Belgian Road Research Centre

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Categorisation and analysis of rejuvenators for asphalt recycling

Dossier

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Categorisation and analysis of rejuvenators for asphalt recycling

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May 2020

Published by: A. De Swaef, Woluwedal 42 - 1200 Brussels

1 Introduction

1.1 Purpose of the dossier

In this dossier, we analyse the different types of products that are either being developed or are already commercially available as a rejuvenator (also called rejuvenating agent) for the reuse or recycling of asphalt pavements.

We propose a categorisation into classes or groups to serve as basis for an analysis to assess the success and risk factors. A number of examples of commercially available products are given for each group.

The categorisation into groups is based primarily on the nature and origin of the product. For each group, we analyse the different rejuvenators, identifying the pros and cons of the various types, while focusing on the following elements:

- origin and production process;
- chemical composition;
- action – working mechanism;
- availability and practical experience;
- health, safety and environment (HSE) and sustainability aspects such as emissions and leaching.

HSE aspects are often closely related. Thus, emissions are evaluated primarily by their impact on the health of those working with the products and those present in the surrounding area, while at the same time their impact on the natural and built environment is evaluated.

Health, safety and environment aspects of the use of these rejuvenators for asphalt recycling are therefore an essential component of the evaluation of asphalt recycling in the broader sustainable development framework.

This evaluation does not discuss the mechanical performance of the products; these aspects are addressed elsewhere, for example in the Re-RACE[1] research project conducted at BRRC. The detailed literature study carried out for that research project also provided useful information for this dossier.

1.2 What are rejuvenators and what are they used for?

The maintenance of existing asphalt pavements results through milling and subsequent processing in large amounts of reclaimed asphalt (RA). RA is successfully reused at high rates by recycling it into new asphalt pavement materials. The functional properties of the old bituminous binder are of essential importance in this context. Reclaimed asphalt is, in fact, more than a black coloured stone and sand fraction (black rock); the residual performance characteristics of the old binder are at least just as important and will be the primary decisive factor for the qualitative success of the asphalt pavement recycling project.

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1 *Rejuvenation of Reclaimed Asphalt in a Circular Economy (Re-RACE)* − a pre-normative research project carried out by the Belgian Road Research Centre (BRRC), over 2 biennial periods (01/06/2017 to 31/05/2019 and 01/06/2019 to 31/05/2021), with the financial support of the Federal State (through the Bureau for Standardisation − NBN and the FPS Economy) [1] [2] [21].

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The higher the recycling ratio, the more important these issues become. The same reasoning applies to multiple recycling, where the RA reused originates from asphalt pavement that was itself produced many years ago incorporating RA as raw material.

Despite decades of experience and research, many questions remain about the quality aspects of the old binder and how it can be improved - particularly with regard to high-quality applications (e.g. in pavement surface layers), higher recycling ratios and multiple recycling, where the "ageing" state of the old bitumen plays a key role. These are typically cases where rejuvenators could be most useful.

Throughout its lifetime, the asphalt pavement is exposed to physicochemical and mechanical influences that adversely affect the performance of the asphalt mixture. The bituminous binder undergoes an oxidative ageing process by contact with the oxygen present in the air, whereby performance properties of the binder may deteriorate over time. This deterioration manifests itself in increasing viscosity, stiffness and brittleness of the material and reduced strain recovery capacity (lowered flexibility or elastic recovery). At the asphalt level, this results in higher risks of cracking and fatigue failure and lower workability of asphalt mixtures containing RA.

If these processes persist, the bituminous binder may lose its functional properties; the RA will be reduced to nothing more than black rock.

At the chemical level, oxidative ageing is reflected in a changing generic composition of the binder. A frequently used term in this context is "SARA fractions" (Figure 1). SARA is an acronym that stands for Saturates, Aromatics, Resins, Asphaltenes, referring to the four subfamilies or main fractions of bitumen. The first three fractions (saturates, aromatics and resins) are known under the group name of maltenes or maltene fraction.

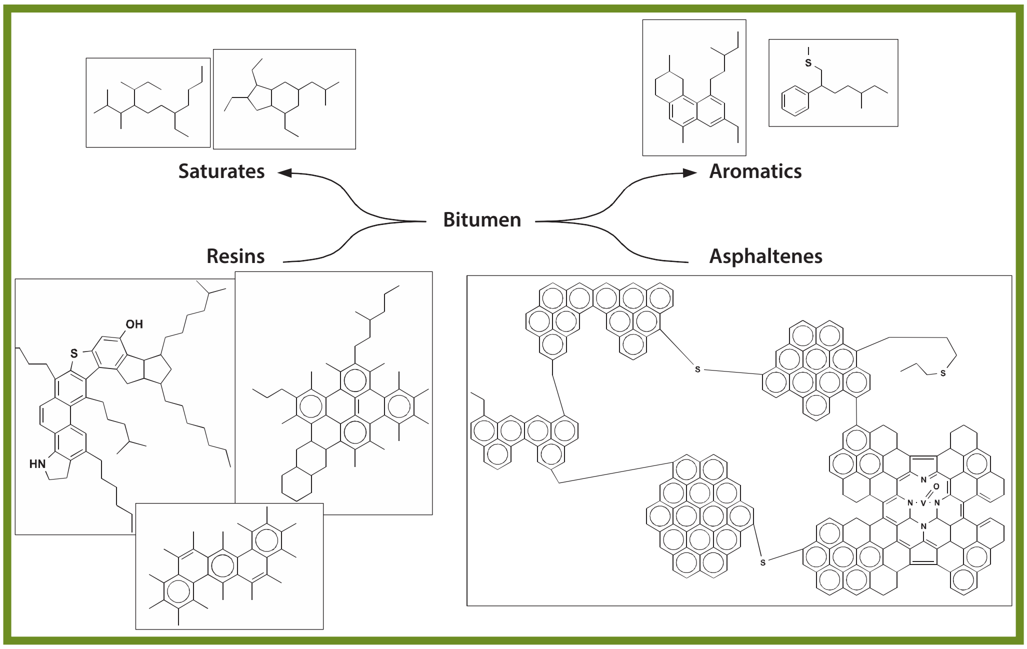

Figure 1 – *Main fractions of bitumen with some typical examples of molecular structures (source: [3])*

A chromatographic separation technique based on the different polarities of the various subfamilies, both maltenes and asphaltenes, can be used for the quantitative determination of the SARA fractions.

An understanding of the relative proportion of these fractions provides detailed information about the colloidal (sol-gel) structure of a binder. Thus, ageing is correlated with an increase in the asphaltene content at the expense of the maltene fraction, resulting in an increasing gel structure of the binder (Figure 2). This increasing ordering in the colloidal structure of the bituminous matrix is known as steric hardening [4]. The increase in both the asphaltene content and the ordering is reflected in an increased viscosity of a bituminous binder.

