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Assessment of the binder blending in bituminous mixtures based on the development of an innovative sustainable infrared imaging methodology

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Abstract

Reclaimed Asphalt (RA) is more and more used in the road recycling industry because it allows reducing the consumption in non-renewable raw materials such as virgin bitumen which comes from the petroleum distillation. As bitumen is oxidation-sensitive, some technical issues are however raised about the mix design and the binder blending between the aged and virgin binders. Particularly, the question lies on the ability of the virgin binder to mix with the RA aged binder to form a homogeneous product in defined manufacturing conditions. To answer this question, most of road studies extract with a chlorinated solvent the total bituminous binder from the asphalt mixture to characterize then oxidation or rheological properties. However, this solvent extraction technique is based on a complete binder dissolution which may alter physicochemical properties of the mixture. The objective is also to develop a solvent-free and non-destructive methodology to in situ assess the binder blending in manufactured mixtures. Using infrared imaging ATR microscopy, homogeneity is defined from spatial distributions in carbonyl functions and the methodology is developed on modeled binder mixtures. The influence of the aged binder temperature and mixing time is then investigated on the binder blending. Results show that high and close temperatures between binders are necessary but not sufficient to obtain a homogeneous mixture whereas a longer mixing time improves the binder blending. The developed chemomap methodology also allows demonstrating the influence of manufacturing process parameters on the binder blending in road asphalt mixtures. At the binder scale, the present work constitutes an
interesting, rapid and economical approach to optimize the manufacturing parameters of the asphalt mixture design. The innovative infrared imaging methodology also opens perspectives to gain a better knowledge about molecular distributions and homogeneity of any hydrocarbon mixture which constitutes an essential criterion for the performance of more sustainable materials.

Graphical abstract

Homogeneity assessment in binder mixtures using the combination of a novel solvent-free infrared methodology and the statistical treatment of carbonyl spatial distributions

Highlights

- A solvent-free chemomap methodology is developed to assess the binder blending
- Homogeneity of bituminous mixtures is defined from carbonyl spatial distributions
- Chemomap helps optimizing manufacturing process parameters of recycled materials
- High and close binder temperatures are necessary to obtain a homogeneous mixture
- A longer mechanical mixing time guarantees a more efficient binder blending

Keywords: bitumen, recycling, blending, infrared imaging microscopy, novel sustainable methodology, solvent-free

1. Introduction

Bitumen is a vacuum residue of petroleum distillation which is largely used in the road construction industry to bind mineral aggregates together. For the mix design of pavement layers, asphalt mixtures are generally composed (by weight) of 95 % virgin mineral aggregates and 5 % virgin bitumen.
Nevertheless, due to the non-renewable oil resources reduction and the constant increase of petroleum cost, significant efforts are undertaken to reuse existing stocks of Reclaimed Asphalt (RA) coming from the demolition of aged road pavement (Zaumanis et al., 2016).

However, bitumen is sensitive to oxidation phenomena occurring during the long-term ageing. Oxidation mechanisms are complex and bitumen ageing often depends on several factors including the exposure to air and the presence of catalytic or inhibitor inorganic compounds in the mastic (Makowska et al., 2017). But reactions with oxygen (from air) lead to general composition changes in the bitumen structure such as an increase in the asphaltenes, sulfoxides, ketones and carboxylic acids content (Lesueur, 2009). To assess bitumen ageing, some studies also focus on a better characterization of the asphaltenes content in bitumen (Boysen and Schabron, 2013; Handle et al., 2017; Michon et al., 1996) and other authors also assess the evolution in chemical carbonyl and sulfoxide functions in the infrared spectrum to track bitumen ageing (Lamontagne et al., 2001; Makowska et al., 2017; Poulidakos et al., 2014).

Hence, according to the bitumen ageing state and manufacturing conditions (temperature, mixing..) of asphalt mixtures, the mix between the aged binder and the virgin one may be not complete, what may conduce to possible microcracks in the mastic (Rinaldini et al., 2014). In the road recycling technology, technical questions are raised about the binder mix design (Lo Presti et al., 2016) and the binder blending.

