al. Subcritical Hydrothermal Liquefaction of Microalgae Residues as a Green Route to Alternative Road Binders. *ACS Sustain. Chem. Eng.* 2015, *3*, 583–590. [CrossRef]
- Abo-Shanab, Z.L.; Ragab, A.A.; Naguib, H.M. Improved Dynamic Mechanical Properties of Sustainable Bio-Modified Asphalt Using Agriculture Waste. Int. J. Pavement Eng. 2021, 22, 905–911. [CrossRef]
- Sun, D.; Lu, T.; Xiao, F.; Zhu, X.; Sun, G. Formulation and Aging Resistance of Modified Bio-Asphalt Containing High Percentage of Waste Cooking Oil Residues. J. Clean. Prod. 2017, 161, 1203–1214. [CrossRef]
- Al-Sabaeei, A.M.; Napiah, M.B.; Sutanto, M.H.; Alaloul, W.S.; Yusoff, N.I.M.; Khairuddin, F.H.; Memon, A.M. Evaluation of the High-Temperature Rheological Performance of Tire Pyrolysis Oil-Modified Bio-Asphalt. *Int. J. Pavement Eng.* 2021, 23, 4007–4022. [CrossRef]
- Borghol, I.; Queffélec, C.; Bolle, P.; Descamps, J.; Lombard, C.; Lépine, O.; Kucma, D.; Lorentz, C.; Laurenti, D.; Montouillout, V.; et al. Biosourced Analogs of Elastomer-Containing Bitumen through Hydrothermal Liquefaction of: *Spirulina* Sp. Microalgae Residues. *Green Chem.* 2018, 20, 2337–2344. [CrossRef]
- López-Montero, T.; Miró, R. Ageing and Temperature Effect on the Fatigue Performance of Bituminous Mixtures. *Mater. Constr.* 2017, 67, e126. [CrossRef]
- 23. Zhang, R.; Sias, J.E.; Dave, E.V. Evaluation of the Cracking and Aging Susceptibility of Asphalt Mixtures Using Viscoelastic Properties and Master Curve Parameters. J. Traffic Transp. Eng. 2022, 9, 106–119. [CrossRef]
- Yang, S.L.; Baek, C.; Park, H.B. Effect of Aging and Moisture Damage on Fatigue Cracking Properties in Asphalt Mixtures. *Appl. Sci.* 2021, 11, 10543. [CrossRef]
- Casado-Barrasa, R.; López-Montero, T.; Castro-Fresno, D.; Miró, R. Evaluation of the Rejuvenation of Asphalt by Means of Oil-Saturated Porous Aggregates. *Constr. Build. Mater.* 2022, 318, 125825. [CrossRef]
- 26. Nayak, P.; Sahoo, U.C. A Rheological Study on Aged Binder Rejuvenated with Pongamia Oil and Composite Castor Oil. *Int. J. Pavement Eng.* 2017, *18*, 595–607. [CrossRef]
- Oldham, D.; Rajib, A.; Dandamudi, K.P.R.; Liu, Y.; Deng, S.; Fini, E.H. Transesterification of Waste Cooking Oil to Produce A Sustainable Rejuvenator for Aged Asphalt. *Resour. Conserv. Recycl.* 2021, 168, 105297. [CrossRef]
- Ma, J.; Sun, D.; Pang, Q.; Sun, G.; Hu, M.; Lu, T. Potential of Recycled Concrete Aggregate Pretreated with Waste Cooking Oil Residue for Hot Mix Asphalt. J. Clean. Prod. 2019, 221, 469–479. [CrossRef]
- Ziari, H.; Ayar, P.; Amjadian, Y. Laboratory Evaluation of Short- and Long-Term Aging Resistance of Rejuvenated RAP Mixtures. J. Mater. Civ. Eng. 2023, 35, 04023428. [CrossRef]
- 30. Ghabchi, R.; Pereira Castro, M.P. Characterisation of a Hybrid Plant-Based Asphalt Binder Replacement with High Reactive Phenolic Monomer Content. *Int. J. Pavement Eng.* **2021**, *23*, 4675–4696. [CrossRef]
- Crucho, J.M.L.; Neves, J.; Capitão, S.D.; Picado-Santos, L.G. Mechanical Performance of Asphalt Concrete Modified with Nanoparticles: Nanosilica, Zero-Valent Iron and Nanoclay. *Constr. Build. Mater.* 2018, 181, 309–318. [CrossRef]
- 32. Tayh, S.A.; Muniandy, R.; Hassim, S.; Jakarni, F.; Aburkaba, E. An Overview of Utilization of Bio-Oil in Hot Mix Asphalt. *WALIA J.* 2014, *30*, 131–141.