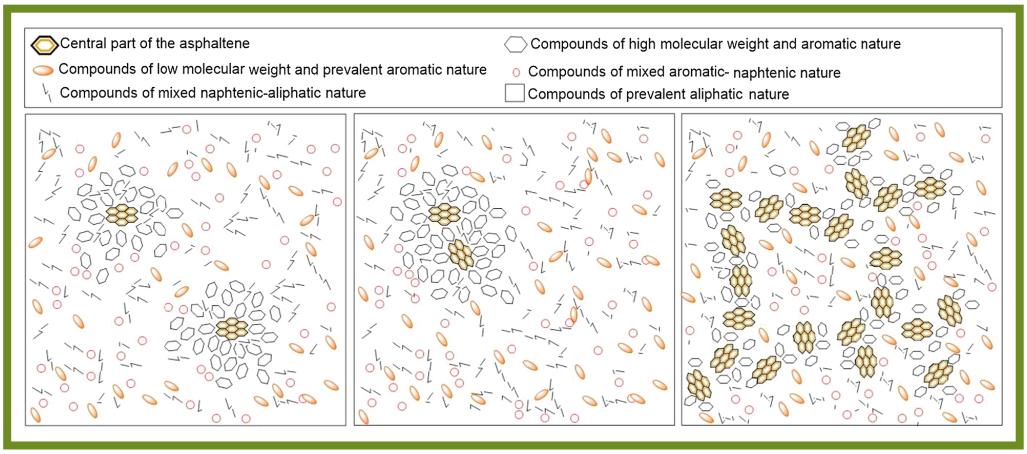

Figure 2 – *Schematic representation of the sol-gel structure of bitumen (source: [5]): left = sol type, central = flocculation of asphaltene micelles; right = gel type*

In the traditional approach of asphalt recycling, the aim is to reduce the increased viscosity of the old binder by adding a new soft bitumen, i.e. one with lower viscosity and a higher penetration or Pen value. In Belgium, dosing of the fresh soft bitumen is calculated using a classical mixing rule (logarithmic Pen rule[2]), based on the required penetration value of the bituminous blend (old and new binder combined) in the asphalt mixture with RA.

As an alternative to the above solution using soft bitumen, the sector is searching for other ways which, in addition to the above effect on viscosity, should combine further positive effects: the use of so-called **rejuvenators** [6].

A rejuvenator is an additive that is added to the reused reclaimed asphalt to cause it to interact with the old binder and thus regenerate and restore the original properties as much as possible. The rejuvenator thus has a positive effect on the empirical and rheological properties (of the old and therefore of the old/new binder blend), yet without it being considered capable of undoing the irreversible oxidation of the old binder.

[2] The calculation rule for the relationship between the penetration values of old binder, new binder and resultant binder blend is as follows:
$\log pen_m = (b_0/100)\times \log pen_0 + (b_n/100)\times \log pen_n$,
where pen_m = penetration value of binder blend; pen_0 = penetration value of old binder;
pen_n = penetration value of new binder; b_0 = percentage of old binder, and b_n = percentage of new binder; b_0 and b_n are (rounded to integer) numbers from 0 to 100,
where $b_0 + b_n = 100$.

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The rejuvenator is used to adjust and improve both the physical and chemical properties of aged binder. Ideally, recycling of RA is aimed at making the asphalt mixture more flexible again, improving the adhesion between aggregate and bitumen, reducing the viscosity, and restoring the binder's performance that has been partially lost through ageing [7].

There is a wide range of commercially available rejuvenators (see further in this dossier). The action of these additives largely relies on one or more of the following effects (hereafter designated with codes A, B and C).

A) Viscosity-lowering or softening effect
Because rejuvenators physically appear in the form of oil, their addition invariably results in a lowering of the viscosity (of the maltene fraction) of aged bitumen. The viscosity of the added rejuvenator and the new binder must be such that the combination of rejuvenator + old and new bitumen ultimately attains the appropriate viscosity in the blend. This effect can be considered as a softening of the old binder. In addition, a lubrification effect may be present: when adding a liquid product, its wettability will improve the workability of the aggregate fraction in the asphalt mixture.

B) Chemical composition compensation effect (maltene to asphaltene ratio)
Rejuvenators from petrochemical sources are rich in aromatics and therefore restore the balance in the generic composition (SARA fractions) of an aged binder by re-enriching the maltene fraction.

C) Dispersant effect
Some rejuvenators act as a dispersant or compatibiliser and as such are capable of breaking or disrupting the interactions or intermolecular associations between the numerous asphaltenes present (due to oxidation). Their action can in this case be considered as a "remobilization" of aged binder.

In the English literature, the aforementioned effects are sometimes distinctively designated by the terms "softening agents" (code A) and "recycling agents" for additives that also act on the chemical composition (code B) and/or the structuring of the bitumen matrix (code C). These terms are sometimes used interchangeably, but various authors emphasize that the two terms should be clearly distinguished [8, 9].

The current application of soft bitumens, too, utilizes the viscosity-lowering effect of binders with low asphaltene content.

Precise details about the chemical composition and working mechanisms of the various potential rejuvenators are generally not published by the producers, but remain undisclosed and protected as trade secrets.

Dosing of rejuvenator needed, takes into account the properties of both the old binder and the rejuvenator as well as the calculation rule for blending both (blending chart). The amount of rejuvenator has to be such that the combination of old and new bitumen with rejuvenator has the appropriate viscosity to ensure smooth mixing and coating of the new asphalt mixture.

The way in which the rejuvenator is added at the asphalt mixing plant, also plays a role. In theory, various possibilities can be considered (Figure 3).

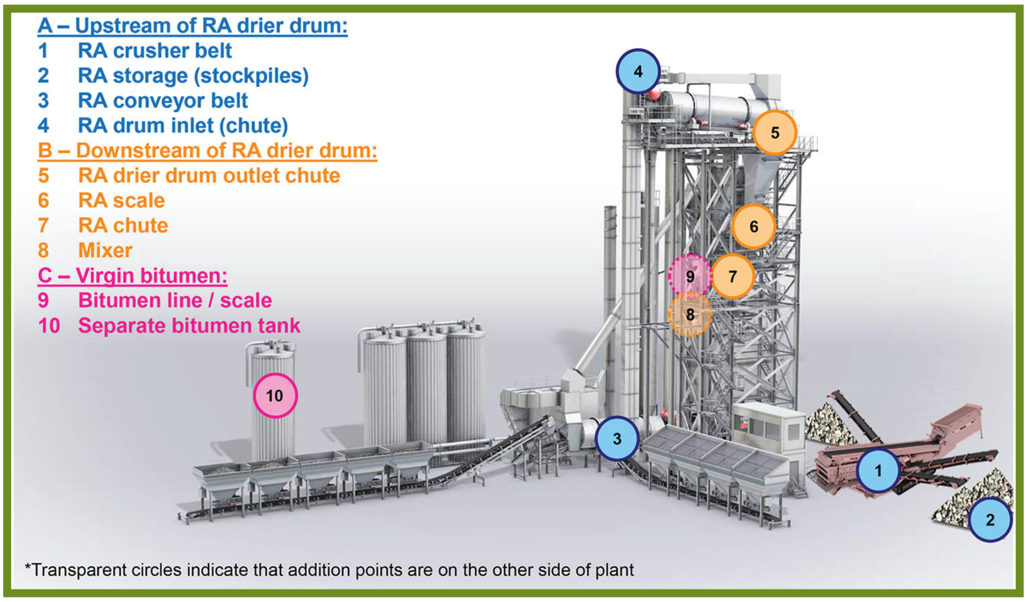

Figure 3 – *Schematic illustration of the various methods by which, or the locations at which, a rejuvenator can be added during asphalt production (source: [10])*

Figure 4 – *Addition of rejuvenator to RA on the conveyor belt by means of a spraying system (source: BRRC [21])*

However, in practice, the following methods are mainly used:

- controlled addition, via the regular bitumen line, of the rejuvenator already mixed into the bitumen (blend made by the bitumen supplier (location 10 on Figure 3);
- controlled addition, via a shielded line, directly to the mixer (location 8 on Figure 3);
- addition or spraying in the open air, using a spraying system (volumetric dosing), of pure rejuvenator on the reclaimed asphalt conveyor belt to the parallel drum dryer in the asphalt mixing plant (Figure 4) (location 3 on Figure 3).