Several studies have been conducted to assess the degree of blending between the virgin and aged bitumens through various experimental approaches including dynamic modulus prediction on asphalt mixtures (Copeland et al., 2011; Delfosse et al., 2016), microscopic intergranular space observation (Cavalli et al., 2017; Navaro et al., 2012), rheological approach on binders (Rinaldini et al., 2014; Shirodkar et al., 2011) or by considering a stage extraction progressive method (Bowers et al., 2014; Delfosse et al., 2016; Huang et al., 2005). Although interesting results, the two last approaches dissolve the total hydrocarbon binder with a chlorinated solvent which may alter the physicochemical properties of the extracted binder (Stimilli et al., 2015; Ziyani et al., 2017) or induce, by dissolution, important structural modifications in bitumen with distorted molecular weight distributions (Themeli et al., 2017).

Therefore, the objective of the paper is to develop a novel solvent-free and non-destructive method to assess the binder blending in bituminous mixtures. As the blending phenomena are still misunderstood at the complex asphalt mixture scale, the study also proposes a modeled experimental approach to
analyze binder mixtures (without granular parts) produced in various manufacturing conditions. The influence of the aged binder temperature and mixing time is then investigated.

For this purpose, the “blend” term has been precisely defined. According to (Nahar et al., 2013), the blend supposes that the identity of two mixed components is lost in order to create a new product for which the colloidal assembly is unique, molecules being rearranged. The blend also refers to a homogeneity property. In this paper, the “blend” is defined as the ability of two components to create a homogeneous product where the chemical composition is identical everywhere at the scale observation of the study. Using the infrared imaging ATR (Attenuated Total Reflectance) technique, homogeneity has been assessed through spatial distributions of the carbonyl function resulting from the bitumen oxidative ageing. A specific methodology, called chemomap, has been then developed to better quantify homogeneity of binder mixtures from obtained spatial carbonyl distributions. After its validation, the associated innovative methodology has been used to demonstrate the influence of manufacturing process parameters (mixing time, temperature) on the binder blending.

2. Materials and methods

2.1. Materials

Two virgin and aged binders were tested:

- The first virgin binder is called LHV (for Laboratory Hard Virgin binder) and has a 50/70 penetration grade according to EN 12591 standard,
- The second aged binder is called LHA (for Laboratory Hard Aged), it was obtained after a RTFOT (EN 12607) + PAV (EN 14769) ageing procedure performed on a virgin binder (35/50 penetration grade) coming from a second refinery. The RTFOT (Rolling Thin Film Oven Test) constitutes a first short term ageing which heats the bitumen in 1.25-mm thick moving films at 163°C for 75 min (Lesueur, 2009). The binder was then exposed to high pressure (2.1 MPa) and temperature (100°C) for 20 hours for the second PAV (Pressure Ageing Vessel) procedure, what allows simulating the in-service ageing of the bituminous binder after 5 to 10 years. The combination of two laboratory procedures also allows obtaining an advancing ageing state of the LHA binder.
A last Site Hard Aged (SHA) binder was used, it was naturally aged in pavement layers. It was extracted by a chlorinated solvent from RA materials according to the NF EN 12697-3 standard.

To implement the sampling method development, mixtures (aged binder/virgin binder) were prepared according to simplified parameters: an identical ratio between binders of 1 was defined (figure 1A) and a total binder mass of 80 grams was cautiously chosen, so that enough matter can be mixed using the mechanical blade action.

Four mixtures were prepared from selected binders in specific manufacturing conditions (difference of temperatures, mixing time) which are gathered in Table 1. These mixtures are codified X/Y/Z/t according to the following nomenclature where X is the virgin binder, Y is the aged binder, Z is the temperature difference (ΔT) used for the sample and t is the mixing time in seconds.

