Renewable binders from waste biomass for road construction: a review on thermochemical conversion technologies and current developments

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Abstract

Biobinders (binders manufactured from biomass) are becoming popular in asphalt engineering due to growing environmental concerns of greenhouse gas emissions from the use of fossil fuels and depleting petroleum bitumen reserves. Waste biomass products are sources of particular interest due to their widespread availability and impact on sustainability, however, they generally need to be thermochemically treated before being used as biobinders. Although biobinders can exhibit good performance in terms of resisting common distresses affecting road pavements, they are still relatively unknown and the uncertainty around them discourages their further use. In this context, this review aims at providing a link between biomass thermochemical conversion technologies and their respective products that may be used as biobinders in pavement engineering. For this purpose, firstly, a detailed insight of the biomass thermochemical conversion technologies available for the manufacture of biobinders is provided. Specifically, solvent liquefaction and pyrolysis are compared and the operating parameters affecting the production of biobinders from solvent liquefaction are explored. Secondly, the review focuses on providing an overview of current biobinder studies for asphalt mixtures with an emphasis on the feedstock utilised and their key engineering properties. The review shows that biobinders' performance highly depends on the biomass source and the technology applied to produce them. Finally, summary tables provide researchers with a quick but insightful way of identifying potential biobinder feedstocks according to certain properties.

Keywords: biomass, bio-oil, thermochemical conversion, biobinder, sustainability, recycling

Abbreviations including units and nomenclature

CO_2: Carbon dioxide
LCA: Life Cycle Assessment
HTL: Hydrothermal Liquefaction
EIBP: Environmental Impact of Biomass Pre-processing
SLR: Systematic Literature Review
Wt. %: Weight percentage
Atm: atmosphere
K_2CO_3: Potassium carbonate
Sp.: species
MPa: Megapascal
MJ/kg: Megajoules per kilogram
Rpm: Revolutions per minute
PG: Performance Grade
kW: Kilowatt
RTFOT: Rotating Thin Film Oven Test
$|G^*|/\sin\delta$: Superpave rutting parameter, the norm of the complex modulus over the sine of the phase angle
VOCs: Volatile Organic Compounds
SBS: Styrene-butadiene-styrene
PAV: Pressure Ageing Vessel
RA: Recycled Asphalt
PEA: Polyethyl acrylate
PMA: Polymethyl acrylate
PBA: Polybutyl acrylate
DBP: Dibutyl phthalate
EMS: Epoxidized Soybean Soyate

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1. Introduction

Most bituminous binders used for pavement materials are derived from fossil fuels [1]. Petroleum bitumens and modified bitumens (bitumens designed to change the performance of straight run bitumen altered by one or more chemical agents such as polymers, waxes and crumb rubber) [2], are the most common materials used as binders in asphalt mixtures. In Europe, the overall consumption of bitumen remains high and relatively stable, varying from 12.89 million tonnes in 2016 to 10.74 million tonnes in 2019 [3]. In addition, bitumen and asphalt mixture demand is predicted to further increase after years of low spending and will be driven by increased expenditure on road maintenance to accommodate for repair backlogs [4]. In the US, the production of hot and warm mix asphalt mixtures has been on the rise since 2016 due to increased construction activity, highlighting their high demand for bitumen and bituminous mixtures (Figure 1) [3]. Fortunately, efforts to use more sustainable materials in all areas of construction have greatly increased. This rise in production coupled with the urge to minimise the usage of fossil fuels has developed a drive to produce binders from alternative sources globally, particularly from bio-renewable materials or biobinders.

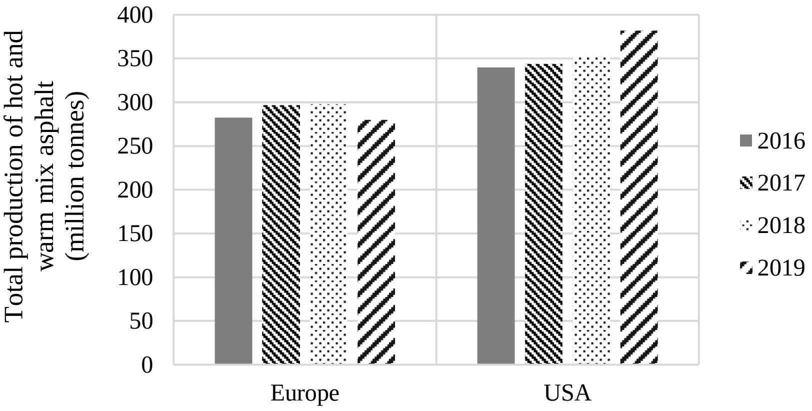

Figure 1: Total production of hot and warm mix asphalt (in million tonnes) between 2016 and 2019 [3].

Biobinders are defined as asphalt binder alternatives made from non-petroleum-based renewable sources, which should not impact on food production, and have environmental and economic benefits [1]. They can be produced from a range of sources including vegetable oils, algae and swine manure [5]. Not only do they have the potential to reduce petroleum bitumen demand, biobinders have also exhibited good performance in terms of resisting the common distresses affecting pavements depending on their composition [5]. Therefore they are receiving increasing attention in pavement engineering as effective alternatives to petroleum-based binders.

Manufacturing biobinders from biomass has gathered interest in recent years in light of environmental concerns with conventional bituminous binders. According to the US National Academy of Sciences, approximately 550 million dry tons per year of cellulosic biomass can be produced by 2020 without any major impact on food production or the environment [6, 7]. Fossilised biomass, like bitumen, has been heavily exploited for decades as coal and oil. The burning of fossil fuels uses ‘old’ biomass and converts it to ‘new’ CO_2, contributing to increased greenhouse gas emissions. On the other hand, burning ‘new’ biomass contributes no new CO_2 to the atmosphere as the released CO_2 is absorbed and recycled back into replanted biomass through photosynthesis in a cyclical process; this balance makes ‘new’ biomass carbon neutral [8, 9]. Unlike fossil fuels, biomass is abundantly available around the world on a renewable basis, either through natural processes or as a by-product of human activities i.e. organic wastes [8, 10].

1.1. Biomass sources

Sources of biomass can be categorised into four main groups: woody plants and agricultural products, herbaceous plants/grasses (all perennial crops), aquatic plants and manures (waste biomass) [8]. Within this grouping, biomass sources can be further subdivided into those with high- and low-moisture contents. ‘Dry’ biomass such as wood chips and sawdust are naturally more suited for gasification, pyrolysis or combustion, whereas aquatic plants and manures are inherently high moisture materials and therefore more suited to ‘wet’ processing techniques [8]. The herbaceous plant sugarcane has a high-moisture content and so would be suitable for a ‘wet’ conversion process. On the other hand, switchgrass, another herbaceous plant, has a much lower moisture content. Apart from moisture content, other factors should be considered when selecting an appropriate conversion method, especially in relation to those sources of biomass which lie between ‘wet’ and ‘dry’. These include:

1. Moisture content (intrinsic and extrinsic)
2. Calorific value
3. Proportions of fixed carbon and volatile components
4. Ash/residue content
5. Alkali metal content
6. Cellulose/lignin ratio

For ‘dry’ biomass conversion processes such as pyrolysis, the first five properties are of interest while for ‘wet’ processes like hydrothermal liquefaction (HTL) the moisture content and the cellulose/lignin ratio are the most important [8].