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2 Categorisation of products by origin

Taking into account the aim of rejuvenators (to compensate for the affected properties of the old bitumen) and the obvious need for compatibility with both bituminous binders (blend of old and new binder in case of asphalt mixture with RA) as well as with the mineral constituents, researchers explore a broad spectrum of substances of various origins while developing potential rejuvenators.

For the purpose of clarity, we have placed the various products into categories or groups, based on their origin.

In the literature, different types of rejuvenators are identified, which can be summed up as follows:

- aromatic extracts and naphthenic oils, specially distilled from crude petroleum;
- oils of biological origin, directly derived from plant production (agro-industry or forestry) or specially engineered for this purpose (by-products; engineered bio-based oils);
- all kinds of recycled and treated cooking oils and fats or industrial oils (machine and engine oils);
- a residual category of specifically engineered additives.

In general terms, latter products may be categorised by origin into petrochemical derivatives (as is also the case for bitumen) on the one hand, and alternative products of vegetal or biological origin, on the other hand. Moreover, these products can further be grouped into purposefully produced materials and into materials derived from the recycling of resources previously used for other purposes.

The combination of both perspectives results in a categorisation into four quadrants (complemented with a residual category), as shown in Table 1.

Origin	Originally manufactured or derived	Recycling of waste
From petrochemical industry/ petroleum	1 Aromatic extracts and naphthenic oils derived from petroleum	2) *Waste-derived oils:* recycling of machine oils
Vegetal/biological	4) Vegetal oils from agro-industry 5) Engineered bio-based oils (e.g. tall oil derivatives))	3) *Waste-derived oils:* recycling of food oils
Residual category	6) Various specifically engineered additives	

Table 1 – *Categorisation of rejuvenators into groups (1 to 6) by origin*

Below we will discuss each of these groups in detail. First, we will briefly analyse the potential suitability of the different rejuvenators, focusing on the following elements:

- name, origin and production process: provides information about the origin and type of product;
- chemical composition: provides information about the chemical groups as active ingredients which is relevant to the understanding of the products action;
- action: only viscosity-lowering or softening effect (code A); rebalancing the chemical composition (code B), or as dispersant for asphaltenes (code C);
- availability and practical experience including examples of commercially available products. This provides some information about practical experience and research conducted in this area. It should be stressed that this is a non-exhaustive list of potential products, which is not intended to be all-inclusive;
- health, safety and environment (HSE): information regarding to the possibilities and any problems that may be encountered with operational and sustainability aspects in day-to-day practice.

Where no problems are expected, this is indicated accordingly.

The following HSE-factors are assessed:

- toxicity;
- thermal stability, flash point;
- odour nuisance;
- emissions;
- leaching (of heavy metals in particular).

Information about the flash point temperature is important for assessing the risk of fire (flammability). The flash point of a chemical (liquid) is the lowest temperature under controlled conditions (at 1 bar while in contact with air) at which application of a flame, spark or incandescent object causes the vapour of the liquid to ignite.

This issue is particularly problematic when the flash point exhibits a low value - for example around or less than the usual asphalt production and processing temperature (> 150 °C up to 180 °C). Due to the nature of rejuvenators, this characteristic must be carefully monitored at all times.

The European Construction Products Regulation requires producers to publish these safety data on the MSDS (*Material Safety Data Sheet*).

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3 Systematic discussion by rejuvenator category

3.1 Group 1: aromatic extracts and naphthenic oils derived from crude oil

3.1.1 Origin and production process

This first group of rejuvenators is obtained by distillation of crude oil (separated into fractions based on difference in boiling point), as is the case with the bitumen itself (Figure 5).

Given the intended action of the rejuvenator, which includes counteracting the high viscosity of the aged bitumen, research is focused mainly on fractions with a high boiling point and a viscosity lower as compared to bitumen (as set out in § 1.2).

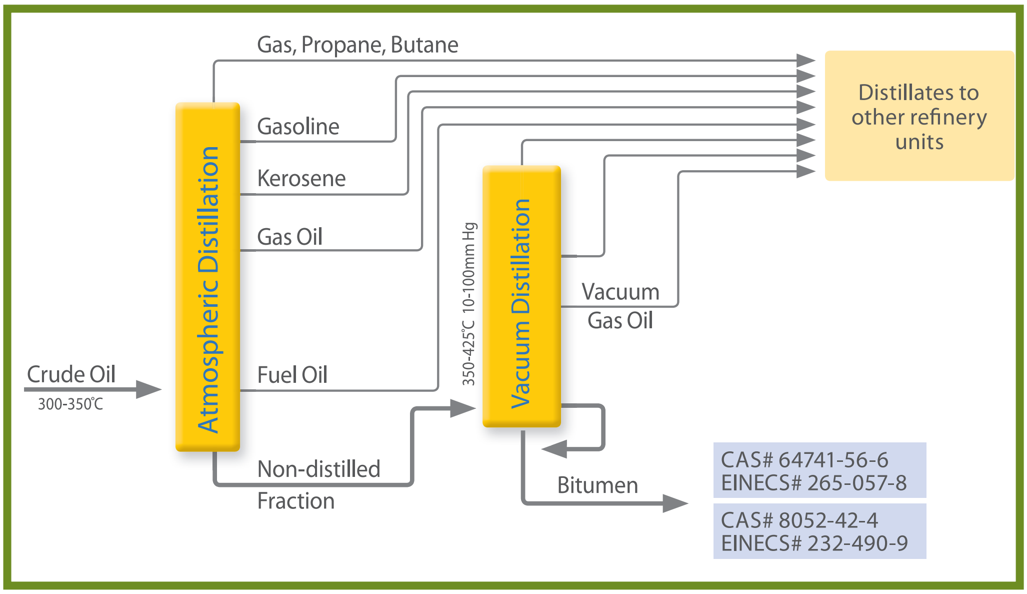

Figure 5 – *Simplified schematic diagram of crude oil distillation (source: [11])*

At present, the conventional method of reactivating a severely aged binder in RA for reuse is adding a soft paving grade bitumen with high penetration value. Soft paving grade bitumens are in fact characterized by a lower viscosity and in many cases also a higher maltene content (and therefore a lower asphaltene content). This counteracts both the high viscosity of the old bitumen as well as the increased concentration of asphaltenes due to oxidation.

Hydrocarbon oils, which are also obtained following the distillation of crude oil, are a potential alternative to this conventional approach. These oils are characterised by a low viscosity and comprise an aromatic fraction allowing the SARA balance to be restored (by enriching the maltene fraction).