Influent parameters correspond to:

- the temperature difference between the aged and virgin binder: ΔT: 0°C or 40°C
- the mixing time: 30 or 120 seconds

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Codified Mixture</th>
<th>Virgin binder</th>
<th>Aged binder</th>
<th>ΔT (°C)</th>
<th>Mixing time (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LHV/LHA/40/30</td>
<td>LHV</td>
<td>LHA</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>LHV/LHA/0/30</td>
<td>LHV</td>
<td>LHA</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>LHV/LHA/40/120</td>
<td>LHV</td>
<td>LHA</td>
<td>40</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>SHA/SHA/0/120</td>
<td>SHA</td>
<td>SHA</td>
<td>0</td>
<td>120</td>
</tr>
</tbody>
</table>

Table 1: Codification of tested binder mixtures according to the X/Y/Z/t nomenclature (X: virgin binder; Y: aged binder; Z: difference of temperatures between binders, t: mixing time)

All mixtures were prepared according to an identical mixing procedure. For example, for the first mixture (LHV/LHA/40/30), 40 grams of the LHA aged binder were firstly poured on the bottom of a silicone mold which was conditioned during 60 minutes at 120°C in an oven, this procedure avoids any further cooling of the sample. Then, a similar mass of the LHV virgin binder was carefully deposited at a controlled temperature (160°C) on the aged binder layer. A temperature difference ΔT (equals to 40 °C)
is also introduced between the aged and virgin binders. After some seconds, the obtained two-layered binder system was stirred with a blade at a controlled rotation speed of 200 rpm during 30 seconds. The blade geometry and rotation speed were fixed. The final mixture was finally cooled to obtain a cold disk (67 mm × 20 mm) (diameter × height) (figure 1B).

Figure 1: Experimental procedure in laboratory for the preparation of binder mixtures

For the second LHV/LHA/0/30 mixture, the temperature difference of 0°C means that the temperature of the first LHA layer is 160°C and the temperature of the LHV binder equals to 160°C. In Table 1, the fourth mixture is a control sample, it was prepared by pouring a SHA layer (at 160°C) on another one at 160°C. The deposit was performed in two times according to the previous mixing time and the sample was mixed during 120 seconds. Under these defined optimal manufacturing conditions, this mixture allows validating the homogeneity definition in a mixture and the development of the statistical infrared imaging methodology (3.1.).

2.2. Method: Infrared imaging microscopy in ATR (Attenuated Total Reflection) mode

Imaging ATR (Attenuated Total Reflection) is an analytical non-destructive technique to obtain important information about the spatial distribution of different components in the sample (Tay and Kazarian, 2009). It is particularly present in several research fields such as pharmaceutical domain (Dole et al., 2011; Heussen et al., 2012), paint film analysis (Kaszowska et al., 2013) and miscibility of polymer blends (Zhou et al., 2009, 2007). The device is composed of an infrared microscope and a spectrometer for which the analysis principle is completely detailed in (Lopes et al., 2016). Sample molecules are excited with an electromagnetic wave, what conduces to the vibration of organic molecular bonds at specific wavelengths detected on the obtained infrared spectrum.
2.2.1. Acquisition of chemical mappings in ATR mode

An infrared Spotlight 400 microscope (Perkin Elmer) was also used according to the ATR (Attenuated Total reflection) mode with a germanium crystal. In the ATR mode, little or no sample preparation is required. Only sample surface flatness is necessary to assure a proper contact between the sample and the crystal. During the analysis (figure 2), internal reflections of the entering infrared beam occur producing a resulting evanescent wave which penetrates the sample on a 1-2 µm thickness. The spectral data are then collected from the 2D sample surface thanks to a focal plane detector (FPA) which can simultaneously record thousands infrared spectra (Gabrienko et al., 2015).

![Germanium micro-ATR accessory](image)

Figure 2: Analysis principle of the sample surface using the germanium micro-ATR crystal (Tay and Kazarian, 2009)

The acquired 2D chemical mapping is generated from infrared spectra which are obtained for each pixel size. In the study, acquisition parameters of the chemical mappings were: 1 scan/pixel, a pixel size of 1.56 × 1.56 µm², a spectral resolution of 8 cm⁻¹, a wavenumber interval from 4000 to 744 cm⁻¹. The dimensions of analyzed zones were fixed to 200 × 200 µm².