Over the last decade, there has been an increase in biobinder development technologies from biomass that are applicable to road construction. These technologies have evolved taking into account the available biomass and physico-chemical treatment needed to be applied to reach an optimum, consistent state. Biomass used as a source of road biobinders can be divided in two categories: liquid hydrophobic (mainly lipidic) biomass and solid biomass that needs to be converted (i.e. pyrolysed or liquefied). Liquid biomass includes vegetable oils and wood by-products such as pine rosin and pitch. Today, major full-scale developments have been made with this type of biomass where the processes are mainly physical blending and well-known chemical modifications such as transesterification of vegetable oil and polymerisation of rosin [11-13]. Considering the global consumption of bitumen, liquefied biomass cannot cover the demand alone as there are many other competing uses including the increasing demand to produce biofuels and chemicals such as biodiesel and bioethanol [14]. This is why more studies have shifted the focus to the second category (solid biomass). Conventional agricultural and wood by-products can provide large quantities of biomass so long as they are not used for the food industry. Depending on the moisture content of biomass, two main types of thermochemical processes can be used: solvent liquefaction and pyrolysis. Using biogenic sources for biobinder production can help reduce emissions and diverts the biomass away from combustion and into sustainable development. In terms of producing asphalts with novel biomaterials, waste biomass products are particularly interesting. Recycling biomass waste products can minimise waste destined for landfill and reduce greenhouse gas emissions by substituting the biowaste into conventional asphalt binders [15]. Life cycle assessment (LCA) in the road industry is an important tool used to measure and compare the key life-time environmental impacts of asphalt products and laying processes [16]. This includes energy consumption and greenhouse gas emissions. The production of 1 tonne of bitumen (including crude oil production, transport, refinery and storage) amounts to a total of approximately 226 kg of CO_2 emissions to the atmosphere [17]. As more novel materials and laying techniques emerge, LCA provides a framework for assessing the environmental benefits of biobinders and so researchers and LCA practitioners should focus on expanding the current databases to accommodate these novel materials [18]. Albeit novel, biobinders have proven to be beneficial in reducing emissions. One study which investigated the production of a biomodified binder via HTL from swine manure observed a significant reduction in greenhouse gases with an 81% drop in CO_2 emissions, whilst also reducing the emission factors of the conventional binder in the mixture (Figure 2) [19]. Similarly, the index for the Environmental Impact of Biomass Pre-processing (EIBP) is a comparable method to LCA that includes carbon footprint reduction and pollutant impacts from by-products and residuals [20]. It is considered to be a more feasible method to make a more generalised comparison between various pre-combustion processes, including HTL, pyrolysis, gasification and anaerobic digestion. A lower EIBP value suggests a better environmental impact. In this study, anaerobic digestion process has the lowest EIBP for most feedstocks studied, whereas HTL had the highest values. Despite this, HTL had an "extremely high environmental impact improvement potential" [20]. The authors found no strong correlations between energy conversion efficiency and EIBP and concluded that environmental impact should be considered separately when optimising biomass pre-combustion processes.

This review attempts to provide a link between biomass thermochemical conversion technologies and their respective products that may be used as biobinders in pavement engineering. For this purpose, firstly, the main biomass thermochemical conversion technologies are compared, and a review of the parameters influencing liquefaction products is provided. Next, it presents an overview of the recent biobinder studies reported in literature with an emphasis on the feedstock used and their performance-related properties. The studies are classified depending on the technology used to obtain the biobinder, including a specific section dedicated to the use of biobinders with recycled asphalt. The limitations to why biobinders have not been produced at industrial scale are also presented. Based on this, summary tables of the currently known properties of different biobinders have been compiled from the literature. The tables aim at providing a quick but insightful way of identifying potential biobinder feedstocks with certain desirable properties and help researchers identify gaps and potential research opportunities in the field.

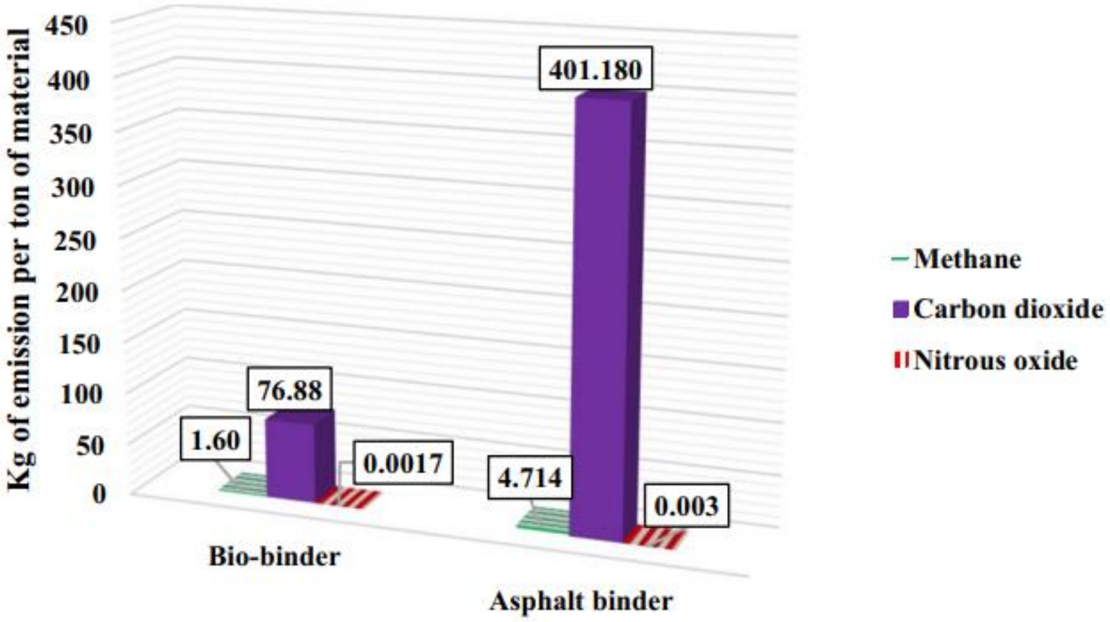

Figure 2: Greenhouse gas emissions from an HTL-derived swine manure biobinder compared to a conventional asphalt binder [19].

2. Comparison of main biomass thermochemical conversion technologies

The main biomass thermochemical conversion technologies for biofuels and chemicals are gasification, pyrolysis and solvent liquefaction. The conversion of carbon-containing solids at high temperatures (700-1000 °C) and under oxygen-starved conditions is referred to as thermal gasification [21]. Biomass gasification for the purpose of producing biobinders for road construction has not been studied and is therefore not relevant in this case. As a result, the focus in this section is on pyrolysis and solvent liquefaction as these are the techniques primarily used to produce biobinders.

Pyrolysis and liquefaction are two direct methods considered to be both time saving and relatively simple, and so they are used extensively [22]. They are comparable technologies as they both extract bio-based intermediate products, referred as a bio-oil or biocrude product respectively. There are complex reaction pathways associated with these technologies and currently many research groups are focusing on understanding them [23].

Although similar, there are considerable differences between these two conversion technologies. During pyrolysis, biomass is decomposed in the absence of oxygen within temperature and heating rates ranging from 300-900 °C [24] and less than 0.005 °C/s to more than 10,000 °C/s respectively [25]. Pyrolysis can be classified as slow, intermediate, fast and flash pyrolysis depending on the operating conditions, with fast and slow pyrolysis being the most commonly used processes [21]. Slow pyrolysis operates at relatively low heating rates and temperatures with long residence time. The main target product is often solid char i.e. traditional charcoal making process [26]. Intermediate and fast pyrolysis use moderate to high heating rates and temperatures, with fast pyrolysis characterised by shorter residence time. Flash pyrolysis uses the highest heating rates and shortest residence time, with a reaction time only lasting several seconds or less. Flash pyrolysis requires the use of special reactors and a sample particle size of approximately 105-250 μm [27, 28].

In pyrolysis, low temperatures and long residence times favour the production of char, whereas high temperatures and long residence times favour the production of the gaseous products. If the purpose is to maximise the yield of the liquid product (bio-oil), moderate temperatures, high heating rates and short residence times are required [26, 29]. Pyrolysis oil or bio-oil, recovered from the condensable vapours and aerosols produced during the process, is composed of a complex mixture of oxygenated organic compounds, including alcohols, aldehydes, esters, saccharides, phenolic compounds, carboxylic acids and lignin oligomers [21]. Bio-oil usually has a high yield of 70-80 wt. % [28].

Liquefaction, also referred to as solvent liquefaction, converts biomass into liquid fuels by processing in a hot, pressurised liquid environment for a period of time, in order to break down the solid biopolymeric structure to mainly liquid components [30]. Various solvents can be utilised such as water and methanol, non-polar solvents like toluene and tetrahydronaphtalene and ionic liquids like 1-ethyl-3-methylimidazolium chloride [21]. Solvent liquefaction undertaken in water is typically referred to as hydrothermal processing, hydrothermal liquefaction or hydrous pyrolysis. It is particularly attractive for wet feedstocks that are handled as slurries. Unlike pyrolysis, HTL does not required feedstock drying, therefore saving on high dewatering costs. This in turn increases the economic return of fuel production largely due to the wet nature of biomass feedstocks [23].