3.1.2 Chemical composition

These are oils distilled from crude oil, also known as aromatic extracts or as light and heavy naphthenic oils. In a next step, latter fractions can be chemically treated, for example, by hydrogenation (reduction by hydrogen) of aromatic compounds, whereby a higher content of saturated hydrocarbons is obtained and the content of aromatics decreases.

Producers ensure compliance with legal requirements by fine-tuning the chemical composition. Packaging and labelling requirements are governed by Regulation (EC) No 1272/2008 [CLP] Annex VI Note L (which relates to base oils in hydrotreated, heavy naphthalenic petroleum distillates) [12]. These substances need not be classified as carcinogenic if it can be shown that they contain less than 3 % DMSO extract (as measured by test method IP346).

It should, however, be noted that aromatic extracts or untreated heavy naphthenic oils may possibly contain a non-negligible percentage of aromatic compounds (such as naphthalene). Because the chemical composition of naphthalene has, by definition, an unsaturated aromatic ring structure (naphthalene is the simplest and lightest PAH in terms of molecular weight), the question arises as to how this affects its environmental properties. In fact, the International Agency for Research on Cancer (IARC) classifies polycyclic aromatic hydrocarbons (PAH) as substances with proven carcinogenic properties [13].

3.1.3 Action

Oxidative ageing modifies the chemical composition of bitumen in that it alters both the asphaltene to maltene ratio and the resins to aromatics ratio. More specifically, bitumen ageing leads to an increase in the asphaltene content at the expense of the maltene fraction (e.g. amount of aromatics), thereby unbalancing the generic composition of the bitumen. These rejuvenators are precisely intended to restore the generic balance in the composition of the total binder (see § 1.2, code B).

In addition, latter rejuvenators have a lowering effect on the viscosity of the old binder and therefore act as a softener as well (see §1.2 code A). The lowering of the viscosity may cause the stiffness of the binder to decrease at ambient temperatures, thereby also compromising the resistance to rutting.

3.1.4 Marketability, availability and practical experience

The products of this group have already been the subject of numerous studies in several regions worldwide. Of all rejuvenators, this group boasts the most experience with its long history in the asphalt industry (over fifty years of experience has been gained with the oldest one [14]).

From the 1960s, rejuvenators have been used in attempts to restore old asphalt pavements, primarily by spraying the rejuvenator onto the road surface, which would then penetrate the old asphalt layer.

Currently there is renewed research into these resources in order to quantitatively boost asphalt recycling or improve its quality.

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Although we do not intend to provide an exhaustive product list, we have included, by way of example, a number of more or less commonly used products of group 1 (for derivatives from the petrochemical industry), such as:

- *Nygen 910* from Nynas AB;
- *Regenis* from Total S.A.;
- *Reclamite* from Tricor Refining LLC;
- *Cyclogen* from Tricor Refining LLC;
- *ValAro 130A* from PBF Energy Inc.

3.1.5 Health, safety and environment issues

To ensure the safe handling of these products, attention must be paid to the following HSE aspects:

- Flash point

All relevant safety information is provided by the Material Safety Data Sheet (MSDS).

- Thermal stability

This aspect is not expected to pose any problems for this group, as the products are themselves the result of a distillation process at high temperature.

- Emissions

These oils may contain light and therefore volatile compounds (e.g. aromatic or saturated compounds). The gas emissions generated by their processing can lead to health problems. Some distillation products are considered to be (partially) carcino-genic (including diesel) and are therefore problematic in terms of health and safety.

Sufficient information on this aspect is not always available, and therefore requires due attention. Caution must certainly be exercised when spraying the product on RA.

The manner in which the product is added in the asphalt mixing plant (manual processing, spraying, in open air, etc.) determines to a significant extent the risk sensitivity for HSE issues in the field. The product is best added through an automated process via a (bitumen) line or direct injection into the bins where the heated RA is stored, prior to further processing in the asphalt mixer.

A ready to use blend of the rejuvenator with bitumen is prepared in advance during the production process in order to reduce emissions from the pure product; this step also applies if the product is added at ambient temperature. The low dosage will then limit risks in terms of emissions and HSE issues at the asphalt plant.

3.2 Group 2: recycled from waste oil (machine oil)

3.2.1 Origin and production process

Machine oils such as engine oil, lubricating oil, etc. collect some contaminants throughout their lifetime, and at the end of their user's phase, they are discarded as waste oil, but they also contain certain fractions that can be recycled. The waste oil is collected through a professional circuit and then reprocessed (separated into different fractions) by a heavy distillation process (including vacuum distillation). The distillation residue is a heavy fraction that can be used as a bitumen substitute or extender.

These products are referred to as waste-derived oils, and include:

- REOB (Re-refined Engine Oil Bottoms; this name is used by road authorities in the US);
- VTAE (Vacuum Tower Asphalt Extender; this name is used by refineries);
- other similar or derived group names[3] include EOR (Engine Oil Residue), RHVDB (Re-refined Heavy Vacuum Distillation Bottoms), VTB (Vacuum Tower Bottom), WEOR (Waste Engine Oil Residue).

Figure 6 schematically shows the different steps in the re-refining of waste oil to recycled lubricating oils and base oils [15].

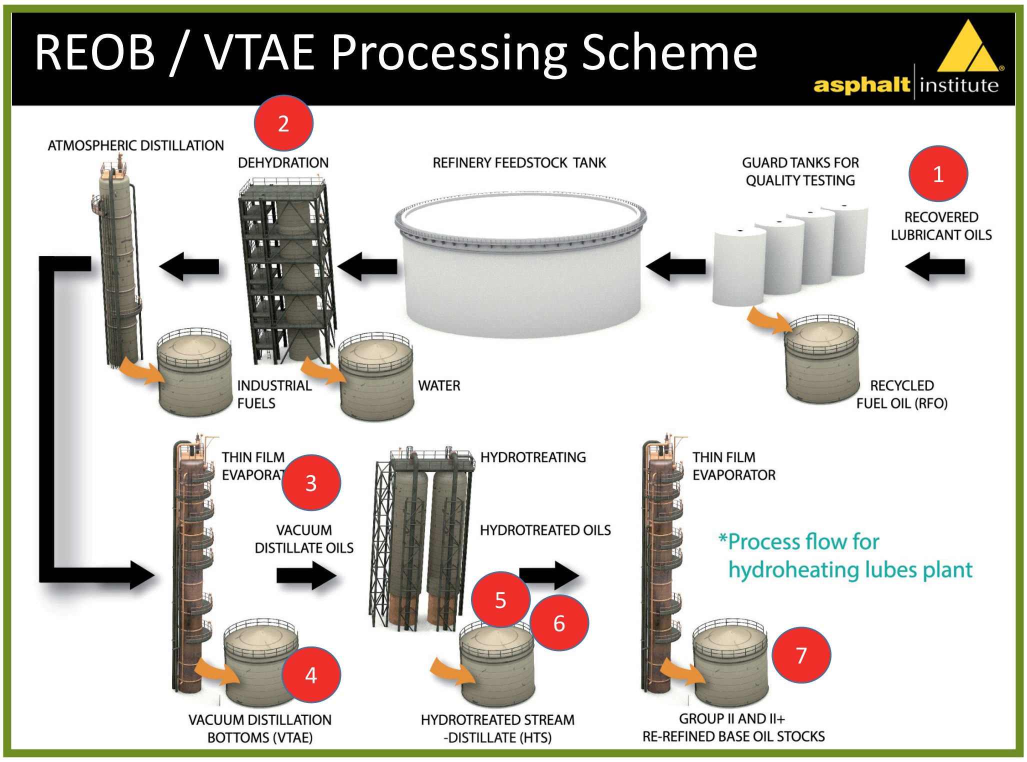

Figure 6 – *Schematic representation of the REOB/VTAE processing process (source: [15])*

[3] The letter B (or R) in the names stands for bottoms (or residue), the non-distillable fraction.