2.2.2. Chemical mappings of pure binders

To monitor the bitumen ageing in mixtures, pure virgin and aged binders were firstly analyzed to identify the infrared marker to use. A little mass of each binder (less than 0.5 g) was deposited on a glass substrate. The analysis was performed on a 200 × 200 µm² surface of the matter summit where the surface is considered plane. The surface flatness can be easily validated by the visualized image clearness. The crystal was then put in contact with the sample surface, no additional pressure was used. Chemical mappings were recorded and appear on figure 3A.
Figure 3: Infrared analysis of pure virgin and aged binders: (A) acquired chemical mappings (B) associated spectra on a 1.56 × 1.56 µm² surface, (C) carbonyl spatial distributions

Using an identical color scale, chemical mappings are mostly composed of a green zone (figure 3A) attributed to an absorbance value of 0.010 which highlights that the crystal/sample contact level is similar for both binders. Local red zones are observed, they correspond to physical defaults of the crystal surface which was previously damaged by the analysis of harder materials, as already discussed by (Tay and Kazarian, 2009). Spectra 1 and 2 (figure 3B) are respectively defined on chemical mappings of the virgin and aged binders, their comparison highlights the presence of a carbonyl peak around 1700 cm⁻¹. As the baseline is spectrum-dependent for the imaging ATR technique, a treatment (valley to valley) (figure 3B) was performed to obtain spatial distributions in carbonyl functions. More precisely, the spectrum 2 was used to correctly define the integration limits of the carbonyl function, they were fixed between 1720 and 1665 cm⁻¹. Whatever the presence of the carbonyl peak, the corresponding absorbance has also been integrated between these limits for each infrared spectrum of each pixel (1.56 µm × 1.56 µm) thanks to the software treatment. All obtained calculated values are represented by a color level on the carbonyl spatial distribution (figure 3C). The color scale extrema were finally fixed between 0.000 and 0.003 to highlight difference of oxidation between binders.
Therefore, figure 3C displays spatial distributions in the carbonyl absorbance area and concentration for the LHV and LHA pure binder surfaces. Using the same color scale, the carbonyl spatial distribution of the virgin binder is green, it corresponds to a carbonyl absorbance area of 0.000 and indicates a non-oxidized virgin binder (figure 3C). The carbonyl spatial distribution of the aged binder is red, indicating a carbonyl absorbance area of 0.003. The aged binder displays also an advanced oxidation. Therefore, the carbonyl function can be used as a marker to monitor the bitumen ageing.

2.2.3. Infrared analysis of binder mixtures using a specific chemical/statistical combined methodology called chemomap

Once the bituminous cold disk was splitted (figure 1B), sub-samples were removed with a cold blade (figure 4B) on the Left, Middle and Right locations of the sample Internal face, they are noted (LI), (MI) and (RI) (figure 4A).

Figure 4: Sampling procedure of sub-samples to analyze with the ATR imaging microscopy

Three sub-samples were chosen to observe variability in oxidation at different locations. 200 × 200 µm² chemical mappings were obtained at these locations (LI) (MI) and (RI) and the spatial distributions of the carbonyl function were obtained by integrating the infrared peak between the same integration limits that previously used (1720-1665 cm⁻¹). For example, figure 5A displays the carbonyl spatial distribution of a sub-sample which was located at a left intern (LI) side of a mixture internal face. Different orange (spectrum 13, 5B) and green (spectrum 14, 5B) absorbance zones are observed, what allows highlighting an oxidation heterogeneity in the mixture.

In order to compare obtained carbonyl spatial distributions according to an accurate and reliable way, the exploitation procedure has been pursued and we have developed a specific statistical treatment to quantify these visual infrared 2D data. That corresponds to the conversion of a chemical mapping into a matrix of micro carbonyl absorbance values which was exploited to plot a statistical curve (figure 5).
Figure 5: Treatment principle of chemical mappings: analysis of a mixture sub-sample (A) with associated spectra (B), map conversion in a matrix (C) and into the associated statistical curve (D)