Solvent liquefaction can produce fractionated and hydrolysed plant polymers [31], partially deoxygenated liquid product (biocrude) [32] or syngas (gasification product) [33]. As reaction temperature increases, pressure must be increased in order to avoid the boiling of the water in the biomass (Figure 3). Extraction of high-value plant chemicals including resins, phenolics, phytosterols and fats occur at around 100 °C. At around 200 °C and 20 atm, fractionation of biomass takes place to yield cellulose, lignin and hemicellulose degradation products like furfural. According to Elliott et al. [30], a further increase in temperatures and pressures (300-350 °C, 120-180 atm) can hydrolyse the cellulose to glucose and more extensive chemical reactions take place, yielding a hydrocarbon-rich liquid product known as biocrude. For the purpose of biobinders, the biocrude liquid is the desired product. It is important to note that although visually resembling bio-oil, biocrude has a lower oxygen content and is less miscible in water, making it more amenable to hydrotreating [30]. Gas products with a significant fraction of methane are primarily achieved at around 600-650 °C and 300 atm [21].

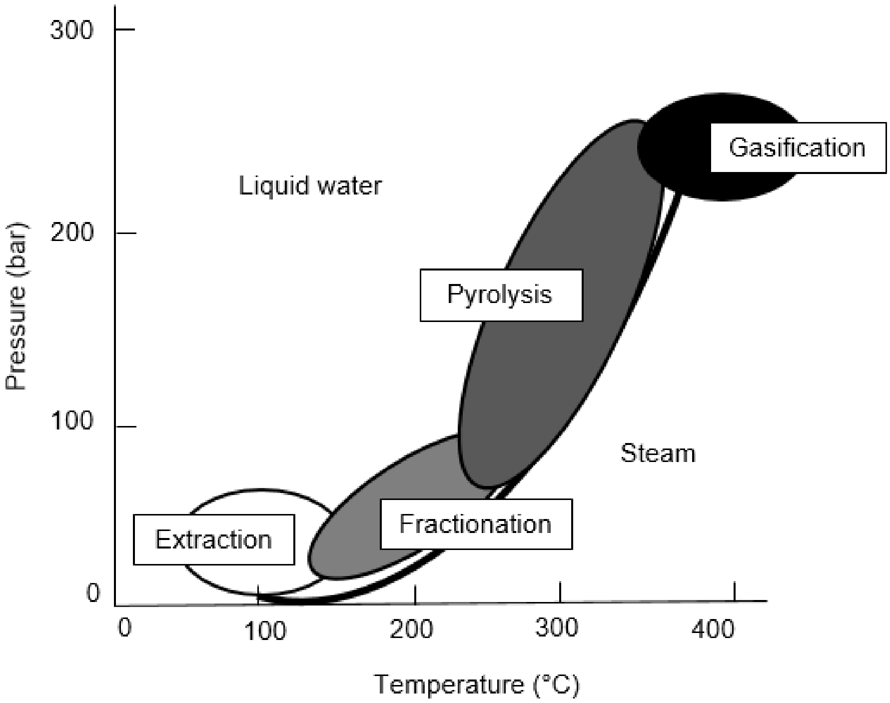

Figure 3: Temperature/pressure regimes for hydrothermal processing [21].

The use of catalysts is not common in pyrolysis, whilst the solvents used during liquefaction can act as catalysts and deliver premium products in comparison to those acquired through pyrolysis [23]. Additionally, the biocrude oil produced from liquefaction is far more stable and less corrosive than the one obtained from fast pyrolysis. This is due to a higher heating value and lower oxygen and moisture content. Equipment handling and storage costs are therefore reduced [23, 34-36]. The less oxygenated and more stable liquefaction product could therefore be more easily stored, transported and upgraded [37]. Studies report that pyrolysis oils can contain between 35-50% oxygen on a water free basis [9, 35, 38]. In comparison, HTL biocrude produced from a continuous-flow reactor contains between 5 and 18% oxygen for lignocellulosic, macro and microalgal biomass feedstocks [30, 39-42]. The high-water content found in the fast pyrolysis product is also a major concern as it would be immiscible with hydrocarbon products including bitumen. As a result, a lower moisture content in the product yield is desirable, such as those achieved via HTL. Overall, liquefaction can be considered a more competitive technology for biomass conversion to bio-bitumen-like products than pyrolysis, as indicated by their typical parameters in Table 1 proposed by Dimitriadis and Bezergianni [23].

However, the high-pressure conditions during liquefaction raise investment costs of the equipment units. Solvent liquefaction has some key engineering challenges that must be overcome in order to make this technology commercially viable. These include the continuous feeding of biomass slurries into high-pressured reactors, efficient energy integration and product separation from solvent [21].

Table 1: Typical hydrothermal liquefaction and pyrolysis parameters for biomass conversion [23].

Parameter	**Pyrolysis**	**Liquefaction**
Drying	Necessary	Unnecessary
Pressure (MPa)	0.1 – 0.5	5 – 20
Temperature (^{o} C)	370 – 526	200 – 400
Catalyst	No	Sometimes
Heating Value	Low (~17 MJ/kg)	High (~30 MJ/kg)
Oxygen Content	High	Low
Water Content	High	Low
Viscosity	Low	High
Upgrade	Hard	Easy

Both pyrolysis and liquefaction product yield and quality are governed by a range of factors, including biomass feedstock, temperature, pressure, catalyst and residence time. These parameters are highly dependent on the chemical characteristics of the feedstock such as the ratio of protein, lipid and carbohydrate fractions present in the biomass [23]. As liquefaction can provide a more stable product in high yields with relatively low oxygen contents than pyrolysis, it therefore seems to be more suited for the production of biobinders and so it is important to examine it in more detail in order to optimise the technology. As a result, the following section focuses on the effects of the operating parameters that come into play in solvent liquefaction.

3. Liquefaction Operating Parameters

Biocrude product yields vary considerably according due to the nature of the biomass feedstock and the operating parameters during liquefaction, such as temperature and pressure. Each parameter is inter-connected with one another, but their effects are ultimately influenced by the biomass feedstock. Each biocrude product must therefore be individually studied, even if the starting material is the same. The key operating parameters that affect liquefaction products are summarised in Table 2. It is important to note that these studies were not conducted for the sole application of road biobinders. However, it is useful to understand the influence of HTL parameters on product yield, and it is safe to assume they will affect biobinder production in a similar way.

Table 2: Summary of liquefaction parameters and their effects on product yield.

Liquefaction parameter	**Main factors affecting biocrude yield**
Temperature	• Can have a substantial effect on both product yield and properties of liquefaction biocrude • No ideal set temperature for a potential biobinder as product depends heavily on biomass feedstock and all operating parameters involved • General consensus that increasing reaction temperature increases yield up to a certain point, where the biocrude yield then begins to level off or decrease [23], with some attributing a decrease in yield with temperatures over 300 °C to a competition between hydrolysis and repolymerisation reactions involved in the liquefaction process [43, 44]
Pressure	• High pressure increases solvent density, with the resulting high-density medium penetrating efficiently into molecules of biomass components, resulting in enhanced decomposition and extraction • The rate of biomass dissolution can be controlled by maintaining pressure above the critical point, helping to boost the favourable reaction pathways to increase oil or gas yields [45] • The effect of pressure on product yield becomes negligible once supercritical conditions for liquefaction are achieved [45]
Catalyst	• Mostly used to reduce char formation and boost biocrude yield by reducing condensation and/or repolymerisation reactions of intermediate products [23] • Catalyst selection dependent on feedstock used. Selection can have either a positive or negative effect on the desired chemical reactions [46]

	• Different types of catalysts can influence yield even if the same feedstocks are used [46, 47], highlighting the importance of studying each liquefaction product (and potential biobinder) individually
Residence time	• Similarly dependent on feedstock used and other parameters involved • Short residence times (a few minutes rather than tens of minutes) have been reported to decompose biomass effectively and produce high yields for algal and evergreen-type feedstocks [45, 48, 49] • Like temperature, increasing residence time can increase biocrude yields until a certain threshold [23, 46, 50] • This levelling-off possible accounted to cracking of the liquid products to gases and the formation of char [46]
Solvent	• Water is the most popular solvent used in HTL due to being readily available, environmentally benign and inexpensive. Water acts as a solvent, a reactant and a catalyst during HTL, making the process significantly different from pyrolysis [51] • Organic solvents such as methanol and ethanol have lower boiling and critical points than those of water and so milder reaction conditions can be used [52] • High molecular weight products have been obtained from organic solvents in comparison to water for the liquefation of pinewood and algae [52, 53], while others have reported lower yield biocrude products with organic solvents, such as Cheng et al. [54], who studied the liquefaction of white pine sawdust, reinforcing the idea of treating each feedstock individually, even if it comes from the same type of biomass • Combining more than one solvent has also been explored, and Cheng at al. [54] was able to show the advantage of using co-solvent systems over single solvents to produce a greater product yield and biomass conversion • Hydrogen-donor solvents like tetralin can also enhance the yield of liquid products [45, 55]
Biomass-to-solvent ratio	• Generally, the optimum biomass-to-solvent ratio varies accordingly to the feedstock used and the operating parameters [56]. • Most types of biomass contain water and due to its threefold functionality, many researchers have evaluated the overall effect of biomass-to-water content • Similar to temperature and residence time, biocrude yield increases with increasing biomass/water ratio until a certain point, with a too-high water content ratio being undesirable [57]. • Smaller ratios can sometimes lead to higher heavy oil yields [48].