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The numbering in Figure 6 refers to the different (intermediate) products: 1. *Raw feed, unprocessed used oil,* 2. *Dehydrated used oil*, 3. *Vacuum oil*, 4. *REOB/VTAE*, 5. *Hydrotreated 80 base oil*, 6. *Hydrotreated 150 base oil*, 7. *Hydrotreated low sulfur fuel (HT-LS).*

About 12 to 15 % of the (intermediate) products obtained through this re-refining process are REOB/VTAE fractions (number 4 in the figure 6), the remainder are recycled fuel oils and lubricating oils.

3.2.2 Chemical composition

Due to the extremely diverse history of these oils, the exact chemical composition is mostly unclear and unpredictable. However, they are invariably mixtures of different machine oils and the contaminants they contain.

Recycled engine oil may also contain paraffin, originating from paraffinic oil components in REOB/VTAE. Crystallisation at lower temperatures involves risks for cold temperature behaviour and related sensitivity to shrinkage, making it unsuitable for use in cold climates.

Moreover, pollutants present in the waste oils from previous user's phases (such as heavy metals like nickel and chromium) concentrate themselves in this non-distillable fraction, which is detrimental to the environmental properties. They also introduce a wide variety into the material, resulting in variable performance.

3.2.3 Action

This type of rejuvenator mainly acts as a softener (see § 1.2, code A): as an alternative to soft bitumen, the addition of this type of recycled oil-based rejuvenator results in a lower viscosity (higher penetration value) of the resultant binder blend.

Compared with soft bitumen or rejuvenating agents of group 1, less noble raw materials are used. This is probably an interesting and cost-effective way of working for the waste processing sector, but its benefit for the asphalt sector is dubious.

The mechanism of restoring the balance in the generic composition (SARA fractions) (see § 1.2, code B) does not apply here.

3.2.4 Marketability, availability and practical experience

There exists a large variety of such products.

NORA, the US association representing companies in the liquid recycling industry[4], estimates that every year around 160,000 tons of recycled oils of the REOB/VTAE type are produced in North America by seventeen plants, which corresponds to approx. 0.5 % of the total bitumen production there [15, 16]. It is unknown how much of this (alongside its application in roofing asphalt) eventually ends up as rejuvenator used in asphalt. In Europe, GEIR represents the interests of the re-refining industry.

[4] NORA, *An Association of Responsible Recyclers (established as National Oil Recyclers Association)*, www.noranews.org/page/aboutnora: figures stated in the reference [16].
In Europe, GEIR (Groupement Européen de l'Industrie de la Régénération, the European Re-refining Industry section of UEIL (Independant Union of the European Lubricants Industry)) represents 17 waste-oil re-refining companies in 10 EU-countries + Belarus + Turkey; www.geir-rerefining.org.

A working group of the US Asphalt Institute made a literature study in which it discussed twenty-six studies published in the US addressing the use of REOB/VTAE as a bitumen modifier [15, 16]. As regards the influence on the performance of the asphalt produced with it (discussion beyond the scope of this dossier), it appears that no unequivocal conclusion can be drawn about their advantages or disadvantages. About half of the studies noted a slightly positive effect (or no adverse effect), whereas the other half noted a negative effect on performance. This is not surprising considering the great diversity in the origin of this type of products (see above).

3.2.5 Health, safety and environment issues

While the sector of waste oil collection may be properly regulated as far as the environment is concerned, this says nothing about the waste products they treat and their subsequent processing. This gives rise to serious concerns as to:

- composition and presence of pollutants and hazardous substances (carcinogens, mutagens). These pollutants originate from the first cycle where they are utilised as machine oil at high temperatures/loads; their concentrations are rather limited, but during further processing they may build up in the non-distillable fraction that is considered here;
- heavy metals (zinc, chromium and copper). These may give rise to leaching;
- emissions during asphalt production (depending on the composition).

Because of the presence of harmful substances such as carcinogenic PCBs (polychlorinated biphenyls) and PAHs (polycyclic aromatic hydrocarbons), crude untreated waste oils score poorly in terms of HSE issues, but their distillation products perform better in this respect. See also Figure 7: the more intensive the processing (with vacuum distillation) of the crude waste oil, the lower the mutagenicity index (MI) and therefore the less hazardous the product. The mutagenicity index of a chemical is a measure of the risk of causing damage to genetic material such as DNA, whereby these chemicals may also be carcinogenic.

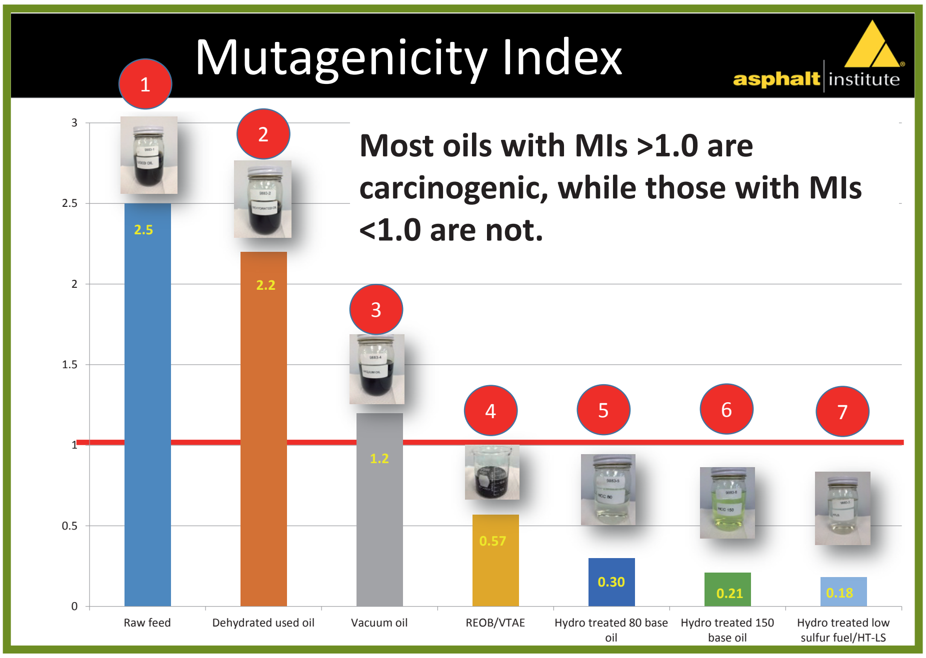

Figure 7 – *Mutagenicity index for a wide range of recycled machine oil derived products such as REOB/VTAE (source: [15])*

The total PAH content (which amounts to around 2000 mg/kg in crude waste oil) falls to less than 100 mg/kg in REOB/VTAE products.