- 33. Abdel Raouf, M. Development of Non-Petroleum Binders Derived from Fast Pyrolysis Bio-Oils for Use in Flexible Pavements; Iowa State University: Ames, IA, USA, 2010; ISBN 2013206534.
- 34. Samieadel, A.; Schimmel, K.; Fini, E.H. Comparative Life Cycle Assessment (LCA) of Bio-Modified Binder and Conventional Asphalt Binder. *Clean Technol. Environ. Policy* **2018**, *20*, 191–200. [CrossRef]
- 35. Wang, H.; Jing, Y.; Zhang, J.; Cao, Y.; Lyu, L. Preparation and Performance Evaluation of Swine Manure Bio-Oil Modified Rubber Asphalt Binder. *Constr. Build. Mater.* **2021**, 294, 123584. [CrossRef]
- 36. Islam, M.N.; Park, J.H. A Short Review on Hydrothermal Liquefaction of Livestock Manure and a Chance for Korea to Advance Swine Manure to Bio-Oil Technology. *J. Mater. Cycles Waste Manag.* **2018**, 20, 1–9. [CrossRef]

- 37. Liu, Q.; Wang, C.; Fan, S.; Shi, S.; Zhang, Z.; Oeser, M. Feasibility Analysis of Bio-Binder as Non-Petroleum Alternative for Bituminous Materials. *Mater. Res. Express* 2020, *6*, 125115. [CrossRef]
- Fini, E.H.; Hosseinnezhad, S.; Oldham, D.; Mclaughlin, Z.; Alavi, Z.; Harvey, J. Bio-Modification of Rubberised Asphalt Binder to Enhance Its Performance. *Int. J. Pavement Eng.* 2019, 20, 1216–1225. [CrossRef]
- Oldham, D.J.; Fini, E.H. A Bottom-up Approach to Study the Moisture Susceptibility of Bio-Modified Asphalt. Constr. Build. Mater. 2020, 265, 120289. [CrossRef]
- 40. Stegmann, P.; Londo, M.; Junginger, M. The Circular Bioeconomy: Its Elements and Role in European Bioeconomy Clusters. *Resour. Conserv. Recycl. X* 2020, *6*, 100029. [CrossRef]
- 41. *EN 1426:2015;* Bitumen and Bituminous Binders. Determination of Needle Penetration. European Committee for Standardization: Brussels, Belgium, 2015.
- 42. *EN 1427:2015;* Bitumen and Bituminous Binders. Determination of the Siftening Point. Ring and Ball Method. European Committee for Standardization: Brussels, Belgium, 2015.
- EN 12593:2015; Bitumen and Bituminous Binders. Determination of the Fraass Breaking Point. European Committee for Standardization: Brussels, Belgium, 2015.
- 44. *EN ISO 2592:2017;* Petroleum and Related Products. Determination of Flash and Fire Points. Cleveland open cup method (ISO 2592:2017). European Committee for Standardization: Brussels, Belgium, 2017.
- 45. EN 12592:2014; Bitumen and Bituminous Binders. Determination of Solubility. European Committee for Standardization: Brussels, Belgium, 2014.
- 46. *EN 12607-1:2014;* Bitumen and Bituminous Binders. Determination of the Resistance to Hardening under Influence of Heat and Air. Part 1: RTFOT Method. European Committee for Standardization: Brussels, Belgium, 2014.
- EN 13302:2018; Bitumen and Bituminous Binders. Determination of Dynamic Viscosity of Bituminous Binder Using a Rotating Spindle Apparatus. European Committee for Standardization: Brussels, Belgium, 2018.
- López-Montero, T.; Maldonado-Alameda, A.; Mañosa, J.; Miró, R.; Chimenos, J.M. Analysing the Potential Use of a Low-Grade Magnesium Carbonate by-Product as a Filler in Hot Asphalt Mixtures. *Int. J. Pavement Eng.* 2022, 1–12. [CrossRef]
- Pérez-Jiménez, F.; Miró Recasens, R. Characterization Procedure of Asphalt Binders with the Cántabro Test. UCL Method. In Proceedings of the Summaries and Papers, 5th Eurobitume Congress, Stockholm, Sweden, 16–16 June 1993; pp. 209–213.