3.1. Summary and findings

Liquefaction biocrude products are overall found to be both more deoxygenated and hydrophobic and contain less water than pyrolysis oils. They are physically less dense but in fact more viscous than the latter [30]. As a result, they are more suited for the production of biobinders. Operating parameters during liquefaction are all closely interrelated, and each play a key part in determining yields. For instance, temperature, residence time and biomass-to-solvent ratio generally increase yield until a certain threshold. The liquefaction process mechanisms and interactions between the parameters have not been clarified much in the literature, although three major steps take place: depolymerisation followed by decomposition and recombination [51]. These processes along with the critical parameters explained above vary extensively according to the feedstock used. As biomass is a complex mixture of carbohydrates, lignin, proteins and lipids, the reaction chemistry and mechanisms of biomass liquefaction are consequently also complex [8, 58, 59]. This coupled with the variability of feedstocks makes it difficult to predict what happens during and after liquefaction. This is a challenge that exists in this field and the complexities of the critical parameters should be studied individually for each feedstock [58].

4. Biobinders

There are three ways in which biobinders can be utilised to decrease the demand of petroleum-based bitumen: (1) as bitumen modifiers (<10% bitumen replacement), (2) as bitumen extenders (20-75% bitumen replacement), and (3) as a direct alternative binder (100% replacement) [60-63]. According to the literature, most current studies focus on using biobinders as modifiers, and adding <10% to the mixture [64]. This is perhaps because of the increase in uncertainty in rheological properties when higher amounts of biobinder are used. Research is still vital to use biobinders as bitumen extenders or direct replacements [61], and therefore there is a need to study further these materials in order to maximise their potential.

Biobinders can be produced from a range of natural resources including agricultural crops, municipal wastes, forestry by-products, sugar, molasses and rice, natural tree and gum resins, natural latex rubber and vegetable oils, amongst many others [1]. However, Kluttz [65] highlighted some issues around substituting other materials for some or all of the bitumen in conventional mixtures. He pointed out that the alternative binder should have predictable properties regarding rheology, adhesion to aggregates, coating behaviour in a mix plant and flow characteristics during construction. Kluttz [65] further added other less obvious assumptions to take into consideration such as predictable leaching characteristics, water solubility, interactions with fuels or oils, environmental issues, odour, mixing with virgin binders and interaction with contiguous mixes. All of these points should serve as starting points when evaluating a new material for a pavement binder. It is important to note that bituminous binders and biobinders greatly differ in terms of their chemical compositions and properties. Bitumen is mostly composed of hydrocarbon molecules with some heterocyclic species and functional groups containing sulphur, nitrogen and oxygen atoms [66, 67]. On the other hand, biobinders are generally composed of a mixture of fatty acid derivatives with an array of compounds, including aromatic and nitrogenous compounds, esters, aldehydes and ketones [68]. This difference in chemical composition presents an added challenge with the development of biobinders, and stresses the importance of characterizing the chemical properties of the biobinder prior to blending with bitumens.

When dealing with the blend of bitumen and biobinders, mixing speed and temperature are important parameters to consider in order to obtain a homogeneous, consistent material that could mimic the rheological properties of petroleum bitumen. Table 3 presents the mixing conditions used by different authors when working on the partial replacement of petroleum-based binders.

Table 3: Main mixing conditions used in biobinder studies.

Mixer type	Temperature (°C)	Mixer speed (rpm)	Time (min)	Type of biomass	Reference
Shear mixer	120	5000	20	Pyrolysed oil	[69]
Shear mixer	180	4000	45	Used oil	[70]
Ribbon mixer	125	3000	30	Tall oil	[71]
Mechanical mixing	125	3000	30	HTL oil from manure	[72]
High speed shear mill	145	3000	5	HTL oil from manure	[72]
Mechanical stirrer	150	2000	0.1 ml each minute	Agricultural waste dissolved in ethylene glycol	[73]
Low shear mixing reactor	160	1500	60	Dehydrated sap	[74]

The following section presents current biobinder studies organised according to the thermochemical technique employed to make the biobinder (where applicable and mentioned). A summary has been compiled from the literature displaying the currently known properties of *various biobinders (Appendix A). It aims at providing a quick but insightful way of identifying potential biobinder feedstocks with certain desirable properties and help researchers identify gaps and potential research opportunities in the field. In addition, Table 4 to*

Table 8 present a short summary of Appendix A, with key improvement and drawback properties of each biobinder.

4.1. Pyrolysis-based biobinder studies

Wood-derived pyrolysis oils have shown to enhance high temperature stability and elasticity, fatigue and rutting resistance [75, 76] and have been recommended as good bitumen modifiers or extenders. Bio-oils can be successfully combined with other waste materials such as crumb rubber from used tires at lower temperatures (around 125 °C) than those used for blending traditional bitumens, with the developed bio-bitumens performing as well or better than conventional asphalt mixtures with ground tire rubber, in terms of rutting, fatigue, moisture sensitivity and low temperature cracking [1, 77].

Similarly, commercially made biobinders such as Eco-Biopave™, made from a mixture of rosin oil, pyrolysed waste materials and natural rubber (Figure 4) have also shown better behaviour at high temperatures with limited emissions of volatile organic compounds (VOCs), as well as good properties against fatigue and cracking after short-term ageing [71]. However, it is agreed that sufficient commercial production of fractionated bio-oil and bio-oil pavement trials are necessary to further understand the ageing mechanisms of these new materials for the technology to be freely applicable.

Figure 4: On the left, biobinder test road section near Adelaide, Australia. On the right, the Ecopave™ biobinder cross-section specimen [78, 79].

Biobinders developed from switchgrass bio-oil, oak wood and corn stover blended at under 10% with bitumen can also result in improvement of the rutting parameter ($|G^*|/\sin\delta$) of the base bitumen [80]. In particular, it has been noted that the rheology of switch grass bio-oils is similar and comparable to that of bituminous binders and can therefore be considered a feasible alternative solution [76, 81, 82] . However, such bio-oils cannot be used as direct replacements on their own due to their low viscosity and high-water content, and therefore require upgrading. Low fractions of biobinders (~10% or less) tend to show the most promising results in terms of improving binder performance without lowering viscosity too much, ensuring a stable performance. Yang et al. [83] suggest that increasing the bio-oil fraction decreases the compatibility with petroleum bitumen, as adding higher dosages increases conglomeration of the asphaltenes, leading to possible stiffening effects or loss of elastic behaviour.

There are studies that have also found promising results with higher blending proportions of biobinders (up to 50% replacement), making the case for treating each biobinder individually and trialling different proportions. Both Mohammad et al. [84] and Yang and Suciptan [85] manufactured biobinders using up to 50% fast pyrolysis bio-oil obtained from pine wood chips. The biomodified mixtures had rutting performance that was similar or better than that of the base binder. In the case of Mohammad et al. [84], almost all the mixtures had adequate moisture susceptibility and showed improved low-temperature performance. However, the mixtures with biobinders revealed less fracture resistance at intermediate temperatures.

Similarly, Zhang et al. [68] studied how a styrene-butadiene-styrene (SBS) modified binder with pyrolysis-derived bio-oil added up to 20% can improve high temperature performance. After RTFOT ageing, temperature sensitivity was lower than that of the base binder but increased with increasing bio-oil content. On the other hand, rutting resistance increased in comparison to the base binder and improved with increasing bio-oil content. Overall, the high temperature performance of SBS-bio-modified binders is promising in this study, but further work is needed to improve its performance and investigate its modification mechanisms as well as storage stability. This emphasises the need for characterising binders before and after ageing, as the biggest challenge with biobinders lies with their ageing susceptibility. Table 4 presents a summary of the pyrolysis-derived biobinder studies with the primary property improvements and drawbacks.

Table 4: Summary of pyrolysis-derived biobinder studies.