More precisely, the carbonyl spatial distribution (figure 5A) was converted into a matrix of micro carbonyl absorbance areas (figure 5C) where each value corresponds to the area absorbance of the carbonyl peak integrated on a spectrum defined on a surface of 1.56 × 1.56 µm² (pixel size). Then, a statistical treatment was undertaken to classify in a refined way micro carbonyl absorbance values into intervals defined with a 0.0001 length. Appearance frequencies of carbonyl absorbance values were determined and converted in percentages. Statistical curves were obtained by plotting appearance frequencies according to micro carbonyl absorbance intervals (figure 5D). On figure 5D, the statistical curve also transposes infrared data of the figure 5A. Two absorbance populations are defined by two curve peaks (two red arrows, figure 5D) and refer to two green and orange zones which were previously observed on figure 5A.

Therefore, a statistical treatment has been developed to quantify infrared data on carbonyl spatial distributions. In the next part, results present the validation of this novel treatment procedure using the SHA/SHA/0/120 control mixture (part 3.1) before studying the influence of the aged temperature and the mixing time on mixture homogeneity (part 3.2).
3. Results

3.1. Validation of the chemical/statistical combined methodology called *chemomap*

To validate the homogeneity definition and the statistical treatment of chemical mappings, the SHA/SHA/0/120 control mixture of two identical binders was tested. Three sub-samples were removed on Left Intern (LI), Middle Intern (MI) and Right Intern (IR) of the mixture internal face, corresponding chemical mappings were acquired, exploited and treated. On figure 6A, the graph displays appearance frequencies of micro carbonyl absorbance areas (Y-axis) according to defined intervals (X-axis). Each curve translates carbonyl data of the infrared analysis of each sub-sample. For the three sub-samples of the analyzed mix, the three observed curves are Gaussian, superimposed and centered on a carbonyl absorbance value of $33 \times 10^{-4}$, what allows validating total homogeneity of the control mixture.

Figure 6: Statistical distribution curves of the control mixture SHA/SHA/0/120: (SHA) Site Hard Aged, (LI) Left Intern, (MI) Middle Intern, (RI) Right Intern

By focusing then on figure 6B, two quantitative parameters are introduced to better assess and compare the position of three curves tops between them:

- the curves peaks average (CPA): it corresponds to the average of all carbonyl abscissa values which are associated to curves peaks. On figure 6B, CPA = Average $(31.5; 32.5; 33.5) \times 10^{-4}$. The CPA indicator allows characterizing the oxidation state of reduced analyzed zones.

- the curves peaks standard deviation (CPSD) which is the standard deviation of all carbonyl abscissa values which are associated to curves peaks. On figure 6B, CPSD = Standard Deviation $1.0 \times 10^{-4}$.
(31.5; 32.5; 33.5) \times 10^{-4}. It allows assessing homogeneity in the mixture from the distance between curves.

Thus, as mixtures were prepared in (50/50) (w/w) proportions in the study (part 2.1), a mixture has been defined as homogeneous if:

- the CPSD is low or equals to $2.0 \times 10^{-4}$
- the CPA is the average of CPA values which are associated to the LHV virgin binder ($7.5 \times 10^{-4}$) and the LHA aged binder one ($19.5 \times 10^{-4}$), suggesting that the positions of mixtures curves are comprised between those of LHV and LHA curves.

Once the infrared imaging analysis of binder mixtures and the statistical treatment validated, the methodology has been applied to study the influence of the aged binder temperature and the mixing time on the binder blending.

### 3.2. Influence of the aged binder temperature on the binder blending

Figure 7 displays statistical curves obtained for the LHV/LHA/40/30 mixture (7A) and the LHV/LHA/0/30 mixture (7B). For these two mixtures, the binder temperature difference respectively equals to 40 and 0°C. Appearance frequencies (Y-axis) of micro carbonyl absorbance areas (from 2D carbonyl spatial distributions) are plotted according to intervals of values (X-axis). Distribution curves of each mixture are compared with those of the virgin LHV binder (green curve with dots) and the aged LHA binder (red curve with dots).

