Aalto University
School of Chemical
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Fawad Ahmed

Diffusion of the rejuvenators into bitumen studied by FTIR-ATR as a function of temperature and bitumen properties

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Supervisor: Professor Terhi Pellinen
Advisor: M.Sc. Michalina Makowska

Aalto University
School of Engineering

Aalto University, P.O. BOX 11000, 00076 AALTO
www.aalto.fi

Abstract of master's thesis

Author Fawad Ahmed		
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Abstract

The ageing of bitumen reduces the ductility of pavement and results in material hardness. Generally, recycling of asphalt is carried out to reduce the negative impact of ageing. In a conventional hot-mix asphalt recycling process, the bitumen from asphalt pavement is blended with the aggregates and rejuvenating agent.

During the recycling process, all materials are mixed at particular temperature for a short period of time. To achieve high quality recycled asphalt mix, proper blending of aged bitumen with added rejuvenator is necessary for effective performance. The role of rejuvenator to reduce the stiffness of aged bitumen is essentially governed by the diffusion of its molecules into the bitumen. Diffusion is a slow occurring process and largely depends on temperature and intermolecular interactions of diffusing molecules

The primary objective of this thesis was to examine the factors limiting the maximum degree of rejuvenation within the realistic time frame, similar to that observed in field. Temperature, viscosity and softening properties of materials were analyzed specifically to deduce their influence on the diffusion of rejuvenating molecules.

Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) was applied to monitor the diffusion of rejuvenator in two different grades of bitumen. The degree of rejuvenation was found to increase with temperature. However, below the softening point of the bitumen, rejuvenation was not visibly proceeding. The rejuvenation level was also found to increase with decreasing viscosity of the rejuvenating agent.

Keywords ageing, rejuvenation, diffusion, FTIR-ATR, softening point, temperature

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1 Introduction

1.1 Background

The aim to establish sustainable environment has encouraged the use of natural resources and low energy consumption technologies. However, with limited natural resources, recycling of materials has gained considerable importance in almost every sector of technology. Recycling of asphalt concrete pavement is one such development in road construction materials. Typically, pavement deteriorates over time due to various factors, such as traffic loading and environmental conditions. Therefore, proper maintenance and recycling must be deployed to avoid the complications of pavement deterioration such as, cracking, surface deformation, potholes and bleeding (Adlinge, Gupta 2013). Bitumen, a crucial subcomponent of asphalt concrete, used in road pavement becomes much stiffer than the desired quality with the passage of time during service life. This hardening of bitumen is caused by ageing. To reduce this negative impact of ageing, raw bitumen of softer grade or recycling agent is added during recycling process.

In most of the recycling techniques, old and new bitumen are mixed to create a recycled bitumen binder of desired properties. Hot in-place recycling (HIP-RC) is vastly utilized technique in the maintenance and rehabilitation of hot mix bitumen pavement on site in one continuous operation. Generally, process begins by heating existing asphalt roadway surface that allows the material to be softened and easily removed by milling or scarifying. Preheating the surface softens the pavement enough to permit scarification. Besides the ease in workability, preheating allows the removal of moisture in reclaimed bitumen pavement, thus preventing severe problematic effects on properties of the recycled mixture (Moghaddam, Baaj 2016). After the scarification, aggregates, bitumen and rejuvenating agent are added to the loosened material and evenly mixed to improve the properties of the final mixture. Finally, the pavement is spread and re-compacted by paving equipment (Russell, Uhlmeyer et al. June 2010). In such conventional HIP-RC process, removed surface materials are mixed with virgin bitumen or rejuvenating agent for a short period of time.