Biobinder	Replacement	Key property improvement	Key property drawback/reduction	References
Oakwood and crumb rubber	100% binder replacement	None	None	[1]

Oakwood and crumb rubber	20% binder extender	Fatigue & moisture damage	None	[77]
Switchgrass oil	100% binder replacement	None	Temperature susceptibility	[86]
Pine wood biomass	Up to 50% binder extender	Rutting & thermal cracking resistance	Viscosity	[84]
Japanese cedar chips	2, 8, 25 and 50% binder modifier and extender	Rutting resistance & temperature susceptibility	Thermal cracking resistance	[85]
Oakwood, switchgrass and corn stover oils	3-9% binder modifier	Rutting resistance	Thermal cracking resistance	[80]
Waste wood resources	5 and 10% binder modifier	Fatigue resistance	None	[75]
Waste wood resources	5 and 10% binder modifier	Rutting resistance & temperature susceptibility	None	[76]
Waste wood resources in the form of wood chips, sawdust and shavings	2, 5 and 10% binder modifier	None	Ageing resistance	[83]
SBS-modified bio-oil	1% SBS, 5-20% bio-oil (binder modifier and extender)	Rutting, temperature susceptibility & ageing resistance	Viscosity	[68]

4.2. Liquefaction-based biobinder studies

HTL-derived biocrude from swine manure has shown to enhance low temperature performance, decrease the rate of ageing, and allow for reduced mixing and compaction temperatures due to the decrease in viscosity, when used at <10% by weight of the base binder [72, 87-90]. The addition of the HTL biocrude from swine manure can yield a more robust binder against oxidation compared to bio-oil from pyrolysis of corn stover or miscanthus [91]. A life cycle analysis was carried out to determine the environmental impact [19]. Even though only 10% of swine manure biocrude was added to the bituminous binder, it was proven to reduce by half the energy consumption and improve the global warming potential index by 7.8%. In other words, this process reduces the emission of carbon dioxide by 5 times compared to the production of bitumen from petroleum. Life cycle studies such as this one present an area of opportunity for biobinders in order to quantitatively show the benefits of their implementation in asphalt binders, and discovering their future potential.

Similarly to pyrolysis oils, HTL biocrudes combined with other modifiers have exhibited good performance. Swine manure biocrude modified with crumb rubber, Gilsonite, SBS and polyphosphoric acid at low proportions (<10%) show improved low temperature performance and enhanced temperature sensitivity, although results become less obvious at higher temperatures [92, 93].

Algae-derived biocrudes are also very popular biobinders. Studies that display the potential of microalgae and HTL to produce binders for pavements, show how the rheological behaviour of the developed biocrude is heavily affected by the operating conditions used.

Dhasmana et al. [94] produced bio-crude from HTL at 300 °C of different algae feedstocks including spirulina, a nanoalgae strain and swine manure. Although all the biobinder blends exhibited similar viscoelastic properties before and after ageing, the algae-derived biobinders were stiffer than those obtained from swine manure. Other algae biobinder studies have claimed a rheological simple material with similar viscoelastic properties to bitumen, if lower temperature ranges (240-260 °C) are used [95, 96]. High molecular weight species that fragment at the higher temperature result in less viscous material that is no longer thermorheologically simple. It is crucial to preserve these heavy species which appear to function similarly to asphaltenes and resins in petroleum derived binders. Future work involves studying how the properties of the hydrophobic fraction vary with microalgae strain. This would helpful in understanding how the main elements and their molecular weight distributions impact the final biobinder viscosity profile. Once the most suitable microalgae residues are chosen, an assessment of their economic viability for road pavement compared to the petroleum distillation process would be beneficial.

Table 5 presents a summary of the liquefaction-derived biobinder studies with key property improvements and drawbacks.

Table 5: Summary of liquefaction-derived biobinder studies.

Biobinder	Replacement	Key property improvement	Key property drawback/reduction	References
Biocrude from swine manure	2, 5 and 10% binder modifier	Thermal cracking & ageing resistance	None	[87, 88]
Biocrude from swine manure	2, 5 and 10% binder modifier	Thermal cracking resistance	None	[89]
Biocrude from swine manure	2, 5 and 10% binder modifier	Low temperature performance, moisture damage & thermal cracking resistance	None	[90]
Biocrude from swine manure with crumb rubber	5, 10 and 15% crumb rubber blended with 5% biobinder	Thermal cracking resistance & temperature susceptibility	None	[92]
Biocrude from swine manure	2, 5 and 10% binder modifier	Thermal cracking resistance	None	[93]
Biocrude from swine manure	5% binder modifier	Rutting, ageing, temperature susceptibility & thermal cracking resistance	None	[72]
Swine manure, miscanthus pellets, corn stover and wood pellets	10% binder modifier	Rutting	Ageing resistance	[91]
Biocrude from swine manure	10% binder modifier	None	None	[19]
			Ageing resistance	[94]

Spirulina sp. algae (microalgae), swine manure, and nanoalgae	Studied as virgin biobinder and blended biobinder with PG 64-22 bitumen in a 1:8 ratio	Thermal cracking resistance & moisture damage		
Scenedesmus sp. Microalgae	100% binder replacement	Similar rheological properties to that of bitumen	None	[96]
Spirulina sp. Residues	100% binder replacement	Temperature susceptibility	None	[95]
Household food waste	5 and 10% binder modifier	Temperature susceptibility	None	[97]

4.3. Biobinder and recycled asphalt studies

The use of bio-oils and biocrude as rejuvenators for recycled asphalt mixtures have also been a focus in recent years. Increasing the recycled asphalt (RA) content is environmentally valuable since it reduces long distance aggregate transport and amount of new bitumen needed in asphalt mixtures [98-100]. In order to make the most of the RA, researchers use new binders and/or additives that re-activate the aged binder by increasing its viscous fraction [98, 101, 102]. In this case, bio and conventional rejuvenators typically improve cracking performance (fatigue and low temperature behaviour) but can be detrimental to rutting performance. Table 6 presents a summary of the biobinder studies with recycled asphalt with the main property enhancements and drawbacks.

Biobinders from swine manure and pongamia oil have been considered suitable rejuvenators with RA, with improved rutting and fatigue resistance and adequate thermal stability [103, 104]. Apart from swine manure, other studies have examined thermochemically treated wood, miscanthus and corn stover with RA, with the objective of understanding how feasible these mixtures could be in cold regions prone to thermal cracking. Results showed that the presence of biobinders improved fracture resistance, and overall it was observed that the biomodified RA mixtures exhibited better low-temperature cracking behaviour to that of conventional hot-mix asphalt [105, 106].

Nevertheless, limited data on accelerated pavement testing is currently available as most studies are restricted to laboratory evaluations [107-111]. One study that has undertaken a full scale accelerated pavement test was Blanc et al. [107], where three mixtures were designed incorporating 50% RA content with three innovative bio-materials and compared with a reference high modulus asphalt mixture. They were tested for one year in order to speed up rutting and fatigue cracking. The authors concluded that all three bio-mixtures present similarly or better performance than the control and confirmed that they can be effectively used in road construction, but further investigation should focus on long-term monitoring to evaluate ageing performance.

Fatty acids from vegetabe oils like soybean and sunflower oils have also been shown to soften aged bitumen [112, 113]. Field investigations have found the biomodified mixtures to have adequate performance after 5 years of service, despite the biomodified binders being more sensitive to ageing than traditional binders. Nevertheless, the authors agree that five years is not long enough to draw definitive conclusions.

The use of biobinders to enhance the properties of petroleum bitumen has been a topic of discussion over several years, however there is limited knowledge on the adhesion properties of bitumens blended with biobinders. Gong et al. [114] and Jiménez del Barco Carrión et al. [115] looked at characterizing the adhesion behaviour of bio-modified bitumen using contact angle measurement and surface free energy. Gong et al. [114] used dosages of 1%, 2%, and 3% of bio-modifier (produced from natural bean oil) with two base binders. They found that the adhesion properties depended on the compatibility between the biobinder and base bitumen used. Jiménez del Barco Carrión et al. [115] combined biobinders with RA binders and concluded that biobinders had great potential to maintain moisture damage resistance of such type of asphalt mixtures. As a result, it is critically important to characterize these properties for innovative materials used.

A main conclusion drawn from RA studies is that high amounts (i.e. 50% RA) could be incorporated into asphalt mixtures with suitable biobinders, restoring their rheological properties and enhancing the performance of the mixture [115-119]. Such bio-derived mixtures with RA can sufficiently pass the design requirements for pavements and perform well at low, intermediate and high temperatures without the need of neat bitumen [120].