**Figure 7: Comparison of statistical curves for LHV/LHA/40/30 (A) and LHV/LHA/0/30 (B), mixtures (LHV) Laboratory Hard Virgin, (LI) Left Intern, (MI) Middle Intern, (RI) Right Intern, (LHA) Laboratory Hard Aged**

<table>
<thead>
<tr>
<th>Curve</th>
<th>CPA</th>
<th>CPSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHV</td>
<td>8.8×10^{-4}</td>
<td>4.9×10^{-4}</td>
</tr>
<tr>
<td>LI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LHA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 7A:** CPA = 8.8×10^{-4}  
CPSD = 4.9×10^{-4}

**Figure 7B:** CPA = 9.0×10^{-4}  
CPSD = 2.0×10^{-4}
Figure 7A highlights that statistical distribution curves of different sub-samples are not identical for the LHV/LHA/40/30 mixture. The curves and associated peaks have different distances between them, which is illustrated by a high CPSD value of $4.9 \times 10^{-4}$. The chemomap methodology also allows rapidly concluding that the LHV/LHA/40/30 mixture is not homogeneous and does not constitute a blend.

By considering the aged binder temperature increase (figure 7B), distribution curves of different sub-samples get closer to each other for the LHV/LHA/0/30 mixture, the CPSD value is reduced from $4.9 \times 10^{-4}$ to $2.0 \times 10^{-4}$. As detailed in the study (part 3.1), the first condition of a homogeneous mixture is validated but the CPA ($9.0 \times 10^{-4}$) value remains close to the LHV virgin one ($6 \times 10^{-4}$). This result suggests that homogeneity of the mix is improved but it is not total. Therefore, closer binder temperatures have also a positive effect on the binder blending but are not sufficient to obtain a totally homogeneous binder mixture.

### 3.3. Influence of the mixing time on the binder blending

Figure 8 shows statistical distributions curves of the LHV/LHA/40/120 mixture whose positions are comprised between the LHV and LHA binder curves.

![Figure 8: Statistical distribution curves for the LHV/LHA/40/120 mixture (LHV) Laboratory Hard Virgin, (LI) Left Intern, (MI) Middle Intern, (RI) Right Intern, (LHA) Laboratory Hard Aged](image)

For this tested mixture, statistical curves of the three sub-samples (LI, MI, RI) are close each other. The calculation of statistical parameters firstly indicates that the CPSD value equals to $2.0 \times 10^{-4}$. Furthermore, mixture curves are centered on an intermediate micro carbonyl value of $14 \times 10^{-4}$ which is very close from the average of the virgin and aged binder CPA values. As defined in the 3.1 part, the two conditions of a homogeneous mixture are fulfilled. In the study, the mixture also appears homogeneous.
according to the *chemomap* method. By comparing the LHV/LHA/40/30 (Figure 7A) and the LHV/LHA/40/120 (Figure 8) statistical curves, a longer mixing time also allows improving blending and leading to a homogeneous binder mixture.

### 4. Discussion

Through the current objectives of a more sustainable society, one of the main challenges for the road construction industry consists in reducing the carbon dioxide emission and the energy consumption during the production of asphalt mixture pavement (Thives and Ghisi, 2017). As most energy is involved in the power plant burner which heats raw materials (aggregated, bitumen) (Thives and Ghisi, 2017), some efforts were also undertaken to reduce the production temperatures of asphalt mixtures and use reclaimed asphalt in the manufacture of road pavement materials.

#### 4.1. Importance to assess the binder blending for the recycling process of asphalt mixtures

Among previous solutions, recycling of asphalt mixtures constitutes a double ecological technology because the incorporation of reclaimed asphalt in asphalt mixtures can lead to significant reductions in energy consumption (Aurangzeb et al., 2014) and greenhouse gas emissions (Zaumanis et al., 2014). However, the addition of reclaimed asphalt under lower manufacturing temperatures may result in to a partial blending between the reclaimed asphalt and virgin binders resulting in poor pavement performance according to (Shirodkar et al., 2013). Therefore, the control of homogeneity leading to high performing mixtures (Celauro et al., 2010), it is important to develop suitable methods to assess homogeneity and the blending between binders. In the road industry, most of studies are based on a binder solvent extraction to address the blending issues (Zhao et al., 2015). But this extraction procedure is time-consuming (Riccardi et al., 2017) and doesn’t take in account the solvent effects on the binder characteristics.