- 50. *EN 12697-17:2018*; Bituminous Mixtures. Test Methods. Part 17: Particle Loss of Porous Asphalt Specimens. European Committee for Standardization: Brussels, Belgium, 2017.
- De la Roche, C.; Van de Ven, M.; Van den Bergh, W.; Gabet, T.; Dubois, V.; Grenfell, J.; Porot, L. Development of a Laboratory Bituminous Mixtures Ageing Protocol. In *Advanced Testing and Characterization of Bituminous Materials*; CRC Press: Boca Raton, FL, USA, 2009; pp. 331–346.
- 52. *EN 12457-4:2002;* Characterization of Waste. Leaching. Compliance Test for Leaching of Granular Waste Materials and Sludges. Part 4: One Stage Batch Test at a Liquid to Solid Ratio of 101/kg for Materials with Particle Size below 10 mm (without or with Size Reduction). European Committee for Standardization: Brussels, Belgium, 2002.
- EN ISO 17294-2:2016; Water Quality. Application of Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Part 2: Determination of Selected Elements Including Uranium Isotopes (ISO 17294-2:2016). European Committee for Standardization: Brussels, Belgium, 2016.
- 54. EN ISO 17852:2008; Water Quality. Determination of Mercury. Method Using Atomic Fluorescence Spectrometry (ISO 17852:2006). European Committee for Standardization: Brussels, Belgium, 2008.
- 55. Oldham, D.J.; Fini, E.H.; Chailleux, E. Application of a Bio-Binder as a Rejuvenator for Wet Processed Asphalt Shingles in Pavement Construction. *Constr. Build. Mater.* **2015**, *86*, 75–84. [CrossRef]
- 56. Fini, E.H.; Kalberer, E.W.; Shahbazi, A.; Basti, M.; You, Z.; Ozer, H.; Aurangzeb, Q. Chemical Characterization of Biobinder from Swine Manure: Sustainable Modifier for Asphalt Binder. *J. Mater. Civ. Eng.* **2011**, *23*, 1506–1513. [CrossRef]
- 57. Fini, E.H.; Al-Qadi, I.L.; You, Z.; Zada, B.; Mills-Beale, J. Partial Replacement of Asphalt Binder with Bio-Binder: Characterisation and Modification. *Int. J. Pavement Eng.* 2012, 13, 515–522. [CrossRef]
- 58. Fini, E.H.; Oldham, D.J.; Abu-Lebdeh, T. Synthesis and Characterization of Biomodified Rubber Asphalt: Sustainable Waste Management Solution for Scrap Tire and Swine Manure. *J. Environ. Eng.* **2013**, *139*, 1454–1461. [CrossRef]
- Mills-Beale, J.; You, Z.; Fini, E.; Zada, B.; Lee, C.H.; Yap, Y.K. Aging Influence on Rheology Properties of Petroleum-Based Asphalt Modified with Biobinder. J. Mater. Civ. Eng. 2014, 26, 358–366. [CrossRef]
- Mogawer, W.S.; Fini, E.H.; Austerman, A.J.; Booshehrian, A.; Zada, B.; Mogawer, W.S.; Fini, E.H.; Austerman, A.J. Performance Characteristics of High Reclaimed Asphalt Pavement Containing Bio-Modifier. *Road Mater. Pavement Des.* 2015, 17, 753–767. [CrossRef]
- Mogawer, W.; Austerman, A.; Booshehrian, A. Performance Characteristics of High RAP Bio-Modified Asphalt Mixtures. In Proceedings of the Transportation Research Board 91st Annual Meeting, Washington, DC, USA, 22–26 January 2011.
- 62. Yadykova, A.Y.; Ilyin, S.O. Rheological and Adhesive Properties of Nanocomposite Bitumen Binders Based on Hydrophilic or Hydrophobic Silica and Modified with Bio-Oil. *Constr. Build. Mater.* **2022**, *342*, 127946. [CrossRef]

- 63. Fini, E.H.; Hosseinnezhad, S.; Oldham, D.J.; Gaudefroy, V.; Fini, E.H.; Hosseinnezhad, S.; Oldham, D.J. Source Dependency of Rheological and Surface Characteristics of Bio-Modified Asphalts. *Road Mater. Pavement Des.* **2016**, *18*, 408–424. [CrossRef]
- 64. 2003/33/EC; Council Decision of 19 December 2002 Establishing Criteria and Procedures for the Acceptance of Waste Landfills Pursuant to Article 16 of and Annex II to Directive 1999/31/EC. Official Journal of the European Communities: Brussels, Belgium, 2003.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.