Table 6: Summary of recycled asphalt and biobinder studies.

Biobinder	Replacement	Key property improvement	Key property drawback/reduction	References
Bio-rejuvenator SYLVAROAD™ Biobinder Biophalt® Bio-additive Epoxidized Soybean Soyate (EMS)	Up to ~5% added to mixtures with 50% RA	Rheological properties including complex modulus and phase angle, fatigue, rutting, thermal cracking resistance & durability in field	None	[98, 107]
Rejuvenator A (regenerated oil and a Fischer-Tropsch wax) and Rejuvenator B (highly viscous material free of polycyclic aromatic hydrocarbons)	6,12 and 18% Rejuvenator A and 9, 18 and 27% Rejuvenator B added to RA mixture	Thermal cracking, rutting & fatigue resistance	None	[101]
Waste vegetable oil, waste vegetable grease, organic oil, distilled tall oil, aromatic extract and waste engine oil	12% added to RA mixture	Rutting, fatigue & thermal cracking resistance	Viscosity, moisture damage & ageing resistance	[111]
Bio-rejuvenator SYLVAROAD™	6.8% added to mixtures with 50% RA	Thermal cracking, rutting & ageing resistance (short-term ageing)	None	[110]
Rejuvenators BituTech RAP SonneWarmix RJT and RJ	9.28% added to mixtures containing 35 and 40% RA	Fatigue, thermal cracking & ageing resistance	Viscosity, rutting & moisture damage	[109]
Crumb rubber with a commercial rejuvenator	3, 5 and 7% rejuvenator added to mixtures containing 0, 30 and 50% RA	Fatigue, thermal cracking & moisture damage	Rutting resistance	[108]

Crude tall oil and soybean oil derivative	3 and 6% added to mixtures containing 50% RA	Thermal cracking resistance	Ageing resistance	[119]
Bio-rejuvenator SYLVAROAD™ Biobinder Biophalt® Bio-additive Epoxidized Soybean Soyate (EMS)	Up to 2.8% biobinder added to mixtures containing 50% RA	Rheological properties including complex modulus, rutting, fatigue, thermal cracking, moisture damage & ageing resistance	None	[118]
Biobinder Biophalt®	1.7% added to mixtures containing 50% RA	Rutting & thermal cracking resistance	None	[120]
Swine manure	5% biobinder added to mixtures containing 40% RA	Fatigue, thermal cracking resistance, temperature susceptibility & durability in field	Viscosity	[103]
Swine manure	% biobinder added to mixtures of 0, 15 and 45% RA	Thermal cracking resistance & temperature susceptibility	Viscosity	[105]
Swine manure, corn stover, miscanthus and wood pellets	5 and 10% biobinder added to mixtures with 0, 15 and 45% RA	Thermal cracking, temperature susceptibility & ageing resistance	Viscosity	[106]
Pongamia oil and a composite oil made from castor oil and coke oven gas	5, 10 and 15% binder modifier	Rutting, fatigue & temperature susceptibility	Viscosity	[104, 121]

4.4. Miscellaneous biobinder studies

Some studies are considered miscellaneous in the sense that they do not adhere or refer to one specific thermochemical technology. Materials such as algae [122], residues from the forestry industry, waste cooking oils, some agricultural wastes and natural fibres such as sugarcane, rice husk and hemp as well as synthetic binders have been used as bitumen modifiers at different percentages [5, 73, 123].

Overall, the materials have shown adequate rheological performance and improve some mechanical properties compared to bitumen (see Annex A for details). They seem to perform better at lower temperatures than conventional bitumens, due to their increased workability, making them more suited to be used in colder climates or as fluxing agents for stiff binders such as those found in recycled asphalt [124, 125]. This renders the study of high-temperature performance more critical with biobinders [126-128]. When ageing was considered, most of them revealed faster ageing rates [129, 130]. Ageing of biomodified binders and mixtures is therefore an unavoidable issue which needs to be carefully studied. A summary of the miscellaneous biobinder studies' key properties is shown in Table 7.

Table 7: Summary of miscellaneous biobinder studies.

Biobinder	Replacement	Key property improvement	Key property drawback/reduction	References
Microalgae	100% binder replacement	None	None	[122]
Forestry industry by-products	5.7%	None	Ageing resistance	[129]
Waste cooking oil	10,30 and 60% binder modifier and extender	Rheological properties & thermal cracking resistance	Fatigue & rutting resistance	[126]
Biodiesel by-product from waste cooking oil (as aged binder rejuvenator)	2-8% binder modifier	Fatigue & thermal cracking resistance	Rutting & moisture damage	[127]
Biodiesel by-product from waste cooking oil (as aged binder rejuvenator)	1.5,1.75 and 2% binder modifier	Fatigue & thermal cracking resistance	Rutting & moisture damage	[128]
Soy fatty acids	1 and 3% binder modifier	Rheological properties including viscosity and complex modulus	None	[112]
		None	Ageing resistance	[131]

Waste coffee grounds	2-8% binder modifier	Rheology & fatigue resistance	None	[123]
Vinasse	10% binder modifier			
Rice husk and wood sawdust	10 and 20% binder modifier and extender	Rutting resistance	Ageing resistance	[130]
Plant resin fluxed with monoalkyl esters from vegetable and animal oils	0.5 and 5% binder modifier	Rheological properties including complex modulus & durability in field (after 5 years)	Ageing resistance	[113]
Sugarcane bagasse, corncobs and rice husk	1 and 2% binder modifier	Rutting & ageing resistance	Moisture damage	[73]
Natural bean oil	1-3% binder modifier	None	None	[114]

4.5. Synthetic binder studies

Synthetic binders have also been studied as alternative binders. Although these are not derived from natural sources and have not been studied extensively, they can still affect the rheological properties of asphalt binders. In particular, Airey and Mohammed [132] investigated the rheological properties of polyacrylates binders, which consisted of polyethyl acrylate (PEA), polymethyl acrylate (PMA) and polybutyl acrylate (PBA). Results indicated that PEA could simulate a ‘soft’ 100/150 penetration grade bitumen, while PMA showed stiff 10/20 penetration grade bitumen characteristics. Airey et al. [60] further studied these binders and blended the polyacrylates with conventional bitumens, which were found to be rheologically similar to SBS polymer modified bitumens.

Bio-rejuvenators manufactured from cotton oil and the plasticizer dibutyl phthalate (DBP) have also been used to restore the properties of conventional and SBS-modified binders [128, 133]. Results showed that the 10% dosage of bio-rejuvenator helps to restore workability and rutting resistance of the long-term aged bitumen to original levels. Low-temperature cracking and *fatigue resistance also improved but not to the level of the virgin conventional and SBS-modified bitumens. A summary of these studies is presented in*

Table 8.

Table 8: Summary of synthetic binder studies.

Biobinder	Replacement	Key property improvement	Key property drawback/reduction	References
Polyethyl acrylate (PEA), polymethyl acrylate (PMA) and polybutyl acrylate (PBA)	100% binder replacement	Rheological properties including complex modulus and phase angle	None	[132]
Polyethyl acrylate (PEA), polymethyl acrylate (PMA) and polybutyl acrylate (PBA)	25-75% binder extender	Rheological properties including complex modulus and phase angle	None	[60]
Cotton oil by-product and dibutylphthalate (DBP) (as aged binder rejuvenator)	5 and 10% binder modifier	Viscosity, thermal cracking & fatigue resistance	Rutting resistance	[133]

5. Current limitations of biobinders

Although the field of biobinders has drastically taken off in the last ten years, the use of bio-derived additives to enhance petroleum bitumen has been around for much longer. The first patent dealing with the production of an alternative binder based on compounds partially derived from biomass was published in 1991 in the US [13]. This binder was obtained from a mixture of natural or modified vegetable resins (tall oil, wood, or turpentine) and was considered an added-value product with high abrasion resistance. Since then, various companies have developed such biobinders based on oils, resins and polymers. The key benefit is reduced asphalt manufacturing process temperatures compared to petroleum binders, corresponding to significant energy reductions [11, 134-138].