The quality of recycled asphalt depends on several parameters of recycling process, such as temperature, materials compatibility and mixing. Incomplete mixing likely influence the properties of recycled asphalt mixture (Karlsson, Isacsson 2003a). Mixing is a combination of mechanical mixing as well as diffusion of materials into each other to form homogeneous mixture. Diffusion is the transport of matter and occurs at micro scale (Karlsson, Isacsson 2003b). To achieve maximum desired quality of recycled asphalt mixture, it is important that molecules of recycling agent diffuse well enough into bitumen component of asphalt mixture. This diffusion in bitumen was previously studied by using spectroscopic techniques. (Karlsson, Isacsson 2003d)

Fourier transform infra-red spectroscopy (FTIR) has previously been applied in the characterization of bitumen for its functional groups and ageing level (Jemison, Burr et al. 1992, Karlsson, Isacsson 2003e). FTIR spectroscopy measures the intensity of infrared light when it passes through the absorbing medium. Infrared light is absorbed by the covalent bonds of molecules present in a material. When any substance diffused into the test sample, the absorbance of the sample changes. Similarly, when bitumen is exposed to FTIR spectroscopy, each component in bitumen absorbs infrared light and the difference in intensity detected shows the nature of functional group present in the bitumen.

Attenuated total reflectance (ATR) exploits the total internal reflectance of infrared light in a non-absorbing prism. Therefore, the spectrum obtained from internally reflected attenuated light due to any absorbing substance in a material in contact with the prism is comparable with the corresponding spectrum recorded if the light passes through the surface layer of material. It is preferably used because of its ease in sample preparation for this work and to avoid any chemical influence by the solvents used in conventional FTIR sample preparation.

In this manner, FTIR-ATR serves convenience in monitoring the changes in bitumen appeared due to diffusion of rejuvenating molecules by detecting the difference in absorption of sample at different time scales. Figure 1 shows a schematic diagram of multiple reflections of infrared light (I0 and I) in non-absorbing ATR prism (white) with bitumen and rejuvenator layers (gray)

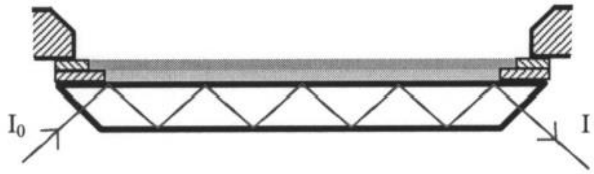
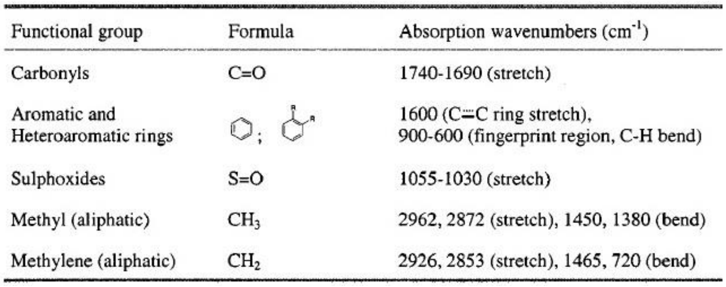


Figure 1 IR beam incident on sample through ATR prism (Karlsson, Isacsson 2003a)

Major changes appeared in the infrared spectral absorption band of carbonyl, aromatics and sulfoxide regimes during rejuvenation process. Due to the fact that carbonyl and sulfoxide signals have been previously correlated (Lesueur 2009) with increase in the stiffening of the binder, the decrease of the intensity of the signals in this region due to dilution of the aged binder could be considered a rejuvenation. Therefore, these functional group systems were studied in the scope of this research work.

The approximated range of wave numbers of these functional group regimes in bitumen spectrum are given in figure 2. Literature shows that the free (non-hydrogen bounded) absorption band of carbonyl group due to oxidation of bitumen was found at 1730 cm^{-1} while aromatic and sulfoxide content can be found at region of 900 to 700 cm^{-1} and at 1030 cm^{-1}, respectively (Petersen, J. Claine., National Research Council (U.S.)., Transportation Research Board.,Committee on Characteristics of Bituminous Materials., 2009).