The main objective of the paper is also to overcome the limitations of the traditional extraction procedure by developing a novel solvent-free methodology to assess the binder blending in asphalt mixtures incorporating reclaimed asphalt pavement.

#### 4.2. Advantages and drawbacks of the developed non-destructive infrared methodology

For this purpose, the use of a non-destructive methods is essential but requires a distinction between binders. An external mineral marker in one binder (Cavalli et al., 2016) can be used to differentiate
binders but the method is indirect and may modify rheological properties of the binder in the mixture.  
Another solution is based on the fluorescence principle: a specific fluorescent binder may be used in the  
mixture (Navaro et al., 2012) but the virgin and aged binders can also differ by their fluorescence  
emissions (Ding et al., 2018). Indeed, the aged binder emits less fluorescence than the virgin one due to  
a decrease in resins according to (Ding et al., 2018). However, this approach remains enough global  
because the technique detects groups of molecules and results are obtained from the physical  
treatment of grey images with an image processing program.  

Inversely, the infrared technique is very efficient to differentiate the virgin and reclaimed binders  
according to (Ding et al., 2016). It also appears more accurate than the fluorescent one because it  
directly detects chemical bonds in bitumen and especially carbonyl bonds which result from the  
oxidative ageing process. Coupling to a microscope, the infrared approach only requires a little  
preparation of the sample.  

Therefore, the infrared imaging technique was preferred to other microscopic techniques and the work  
was focused on modeled binder mixtures to implement the methodology on known samples. The  
bitumen ageing was directly assessed by monitoring spatial distributions of the carbonyl marker on  
different locations of the mixture. It’s the first time that the infrared Imaging ATR technique was used  
for the analysis of binder mixtures, that constitutes an innovative result. The contact between the ATR  
germanium crystal and the sample surface is convenient because the sub-sample is only composed of a  
bituminous matrix. To assess blending kinetics during the manufacturing process, the used methodology  
presents however, the drawback to test sub-samples after a cooling step. Consequently, the extracted  
infrared information may differ between the in-situ process step and the sample cooling one.  

Nevertheless, chemical mappings were acquired on bituminous sub-samples which were extracted at  
different locations of the mixture internal face. In this study, three sub-samples were analyzed and the  
number of samples is sufficient to highlight first oxidation variabilities which may spatially occur in a  
mixture. Nevertheless, a more important representative number of sub-samples should be analyzed in  
order to provide the most accurate and reliable assessment of mixture homogeneity.  

For a better knowledge of bitumen composition and structure, spatial distribution of other functions  
could be also treated. In the study, the carbonyl marker was chosen because it refers to the bitumen  
oxidative ageing. The sulfoxide peak could be also selected as a bitumen ageing marker because an  
increasing absorbance area is observed at $1030 \text{ cm}^{-1}$ between spectra 1 and 2 (figure 3B). Nevertheless,
the sulfoxide peak appears more prone to spectrum baseline variabilities which may be due to some mineral siliceous impurities (around 1000 cm\(^{-1}\)) or to the possible presence of coke which is illustrated by the baseline increase in the LHA infrared spectrum (figure 3, spectrum 2 from 1500 cm\(^{-1}\)) and confirmed by (Tay and Kazarian, 2009). It should be also interesting to monitor spatial distributions of the aromatic C=C bond at 1650-1550 cm\(^{-1}\) to complete spatial molecular information about the presence and concentration of aromatic hydrocarbons (with rings) which are associated to asphaltenes in petroleum studies (Andersen et al., 2017; Gabrienko, 2015).