At present, essentially all studies (academic or commercial) that use biobinders in road construction are limited to small-batch production, and so bio-bitumen, whether blended with bituminous binders or not, cannot compete with traditional bitumen. One of the key obstacles to the deployment of biobinders compared to conventional binders is their price. Indeed, the price of vegetable binders is equivalent to that of synthetic binders and is 3 to 10 times higher than that of petroleum bitumen [139]. This results in an asphalt mixture approximately four times more expensive than the traditional product. Unlike bitumen, it can be safe to assume that the price of biobinders will not be affected by the volatile price of crude oil. A high oil price coupled with further development of renewable technologies will result in a favourable environment for developing biobinders at a much larger scale. Due to the fact that the biobinder technologies are at an early stage, its price is unlikely to fall until a commercial market has been developed and economies of scales take off.

In addition, the process of manufacturing biobinders and then combining them with bitumen tends to be time-consuming and stability of the biobinders is a major issue. Each biobinder has to be carefully studied in detail to understand its chemical and rheological properties, as well as their ageing mechanisms. This building of knowledge is what will help make biobinders more acceptable for widespread use in the future.

Carrying out more studies that look at the sustainability impact and overall carbon footprint of biobinders in comparison with bitumen, such as LCA, will also help build the case for biobinders. In order to help LCA to be useful as a decision-making tool for practitioners and road administrations, cradle-to-grave analysis should be performed, and therefore, more data about the durability of asphalt mixtures containing biobinders should be produced, including full-scale trials and trial sections.

6. Conclusions and final remarks

This review aimed, for the first time, to bring together studies across different disciplines and investigate their effects on biobinders for road construction.

The utilisation of biomass is beneficial to the environment and society as a sustainable form of energy. A vast range of biomass feedstocks can be thermochemically treated and the derived products subsequently used for various applications, including biobinders for road construction. Its availability worldwide makes it an attractive option for researchers looking to find more environmentally-friendly alternatives to bituminous binders.

Liquefaction and pyrolysis are two effective biomass thermochemical conversion technologies that can be used to produce biobinders. Unlike pyrolysis, liquefaction does not require feedstock drying, saving on high drying costs. The recovered products seem to be more stable and less corrosive than the ones obtained from pyrolysis, due to lower oxygen and moisture contents and higher heating values, and are therefore more suitable as biobinders for asphalt mixtures.

However, liquefaction is considered a less developed technology than pyrolysis and so understanding the effects of the operating parameters is essential to optimise biocrude yields and ultimately advance the process. Product yield and quality are impacted by a range of factors, including temperature, pressure, residence time and type of biomass source. These parameters are highly reliant on the nature of the feedstock as well as each other and can vary extensively. Numerous complex reactions take place during the conversion of biomass into biocrude products. The wide variation in different feedstock types and reaction conditions generates a broad but fragmented spectrum of knowledge and makes it essential to individually study each material to produce biobinders.

The concept of biobinders has definitely gained momentum in pavement engineering and a range of studies have been carried out evaluating their influence on asphalt mixtures performance. Biobinders have shown promising performance as bitumen modifiers and extenders. They can enhance the chemical and mechanical properties of conventional asphalt binders. Extensive research has been found on these categories, but less confident results are found in terms of total replacement of conventional bitumen.

The review carried out reveals that biobinder behaviour is dependent on biomass composition. While some biobinders improved rutting resistance, others improved fatigue cracking. However, most biobinders seem to enhance low temperature performance and lower the viscosity of the bitumen. There are no reports of a single biobinder improving all of the desired performance parameters. Therefore, before these materials can be further implemented, their performance in asphalt mixtures needs to be always fully characterised in terms of their chemical, rheological, mechanical and ageing properties. These need to be tested over a whole range of service temperatures depending on the behaviour and nature of the biobinder. Due to their recent use, most of the studies found are focused on laboratory properties. In order to provide confidence to the use of these materials, more data about long-term performance and durability are required; and attention should be paid to future issues such as their recyclability.

Biobinders that are available in large quantities such as through industrial processes, i.e. waste feedstocks, are more attractive in terms of commercial viability than those derived from more involved processes. Due to their availability, these are more likely to become a practical reality in the near future. Comprehensive environmental assessment tools like LCA and EIBP should be incorporated when studying thermochemical processes and biobinders as they can highlight potential research opportunities and help provide a clearer picture of where the technology is heading in the long term. Environmental impact studies should consider the whole life cycle of asphalt mixtures containing biobinders, accounting for their impact during the whole service life of the pavement. For this purpose, future research should focus on their long-term performance and recyclability.

Finally, the price and length of time required to make biobinders are major barriers limiting their widespread use. Current biobinder materials are mostly used for research purposes either at lab or pilot-scale, and so are not presently found at industrial scale. For these reasons, successfully produced biobinders almost exclusively apply to small cycle and pedestrian paths, sidewalks and car parks. Nevertheless, there is a great opportunity for biobinder production costs to decrease as the technology becomes mainstream, their combination with reclaimed asphalt to reduce the final price of the mixture and also for the implementation of a more bio-based and circular economy in the future, where suitably efficient bio-products can then compete and capture markets dominated by petroleum bitumen.

Appendix A. Summary of the influence of biobinder composition on bituminous binders’ properties and performance

↓	Decrease compared to conventional materials
↑	Increase compared to conventional materials
✓	Better comparison to conventional materials
x	Worse comparison to conventional materials
~	Similar performance to conventional materials
-	Not known/specified

Thermochemical Technology used	Ref.	Biobinder	Replacement (%)	Biobinder used as	Rheology	Viscosity	Complex Modulus	Phase Angle	Rutting resistance	Fatigue resistance	Thermal cracking resistance	Moisture Damage	Temperature susceptibility	Ageing resistance	Durability in field
Pyrolysis	[1]	Oakwood and crumb rubber	100	Binder replacement	-	~	-	-	-	-	-	-	-	-	-
	[77]	Oakwood and crumb rubber	20	Bitumen extender	~	~	~	~	~	✓	~	✓	-	~	-
	[81]	Switchgrass oil	100	Binder replacement	-	~	-	-	-	-	-	-	↑	-	-
	[84]	Pine wood biomass	Up to 50%	Bitumen extender	-	↓	-	-	✓	-	✓	~	-	-	-
	[85]	Japanese cedar chips	2 and 8% And 25 and 50%	Bitumen modifier and extender	-	↑	~	↑	✓	-	↓	-	↓	-	-
	[80]	Oakwood, switchgrass and corn stover oils	3-9%	Bitumen modifier	-	-	-	-	✓	-	x	-	-	-	-
	[75]	Waste wood resources	5 and 10%	Bitumen modifier	-	-	-	-	~	✓	-	-	-	-	-
	[76]	Waste wood resources	5 and 10%	Bitumen modifier	-	-	↑	↓	✓	-	-	-	✓	-	-
	[83]	Waste wood resources in the form of wood chips, sawdust and shavings	2, 5 and 10%	Bitumen modifier	-	-	-	-	-	-	-	-	-	x	-
	[68]	SBS-modified bio-oil	1% SBS, 5-20% bio-oil	Bitumen modifier and extender	-	↓ with increase in bio-oil content	-	-	~ slightly weaker than base binder ✓ Stronger rutting resistance after RTFOT ageing	-	-	-	✓less temperature sensitive than base binder. Sensitivity ↓ with increase in bio-oil content both before and after RTFOT ageing	✓	-

Liquefaction	[87]	Biocrude from swine manure	2, 5 and 10%	Bitumen modifier	-	↓	↓ as biobinder content increased	-	~	-	✓	-	-	-	-
	[88]	Biocrude from swine manure	2, 5 and 10%	Bitumen modifier	-	↓	↓	-	-	-	✓	-	-	✓	-
	[89]	Biocrude from swine manure	2, 5 and 10%	Bitumen modifier	-	-	-	-	-	-	✓	-	-	-	-
	[90]	Biocrude from swine manure	2, 5 and 10%	Bitumen modifier	✓for low temperature properties	-	-	-	-	-	✓	Potential to improve	-	-	-
	[92]	Biocrude from swine manure with crumb rubber	5, 10 and 15% crumb rubber blended with 5% biobinder	Bitumen modifier	-	↓ than a common crumb-rubber modified binder. This is less significant at higher temperatures	-	-	-	-	✓	-	↓	-	-
	[93]	Biocrude from swine manure	2, 5 and 10%	Bitumen modifier	-	-	-	-	-	-	✓	-	-	-	-
	[72]	Biocrude from swine manure	5%	Bitumen modifier	✓	↓	↓	↓	✓	-	✓	-	~ can potentially enhance both the high- and low-temperature susceptibility of typical binders	✓ potential to reduce ageing without compromising rutting performance	-
	[91]	Swine manure, miscanthus pellets, corn stover and wood pellets	10%	Bitumen modifier	Ranked differently before and after ageing	↓ in unaged biobinders to that of control but ↑ after ageing	↑ after ageing except for swine manure biobinder (only ↑ at low frequencies after ageing)	↓ for swine manure biobinder after ageing but ~ behaviour at high frequencies ↓ for Miscanthus, and corn stover than control Wood pellet lowest phase angle	✓	-	-	-	Wood pellet most susceptible to temperature and miscanthus least susceptible	Wood pellet highest susceptibility to ageing followed by miscanthus, corn stover, control and then swine manure	-
	[19]	Biocrude from swine manure	10%	Bitumen modifier	-	-	-	-	-	-	-	-	-	-	-
	[94]	*Spirulina* sp. algae (microalgae), swine manure, and nanoalgae	Studied as virgin biobinder and blended biobinder with PG 64-22 bitumen in a 1:8 ratio	Bitumen modifier	~ but more work needed	~	↓ before ageing for virgin biobinders ~ behaviour to aged base binder when blended with bitumen and aged	↓ after ageing for virgin samples ~ behaviour when blended	-	-	✓	↓	-	Stiffer virgin biobinders after ageing, algal feedstocks stiffer than swine manure ~ behaviour to aged base binder	-