Functional group	Formula	Absorption wavenumbers (cm^{-1})
Carbonyls	C=O	1740-1690 (stretch)
Aromatic and Heteroaromatic rings	;	1600 (C=C ring stretch), 900-600 (fingerprint region, C-H bend)
Sulphoxides	S=O	1055-1030 (stretch)
Methyl (aliphatic)	CH_3	2962, 2872 (stretch), 1450, 1380 (bend)
Methylene (aliphatic)	CH_2	2926, 2853 (stretch), 1465, 720 (bend)

Figure 2 Approximated absorption wave number of bitumen functional groups (Karlsson, Isacsson 2003a)

1.2 Research problem

Mixing of old aged binder with rejuvenator must be appropriate in order to achieve desired homogeneity. Complete mixing requires proper mechanical mixing as well as diffusion of rejuvenator into aged bitumen to adjust the stiffness of recycled binder up to the acceptable level. Furthermore, binders phase stability is important to keep the mixture homogeneous. Homogeneous mixing is influenced by factors, such as temperature, binder viscosity and mixing time.

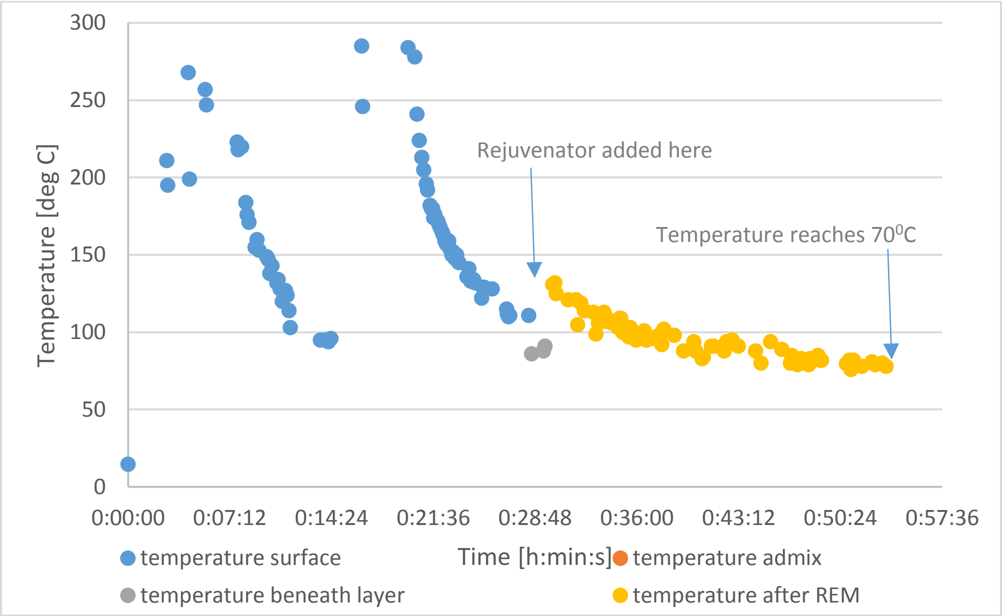


Figure 3 Temperature profile HIP-RC pavement recorded from the field results

Figure 3 presents the temperature recorded from the surface of the HIP-RC treated pavement during the summer of 2016. The rejuvenator is added after the beneath temperature is measured.

The time at which aged bitumen and rejuvenator are at temperatures above 70°C is approximately 30 minutes.

In some cases, total stiffness of recycled bitumen mix turns out to be less than the expected. One hypothetical explanation is that the rejuvenator acts as a lubricant and creates a coating layer around old bitumen and aggregates, thus giving lubricating effect and non-homogeneity of final mix (Karlsson, Isacsson 2003c). Further, rate of diffusion occurring at micro level is also influenced by temperature as shown by (Karlsson, Isacsson et al. 2007a). It is important that rejuvenator diffuses into the aged binder for effective rejuvenation. Therefore, proper mixing time at specific temperatures must be provided to allow rejuvenator to diffuse through the aged binder. Since the rate of diffusion of particular rejuvenator is dependent on temperature changes therefore, level of rejuvenation is assumed to be varied at different temperatures.