Vacuum distillation removes the PAHs from the residue, after which they end up in the heavy oil and lubricant fractions in the form of naphthenic oils. See the products numbered 4 to 7 in the flowchart (the numbering in Figure 7 refers to the numbering of the intermediate products as discussed at the end of § 3.2.1, after Figure 6).

3.3 Group 3: recycled waste cooking oils (oils and fats of vegetable or animal origin)

3.3.1 Origin and production process

The products in this group are recycled waste cooking oils (so-called waste-derived oils / waste vegetal oils / yellow grease), in the English literature known as:

- WCO (waste cooking oil);
- WEVO (waste edible vegetal oil).

Examples are waste sunflower, rapeseed or peanut oil, or certain cooking fats.

3.3.2 Chemical composition

This category includes a broad array of recycled cooking oils and fats, so that a varied chemical composition is to be expected. They are mostly mixtures of fatty acids such as palmitic acid, oleic acid or linoleic acid, supplemented with various contaminants originating from the use phase [17].

These fatty acids are formed when food is heated in cooking oil, because the water in the food cannot be expelled fast enough. This leads to hydrolysis, whereby the fatty acid esters are converted to fatty acids. These acids are, however, highly detrimental to applications in a second life cycle, because the acid (particularly at high temperatures) may give rise to accelerated corrosion (e.g. of metal machine parts) and is highly irritating (e.g. to the eyes or skin). That is why, as a first step in the recycling process, these fatty acids must be converted to esters.

The best known example of such a process is to be found in the production of biodiesel (from waste oil). In this case, unlike the scope of application of rejuvenators, strict requirements apply in terms of composition, such as a limited content of free fatty acids (< 15 %) and being virtually free (< 2 %) of water, impurities and unsaponiables. The production of diesel oil from waste oil therefore generally requires a prior distillation process.

In addition, many fatty acid chains contain one or more unsaturated compounds, thus making these products oxidation sensitive (and therefore also temperature sensitive). Consequently, these products may change over time. These chemical changes may result in potential health risks, for example due to the presence of harmful intermediate compounds such as epoxy compounds.

3.3.3 Action

This type of product mainly acts as a softener (see § 1.2, code A): the addition of this type of recycled oil-based rejuvenator results in a lower viscosity of the resultant binder blend.

Compared with soft bitumen or rejuvenators of group 1, less noble raw materials are used.

The SARA rebalancing mechanism (see § 1.2, code B) does not apply here.

3.3.4 Marketability, availability and practical experience

The products of this category have been the subject of numerous studies, especially in Asia. This is mainly because many cooking oils are used in Asian food culture and a vast amount of publicly funded research is carried out into their potential application after recycling.

Their application as a rejuvenator in the asphalt industry is considered to be an interesting and cost-effective method of waste management by the waste management sector, but its benefit for the asphalt sector is dubious.

These recycled products are far less available on the European market because this type of oils features less prominently in our food culture.

3.3.5 Health, safety and environment issues

As with category 2 (recycled machine oils), group 3 is also made up of resources that originate from waste materials that may have been contaminated during their use with all kinds of substances giving rise to HSE concerns.

While the waste oil collection sector may be properly regulated as far as the environment is concerned, this says nothing about the end products of subsequent processing.

This gives rise to serious concerns as to:

- the composition and presence of pollutants and hazardous substances. A well-known example includes acrolein, which is formed by the decomposition of triglyceride esters. Other pollutants may have originated during the first use phase as cooking oil at high temperatures [5];
- heavy metals, although here they may be expected to be less present than in engine oils (category 2);
- flash point: is low due to the presence of paraffinic components;
- lack of thermal stability (unstable or more hazardous intermediate products).

The application of such products in the asphalt production process may therefore, depending on their composition, lead to unwanted emissions and also odour nuisance during the asphalt production process.

Because of these concerns, caution must be exercised when using such products as rejuvenators in asphalt.

5 After use at high temperatures, frying oils often have a higher acrylamide content due to the contact of starchy and asparagine-rich foods with the heated oil. In the human body, acrylamide can be converted to glycidamide, which is considered to have mutagenic properties.

3.4 Group 4: vegetal oils from agro-industry

3.4.1 Origin and production process

This group of products comprises a wide range of (generic) resources, mainly from agriculture and the processing of harvested crop products in agro-industry, such as:

- sunflower oil;
- soybean oil;
- palm oil;
- castor oil;
- cashew nut oil;
- cotton seed oil;
- linseed oil;
- etc.

In contrast to the oils of group 3 (treatments of recycled waste cooking oils), the oils in this group 4 are not materials that have already gone through their first use phase, but products that have just been harvested and treated.

Compared with the products of group 1, these are not fossil, but renewable raw materials.

3.4.2 Chemical composition

These products are generally mixtures of fatty acids (and esters). More particularly:

- Sunflower oil: contains mainly palmitin, stearin, olein and linoleic acids;
- Soybean oil: contains mainly esters and other fatty acids of soybean oil;
- Palm oil: contains mainly palmitin and olein;
- Castor oil (from Ricinus plant): contains mainly triglyceride of ricinoleic acid;
- Cashew nut oil (oil from the peel of the nut of the cashew tree): consists mainly of phenol derivatives with long side chains (anacardic acids, cardol and cardanol);
- Cotton seed oil: contains mainly linoleic acid and olein;
- Linseed oil: contains mainly linoleic and linolenic acid and, to a lesser extent, olein;
- etc.

The raw materials are of biological or plant origin, and are therefore also referred to as biogenic sources.

3.4.3 Action

These products mainly act as a softener with a viscosity-lowering effect (see § 1.2, code A): the addition of this type of plant oil-based rejuvenator results in a lower viscosity of the resultant binder blend.

Moreover, some particular products of this group may also act as a dispersant for the aged bituminous binder (see §1.2, code C).

3.4.4 Marketability, availability and practical experience

Especially in the US, there are a number of producers who process these raw materials to products to be used as rejuvenators in asphalt recycling. However, over the last years quite some attention was also paid to these products in Europe and even worldwide.

Their marketability is therefore assured. Both studies conducted in the laboratory as well as practical experiences are available.

Although we do not intend to provide an exhaustive product list, we have included, by way of example, a number of more or less commonly used products of this group:

- *Rheofalt HP-AM* from Ventraco Chemie;
- *ReJUVN8* from Sripath Technologies, LLC;
- *RePLAY 18* from BioSpan Technologies Inc.;
- *BituTech RAP* from Engineered Additives LLC and (new name) *Hydrogreen S*™ from PVS Meridian Technologies Inc.
- *Anova 1817 Rejuvenator* from Cargill Industrial Specialities;
- *Biorestor* from BioBased Spray Systems LLC.

3.4.5 Health, safety and environment issues

In this group of products, which are usually obtained and utilised at ambient temperature, such as oils obtained from the pressing of vegetable seeds or fruits, questions arise about their behaviour at higher temperatures (> 150 to 180 °C), more particularly about their thermal stability, flash point, and related emissions and environmental odour nuisance.