Liquefaction	[96]	*Scenedesmus* sp. Microalgae	100%	Binder replacement	~ similar properties to that of bitumen	-	~	~	-	-	-	-	-	-	-
	[95]	*Spirulina* sp. residues	100%	Binder replacement	~ viscoelastic profile to an elastomer-containing bitumen composed of ca. 8% SBS dispersed in bitumen	-	↓	↓	-	-	-	-	↓ water-insoluble fraction appears to be less temperature sensitive than conventional bitumen, particularly at high temperatures	-	-
	[97]	Household food waste	5 and 10%	Bitumen modifier	-	~	-	-	-	-	-	-	↓	-	-
Recycled Asphalt	[98]	Bio-rejuvenator SYLVAROAD™ Biobinder Biophalt® Bio-additive Epoxidized Soybean Soyate (EMS)	Up to ~5% added to mixtures with 50% RA	Bitumen modifier	✓	-	✓	✓	-	✓	-	-	-	-	-
	[101]	Rejuvenator A (regenerated oil and a Fischer-Tropsch wax) and Rejuvenator B (highly viscous material free of polycyclic aromatic hydrocarbons)	6,12 and 18% Rejuvenator A and 9, 18 and 27% Rejuvenator B added to RA mixture	Bitumen modifier and extender	-	↓	-	-	✓	✓	✓	-	-	-	-
	[107]	Bio-rejuvenator SYLVAROAD™ Biobinder Biophalt® Bio-additive Epoxidized Soybean Soyate (EMS)	Up to ~5% added to mixtures with 50% RA	Bitumen modifier	✓	-	-	-	✓	✓	✓	-	-	-	✓
	[111]	Waste vegetable oil, waste vegetable grease, organic oil, distilled tall oil, aromatic extract and waste engine oil	12% added to RA mixture	Bitumen modifier	✓	↓	-	-	↑	↑	↑	↑	-	↓	-

Recycled Asphalt	[110]	Bio-rejuvenator SYLVAROAD™	6.8% added to mixtures with 50% RA	Bitumen modifier	-	-	-	-	✓	-	✓	-	-	✓in short-term laboratory testing	-
	[109]	Rejuvenators BituTech RAP SonneWarmix RJT and RJ	9.28% added to mixtures containing 35 and 40% RA	Bitumen modifier	✓	↓	-	-	x	✓	✓	x	-	✓	-
	[108]	Crumb rubber with a commercial rejuvenator	3, 5 and 7% rejuvenator added to mixtures containing 0, 30 and 50% RA	Bitumen modifier	-	-	-	-	↓	✓	✓	✓	-	-	-
	[119]	Crude tall oil and soybean oil derivative	3 and 6% added to mixtures containing 50% RA	Bitumen modifier	✓	-	↓ at high temperatures	↓ as dynamic modulus |E*| decreases	~	~	✓	-	-	↓	-
	[118]	Bio-rejuvenator SYLVAROAD™ Biobinder Biophalt® Bio-additive Epoxidized Soybean Soyate (EMS)	Up to 2.8% biobinder added to mixtures containing 50% RA	Bitumen modifier	✓	-	✓	-	✓	✓	✓	✓	-	↑	-
	[120]	Biobinder Biophalt®	1.7% added to mixtures containing 50% RA	Bitumen modifier	-	-	-	~ at low temperatures/high frequency, ↓ at high temperatures/low frequency and ↑ at intermediate temperatures and 1 Hz frequency	✓	~	✓	~	-	-	-
	[103]	Swine manure	5% biobinder added to mixtures containing 40% RA	Bitumen modifier	-	↓	-	-	~	✓	✓	~	↓	-	↑
	[105]	Swine manure	5% biobinder added to mixtures of 0, 15 and 45% RA	Bitumen modifier	-	↓	-	-	-	-	✓	-	↓	-	-
	[106]	Swine manure, corn stover, miscanthus and wood pellets	5 and 10% biobinder added to mixtures with 0, 15 and 45% RA	Bitumen modifier	↑ viscoelastic response found to be superior than hot-mix asphalt	↓	-	-	-	-	↑	-	↓	✓potential to perform better than hot-mix asphalt except for corn stover	-
	[104, 121]	Pongamia oil and a composite oil made from castor oil and coke oven gas	5, 10 and 15%	Bitumen modifier	✓	↓	↓	-	✓	✓	-	-	✓	-	-

Miscellaneous	[122]	Microalgae	100%	Binder replacement	~	-	~	~	-	-	-	-	~	-	-
	[129]	Forestry industry by-products	5.7%	Bitumen modifier	~	↓	~	↓	-	-	~	-	-	x	-
	[126]	Waste cooking oil	10, 30 and 60%	Bitumen modifier and extender	✓	-	-	-	x	x	✓	-	-	~	-
	[127]	Biodiesel by-product from waste cooking oil (as aged binder rejuvenator)	2-8%	Bitumen modifier	-	↓	↓	-	x	✓	✓	-	-	-	-
	[128]	Biodiesel by-product from waste cooking oil (as aged binder rejuvenator)	1.5,1.75 and 2%	Bitumen modifier	✓	↓	✓	-	x	✓	✓	x	-	-	-
	[112]	Soy fatty acids	1 and 3%	Bitumen modifier	✓	↓	↓	-	-	-	-	-	-	-	-
	[131]	Waste coffee grounds	2 to 8%	Bitumen modifier	-	↓	-	-	-	-	-	-	~	↓ oxidation rate increase with an increase of coffee ground content but does not exceed that one of the base binder	-
	[123]	Vinasse	10%	Bitumen modifier	✓	-	-	-	-	✓	-	~	-	-	-
	[130]	Rice husk and wood sawdust	10 and 20%	Bitumen modifier and extender	✓	↑	↑	↓	✓	-	-	-	-	↓	-
	[113]	Plant resin fluxed with monoalkyl esters from vegetable and animal oils	0.5 and 5%	Bitumen modifier	-	↓	✓	↑	-	-	-	-	-	x	✓good after 5 years but not enough to draw definite conclusions
	[73]	Sugarcane bagasse, corncobs and rice husk	1 and 2%	Bitumen modifier	✓	-	↑	-	✓	-	-	x	-	↑ with the exception of a rice husk biobinder, age-related hardening effects were smaller at low dosages than the control although this trend changed at higher dosages	-
	[114]	Natural bean oil	1-3%	Bitumen modifier	-	-	-	-	-	-	-	Depends on base bitumen	-	-	-

Synthetic	[132]	Polyethyl acrylate (PEA), polymethyl acrylate (PMA) and polybutyl acrylate (PBA)	100%	Binder replacement	✓except for PBA	-	✓ except for PBA	✓ except for PBA	-	-	-	-	-	-	-
	[60]	Polyethyl acrylate (PEA), polymethyl acrylate (PMA) and polybutyl acrylate (PBA)	25-75%	Bitumen extenders	✓the blends produced similar but not identical rheological properties to SBS PMBs	-	✓	✓	-	-	-	-	-	-	-
	[133]	Cotton oil by-product and dibutylphthalate (DBP) (as aged binder rejuvenator)	5 and 10%	Bitumen modifier	✓	~ 10% bio-rejuvenator is enough to restore the viscosity of the PAV-aged bitumen to its original level	↓	-	x	✓	✓	-	-	-	-

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