1.3 Aims and structure of thesis

This thesis aims to address the influence of following major parameters involved during HIP-RC technique:

1. The influence of viscosity of old binder on blending of aged bitumen and rejuvenator. The effect of bitumen viscosity is important factor to consider as it helps to evaluate the blending ratios of bitumen and rejuvenator as well as selection of blending temperature.

2. Influence of temperature when a bitumen and rejuvenator interacts during blending. It is one of the key parameter in diffusion therefore, it governs the effectiveness of blending during recycling of aged binder by rejuvenating agent. The information about the influence of temperature will help to adjust the temperature required for blending of particular bitumen and rejuvenator.

3. Influence of viscosities of rejuvenators has to be considered in evaluating the rejuvenation level in aged binder. Since it is required that the final mix must adhere desired viscosity level, therefore impact of viscosity of rejuvenator has greater importance in selection of material.

1.4 Limitations of the research

This research covers those parameters that are directly affecting the real time rejuvenation process. Previously rejuvenation of binder was studied in terms of diffusion as well as effects of ageing, temperature and bitumen properties on diffusion (Makowska, Pellinen 2015). This research however was limited to the analysis of rejuvenation by means of concentration of certain functional groups entities in the bitumen during diffusion. Diffusion is a slow occurring process but the recycled asphalt pavement is required to perform starting from few hours after end of compaction (when the surface temperature reaches 70°C). During the HIP-RC technique rejuvenator and bitumen remain at high temperatures for only about 30 minutes, figure 3. Therefore very long periods of time for diffusion at high temperatures are deemed useless in this work and short term blending is studied.

The experimental set-up used in this work proved to be problematic in measurements conducted at 120°C and therefore the temperature range was limited.

The diffusion coefficients were not calculated to show the exact diffusion of rejuvenators and the problem is discussed in further section.

This research work focused on the blending as witnessed by FT-IR and did not focus on the effect on the rheology.

2 Physical and chemical properties of bitumen

2.1 Bitumen composition

Bitumen is a complex material having several chemical groups present, therefore its chemical and physical properties directly influence the mechanisms involved in the recycling process. However, to simplify, the bitumen can be described as a material which consists mainly of carbon and hydrogen atoms with hydrogen-to-carbon molar ratio of 1.5 (Lesueur 2009). Typically, carbon 80-88 wt.% and hydrogen 8-12 wt.% gives a hydrocarbon content superior to 90 wt.\%. Other atoms such as sulfur (0-9 wt.%), nitrogen (0-2 wt.%), oxygen (0-2 wt.%) and traces of metals were also found (Lesueur 2009). Sulfur has been considered as most polar atom present in the form of sulfies, thiols and, upon ageing, sulfoxides (Lesueur 2009). Oxygen typically appeared in raw and aged bitumen in the form of ketones, phenols and, to lesser extent, carboxylic acids (Lesueur 2009). Nitrogen exists in pyrrolic and pyridine structures and also form amphoteric species such as 2-quinolones. Functional groups present in bitumen before and after ageing can be seen in figure 4.

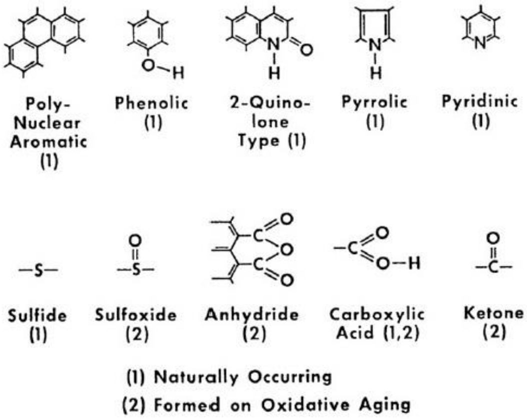


Figure 4 Functional groups in bitumen (Lesueur 2009)