It is also noted that generally, little attention is paid to the HSE aspects of this category. As a result, some of these products continue to pose significant risks that are also associated with lack of knowledge and questions regarding suitable conditions for their use as rejuvenator (see also § 3.3.5).

Categorisation and analysis of rejuvenators for asphalt recycling

3.5 Group 5: bio-based engineered oils

3.5.1 Origin and production process

This group mainly contains oils that are specifically produced from a transformation of biological raw materials, mostly coniferous tree woods, of which crude tall oil (CTO) is an essential intermediate raw material (Figure 8).

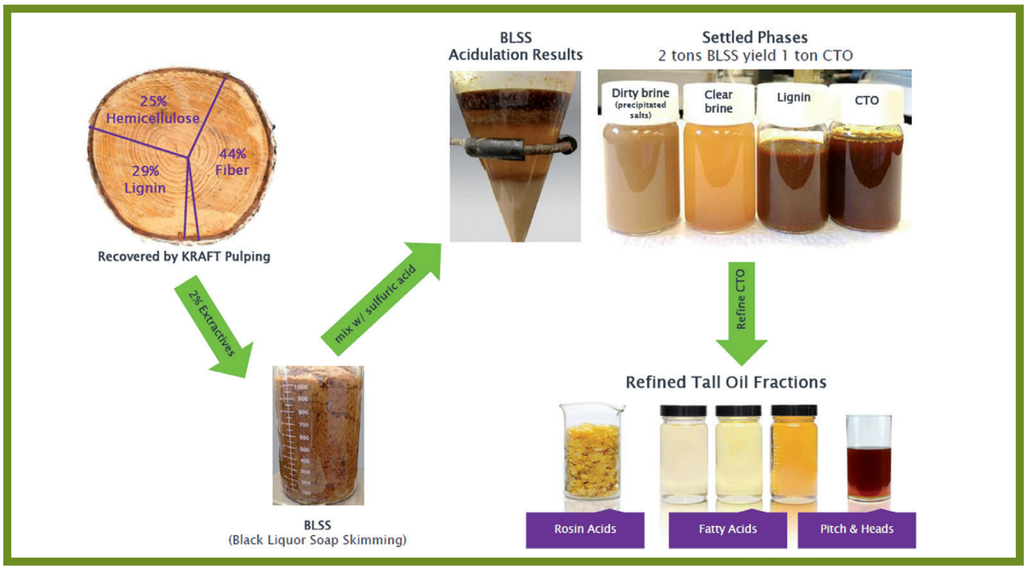

Figure 8 – *Schematic diagram of the production process for bio-based engineered oils (source: [18])*

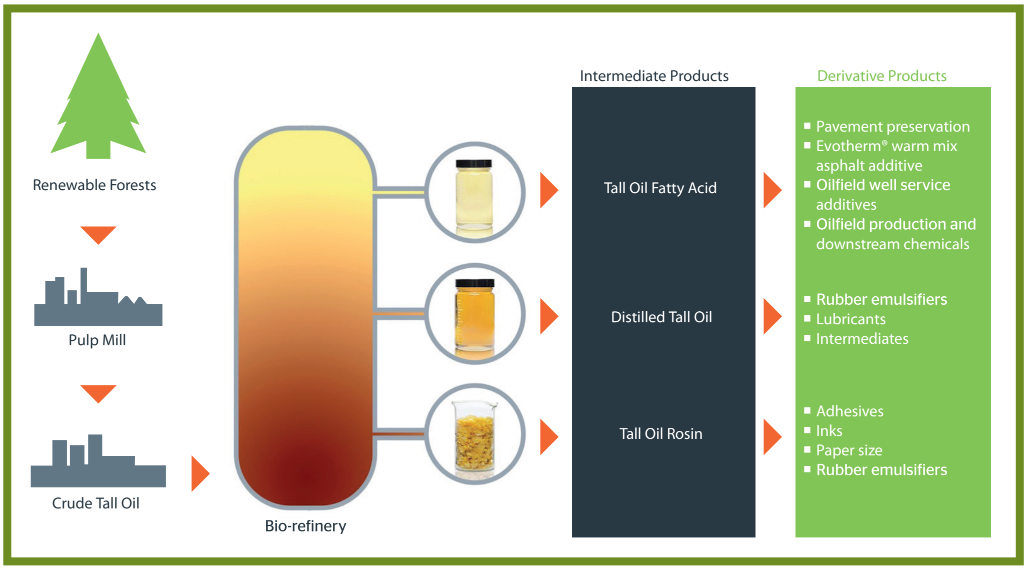

Figure 9 – *Production of tall oil products by CTO bio-refining (source: [18])*

Crude tall oil is a resin product from coniferous tree species belonging to the Pinus genus. It contains a mixture of resin acids, fatty acids, abietic acid and other constituents (terpenes and rosin or colophony), obtained by treating the alkalis originating from the decomposition products of coniferous wood with acid. As such, it is a by-product of the paper industry. Crude tall oil is refined in a bio-refining plant to produce a wide range of chemicals (Figure 9).

3.5.2 Chemical composition

CTO distillation products are diverse and include, among others, Tall Oil Fatty Acids or TOFA (a wide range of fatty acids, mainly C16 - C20 carbon chains), Distilled Tall Oil (DTO) and Tall Oil Rosin (rosin acids).

For application as a rejuvenator in asphalt recycling, however, the fatty acids (top right in Figure 9) first have to be esterified, for the same reasons as outlined earlier (§ 3.3.2) for the production of biodiesel.

3.5.3 Action

Tall oil acts both as a softener (lowering of the viscosity; see § 1.2, code A) and as a dispersant/compatibiliser/remobilizer of the old binder (see § 1.2, code C) [19].

Tall oil therefore belongs to the same chemical family as liquid antistripping agents or emulsifiers.

3.5.4 Marketability, availability and practical experience

Producers in various countries, not only in the US but also in Europe, have widespread experience with this type of rejuvenator. Published literature includes both laboratory studies and practical experience in the asphalt industry.

Although we do not intend to provide an exhaustive product list (see § 1.3), we have included, by way of example, a number of more or less commonly used products of group 5, such as:

- *SylvaRoad RP1000 Performance Additive* from Kraton Chemical;
- *Evoflex* from Ingevity;
- *Delta S* from Collaborative Aggregates LLC;

3.5.5 Health, safety and environment issues

This group involves products that are specially engineered for a well-defined purpose, so that special attention can be paid to certain aspects that could otherwise (e.g. the harvest products of group 4) be more problematic in terms of thermal (in)stability, (too low) flash point or odour nuisance.

Evoflex™ has a flash point of 298 °C (AASHTO test method T48). The flash point of Delta S is higher than 260 °C (according to the Cleveland open cup method). SylvaRoad™ RP1000 has a flash point that is also higher than 280 °C, so this is no longer an issue for hot manufactured asphalt.

3.6 Group 6: various specifically engineered additives

3.6.1 Origin and production process

As the name of the group already suggests, this is a very varied group of specifically engineered products/additives based on raw materials from a variety of sources, both of biological (plant) origin and from the petrochemical industry, including:

- products (bio-oils) obtained through pyrolysis of various types of biomass (Figure 10);
- biogeneric mixtures to which extra additives (e.g. waxes) are added;
- flux oils added bitumen and possibly extra additives.