### 4.3. Identification of manufacturing factors influencing the binder blending

Based on the statistical curves (figure 7), the comparison of CPA and CPSD indicators shows that the aged binder temperature increase positively impacts the binder blending (figure 7). This result is in a good agreement with other studies which have shown that the production temperature has a great positive influence on homogeneity of asphalt mixtures incorporated reclaimed asphalt (Cavalli et al., 2016; Navaro et al., 2012). Furthermore, figure 8 highlights that the mixing time increase improves the binder blending. In relation to the mechanical energy supply, this result is similar to those of other studies performed at the asphalt mixtures scale (Hassan et al., 2015; Navaro et al., 2012; Nguyen, 2013). This study also highlights the significant role of a mechanical energy in the industrial manufacture of heterogeneous materials.

Therefore, results of this study outline the possibility to demonstrate the effect of manufacturing process factors on the blending using an infrared methodology adjusted to the analysis of small quantities of bituminous mixtures.

Nevertheless, the blend between two binders may not happen in a similar way in a binder mixture than in a granular asphalt mixture. The geometric and morphological aspect of granular aggregates may namely reduce the interaction spaces between the binders and a filler addition may also reduce the binder interactions due to the increase in the binder viscosities. This is why the present paper constitutes here a first step to optimize the formulation step and to assure a good quality and performance of more sustainable road materials. The study has also allowed demonstrating the positive effect of a mechanical energy and high binder temperatures on homogeneity of a binder mixture. High and close binder temperatures being a first condition to assure homogeneity, novel research ways must be considered to maintain performance, lower energy and lower greenhouse gas emissions of warm
asphalt mixtures reducing the manufacturing temperature. The use of specific additives lowering binder viscosities should be one of the alternatives to consider.

Other experiments could be interesting to assess the influence of the aggregates addition on the blend properties and the infrared imaging methodology could be also directly applied on granular RA materials to assess local oxidative properties of the RA binder. Particularly, we will take an interest in a future work to the chemomap methodology customization to the binder blending assessment in intergranular spaces of real compacted asphalt mixtures incorporating aggregates and reclaimed asphalt.

Thus, this alternative infrared imaging methodology opens several interesting perspectives to progressively slow down the use of the solvent-extraction procedure in the road industry. It also allows more a rapid analysis of bituminous mixtures. 1 to 3 hours are namely possible for the infrared chemomap analysis of bituminous mixtures in comparison to several days for the binder extraction and analysis from recycled asphalt mixtures.

5. Conclusion

Within the recycling context of asphalt mixtures, most of road studies use the traditional solvent extraction method to assess the degree of blending between the reclaimed asphalt and virgin binders. However, this technique is time-consuming, use Carcinogenic, Mutagenic and Reprotoxic (CMR) solvents and raises questions about the solvent effect on the binder characteristics. The main objective of the paper is to overcome these limitations by developing a novel solvent-free methodology to in situ assess the binder blending in bituminous mixtures. For this purpose, the selected approach was to implement the development of an infrared imaging microscopy methodology to the analysis of modeled binder mixtures produced in laboratory according to specific manufacturing conditions. As aged and virgin bituminous binders differ in oxidation, carbonyl spatial distributions were obtained at different spatial locations of the mixture. Visual chemical mappings were then converted into statistical curves which were compared. Homogeneity has been quantified using two statistical indicators. The development of this methodology has been successfully validated and the influence of the manufacturing temperature and mixing time has been studied on the binder blending. Results show that high and close temperatures between the aged and virgin binders are necessary to obtain a homogeneous mixture whereas a longer mixing time further improves the binder blending. That suggests the necessity to always maintain a mechanical mixing energy during the manufacturing of recycled asphalt mixtures.
Based on the analysis of small bitumen quantities, the developed chemomap methodology is a promising method to get access to a rapid and non-destructive sample analysis while not modifying the bitumen molecular structure by a solvent extraction step. It also constitutes a sustainable tool to optimize manufacturing process parameters in the mix design of recycled asphalt mixtures.

6. Perspectives
For the study of asphalt mixtures containing both organic and inorganic parts, other perspectives are also open to in situ assess chemical properties which were not accessible by solvent-based extraction techniques. More generally, the statistical chemomap imaging ATR methodology could be applied to the monitoring of any chemical infrared bond in any organic mixture such as bitumen/bio-binder mixtures, polymer mixtures or petroleum residues.

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