2.2 Bitumen SARA fractions and their properties

Bitumen is considered as a multi-component system containing various substances and structures. Models of bitumen composition and structure suggest that bitumen is mainly composed of solvent phase, often referred to as maltenes, which further separated into saturates, aromatics and resins as SARA fractions (Karlsson, Isacsson et al. 2007b). The other viscosity enhancing colloidal particles or micro-structures were referred to as asphaltenes (Karlsson, Isacsson et al. 2007b). Saturates are 5-15 wt.% of paving grade and mainly consist of aliphatic chains with very few polar atoms or aromatics rings (Lesueur 2009). Aromatics are the abundant content of bitumen with 30-45 wt.% of total bitumen (Lesueur 2009). Their carbon structure is slight aliphatic with few condensed aromatics rings. Aromatics are slightly viscous than saturates at the same temperature due to high glass transition temperature around -20°C (Lesueur 2009). Resins are considered as polar aromatics which act as a stabilizer for the asphaltenes (Lesueur 2009). Their composition are expected to be close to asphaltenes but contain low molecular weight as well as less complex aromatic structure (Lesueur 2009).

Asphaltenes are the viscosity build up components of bitumen and largely contribute in black color of the bitumen (Lesueur 2009). Although asphaltenes contain more condensed rings and more polar groups but fused aromatic ring structures are the fundamental differentiating feature of asphaltenes from other bitumen contents (Lesueur 2009). In addition, asphaltenes carry permanent electric charges that is thought to arise as a consequence of the high degree of electron de-localization stacking of graphite-like molecules, giving overall negative charge (Lesueur 2009).

Asphaltenes exist as micelles inside bitumen and experience Brownian motion at high-enough temperature (Lesueur, Gerard et al. 1996, Lesueur, Gerard et al. 1997). Therefore, this Brownian diffusion cause increase in electrical conductivities of asphaltenes with temperature (Lesueur 2009). Thermal analysis strongly suggests that asphaltenes are dispersed solid particles and thus supported colloidal nature of bitumen (Lesueur 2009). Resins in bitumen play vital role in the stabilization of asphaltenes. Asphaltenes could only be dispersed in the oily component of bitumen in the presence of resin content (Swanson 1942). However, it is important to mention that resin from one type of crude is unable to stabilize asphaltenes from another type of crude (Koots, Speight 1975). Murgich et al. further explains this fact that the {*shape of the asphaltene molecules allows the aggregation of only those resins that fit its aromatic regions and show the lowest steric interference with its alkyl groups*}(Murgich, Rodríguez et al. 1996).

2.3 Bitumen ageing

In general, bitumen structure is quite complex and various factors affect its composition and rheology. Complexity of bitumen rises due to temperature changes and environmental factors. Furthermore, various molecular mechanisms evolved due to chemical ageing. Molecules undergo oxidation and polymerization processes, and to lesser extent, lighter components evaporation (Lesueur 2009). Consequently, chemical ageing leads to global hardening of the material and increases cracking problems (Lesueur 2009). Usually, chemical ageing is categorized in short-term ageing and long-term ageing. Short-term is a rapid chemical ageing during mixing of hot bitumen thin film with hot aggregate (Hveem, Zube et al. 1960). The second category, called as long-term ageing, occurs within the longer period of time during the service life of the road (Hveem, Zube et al. 1960). Generally, local climate largely causes ageing of bitumen pavement layers. Typically, top layers of pavement are more exposed than the lower layers therefore, top layers are first affected by ageing (Lesueur 2009). It depends of course on the mix formulation, bitumen thickness and the porosity of mix as well (Lesueur 2009). Overall, several factors influence the extent of ageing and all these parameters involved, make it complicated to describe the in-situ ageing process.