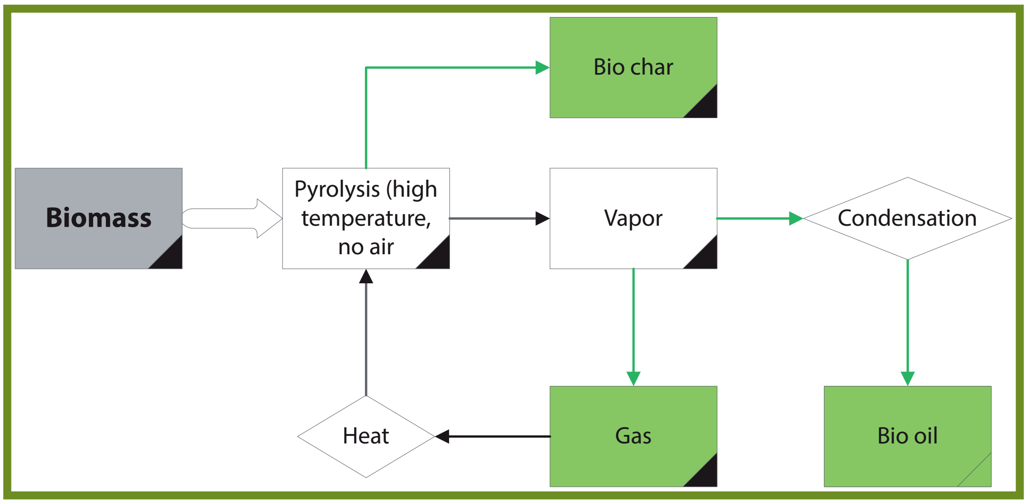

Figure 10 – *Schematic overview of the production of bio-oils by pyrolysis and subsequent biomass condensation (source: [20])*

3.6.2 Chemical composition

The large variety in raw materials used for the products implies that also the chemical composition in this group varies greatly.

- The composition of products obtained by pyrolysis is inherently very diverse because decomposition processes at high temperatures nearly always result in a wide range of chemical compounds. Moreover, a large number of supply sources, of both plant and animal origin, are used which themselves may vary over time.
- Some rejuvenators of vegetal or biogeneric origin (consisting of mixtures of fatty acid esters) are mixed with further additives to extend the action of the rejuvenator (multifunctional additive). A typical example in this context is the addition of synthetic waxes to combine sustainable reuse of RA with asphalt production at lower temperature (warm mix asphalt or WMA).
- Flux oils may originate from the distillation of crude oil (Figure 4), but may also be of vegetal origin. In the first case, they consist of mixtures of aromatic and aliphatic hydrocarbons and are often added to bitumen when applied as a rejuvenator. If they are of plant origin, their composition resembles that of products of group 4 (e.g. esters of rapeseed or linseed).

3.6.3 Action

These products mainly act as a softener to lower the viscosity (see § 1.2, code A). With multifunctional additives, production at lower temperatures or improved bonding properties can also be envisaged. It should, however, be noted that, in general, only limited information is available on the precise action.

Flux oils are obviously substances or derivatives designed to increase the fluidity and decrease the viscosity of the material to which they are added. Their use in other fields of road construction, such as cold bituminous applications, is widely known.

3.6.4 Marketability, availability and practical experience

Experience is rather limited and confined primarily to laboratory studies.

Products to which synthetic waxes have been added could give rise to problems with the properties of the asphalt mixture at low temperature (e.g. cracking).

A non-exhaustive list of products belonging to this group is given below:

- *Storbit-Storflux Plus* from Storimpex Asphaltec GmbH;
- *Bioflux* from Neste Oyj.

3.6.5 Health, safety and environment issues

Due to the variability, it is difficult to provide generic HSE information for this group. This aspect must be examined for each specific product, which falls outside the scope of this dossier.

Pyrolysis products (whereby organic, carbonaceous material is cracked and decomposed by heating it to high temperatures without oxygen being present, i.e. without combustion), generally contain a number of chemical components that require special attention, such as polycyclic aromatic hydrocarbons (PAHs) (alongside other potentially harmful substances).

As a result, many of these products obtained through pyrolysis of biomass give rise to serious doubts and concerns regarding their suitability as additive and as rejuvenator in particular.

4 Conclusions

There is a varied range of products to be used as potential rejuvenators that can qualitatively improve the reuse of reclaimed asphalt in new asphalt mixtures. Due to the diversity of types and the various names and terms used, a categorisation into groups was proposed. This facilitates the discussion of the action and the success or risk factors for each group.

In addition, a number of examples of commercially available products were given for each group.

The categorisation into groups is based primarily on the nature and origin of the product. In general terms, we distinguish petrochemical derivatives (with bitumen being one of them) and alternative products of plant or biological origin.

Categorisation and analysis of rejuvenators for asphalt recycling

These products can further be subdivided into directly produced materials and materials derived from the recycling of materials previously used for other purposes.

Rejuvenators can be categorised by origin into six main groups:

- aromatic extracts and naphthenic oils, specially produced by distillation of crude oil (group 1);
- various recycled and treated oils and fats from industrial activities (machine and engine oils) (group 2) or from the food industry (group 3);
- oils of biological origin (plant production), directly derived from plant production (agro-industry or forestry) (group 4) or specially engineered for this purpose (by-products; engineered bio-based oils) (group 5);
- a residual category of specific products (flux oils, bio-oils from pyrolysis of biomass, etc.) (group 6).

We then analysed each group and discussed the success and risk factors, focusing on the following elements:

- origin and production process;
- chemical composition;
- action;
- availability and practical experience;
- health, safety and environment.

Products specifically engineered for a specific purpose, such as those of groups 1, 4 and 5 (and partially 6), originate from well-defined origins of raw materials. As a result, their properties are better controllable and less variable in time than those of products derived from the recycling of waste oils (groups 2 and 3). Knowledge about the properties of the latter products, both as regards performance and HSE aspects, is more often limited or less publicly available.

The analysis shows that especially in the area of HSE some groups pose significant risks that are strongly related to origin or production process, to heterogeneity and to uncertainty about their history:

- For products obtained at ambient temperature or normally used at ambient temperature, such as (in group 4) oils obtained from the pressing of vegetable seeds or fruits, questions arise about their behaviour at higher temperatures (> 150 °C up to 180 °C as is common during asphalt production), more particularly about their thermal stability, flash point (flammability) and related emissions and environmental odour nuisance;
- For products obtained from the recycling of waste oils, we distinguish between the groups of machine oils (group 2) on the one hand, and the group of cooking oils (groups 3) on the other hand. In both groups, there are risks of emissions of hazardous substances that have been build up in a previous life cycle phase. Moreover, additional risks related to the presence of potentially carcinogenic and mutagenic substances and heavy metals (particularly in the group of machine oils) may arise. There are also questions about thermal stability and possible odour nuisance (particularly in the group of cooking oils);
- For the products in group 6, the varied group of engineered additives, there are serious doubts and concerns regarding their suitability as additive - notably those obtained from pyrolysis of biomass, because this technique usually gives rise to the presence of more hazardous substances such as PAHs.

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