2.4 Effects of ageing on bitumen chemistry

Ageing brings chemical changes in the bitumen composition that affect its rheological properties. Ageing leads to decrease in aromatic content and subsequent increase in resin content whereas, rise in asphaltene content is observed (Lesueur 2009). Therefore, it is generally concluded that aromatics transform into resins which consequently generates more asphaltenes (Lesueur 2009). On the other hand, low reactivity of saturates suggests unchanged chemical effect (Hveem, Zube et al. 1960). In previous researches, it is presented that the asphaltenes produced because of ageing are somewhat different from the initially present asphaltenes in the bitumen (Lesueur 2009). Several researches supported the increase in molecular weights of asphaltenes upon air-blowing, suggesting presence of polymerization reactions (Corbett, Swarbrick 1960, Kats, Glotova et al. 1976). Moschopedis and Speight reported the usual increase in asphaltenes content with the increase in molecular weight from 5600 g/mol to 8000 g/mol upon blowing an Athabasca bitumen for few hours at 260°C. This increase in molecular weight follows with the increase in temperature up to 290°C however, no change was found when the temperature was further increased to 320°C. Moreover, a decrease in H/C, N/C and S/C ratios was observed while O/C ratio was increased (Lesueur 2009). This indicates that the oxygen uptake of asphaltenes develops in parallel, release of nitrogen and Sulphur (Moschopedis, Speight 1977). Similar trend was observed with resins, except the increase in H/C ratio and this suggested the formation of resins from aromatics (Lesueur 2009).

Typically, ageing results in the formation of sulfoxides, followed by formation of carboxylic acids (Lesueur 2009). In literature it was mentioned that organic sulfides, most likely to be dialkyl or alkylaromatics sulfides, present in bitumen were oxidized to form sulfoxides (Petersen, J. Claine., National Research Council (U.S.)., Transportation Research Board.,Committee on Characteristics of Bituminous Materials., 2009). It was postulated that organic sulfides in bitumen reacts with hydroperoxide intermediates that were formed from oxidation of hydrocarbon and results the formation of sulfoxides (Petersen, J. Claine., National Research Council (U.S.)., Transportation Research Board.,Committee on Characteristics of Bituminous Materials., 2009).

As described earlier, bitumen undergoes dual mechanism kinetics when it comes to oxidation reactions, rapid reactions followed by a slower rate reactions (Petersen J.C. 2011). Therefore, ketones and sulfoxides formed at different rates during oxidation and highly depend on the initial composition of bitumen. Figure 5 shows a dual oxidation mechanism of bitumen proposed in (Petersen J.C. 2011), where ketones and sulfoxides produced from common transitory hyderoperoxide oxidation product formed on benzylic carbons (structure VII) (Petersen J.C. 2011). Besides from laboratory experiments, in-situ ageing seems to yield steady-state level not only for sulfoxides but also for carboxylic acids (Lesueur 2009). Generally, oxidation in bitumen is said to proceed in an auto-catalytic way. In addition, photo-oxidation reactions due to ultra-violet light favours polymerization reactions for asphaltenes as well as for lower fractions down to the saturates. These auto-catalytic reactions directly impact on the mechanical properties of bitumen, resulting bitumen hardening.

It is stated in literature that the inherent polarities of ketones and sulfoxides produced during oxidative ageing of bitumen do not directly raises the viscosity parameter of bitumen. However, these entities formed on molecules that can further associates into larger agglomerates resulting in increase of molecular weight and consequent rise in viscosity (Petersen, J. Claine., National

Research Council (U.S.)., Transportation Research Board.,Committee on Characteristics of Bituminous Materials., 2009). Sulfoxide functional groups have greater inherent polarity than ketones, however the effect on viscosity is relatively low. This is because the similar fact that sulfoxide functional groups formed on molecules identified with less strongly associated components of the bitumen (Petersen, J. Claine., National Research Council (U.S.)., Transportation Research Board.,Committee on Characteristics of Bituminous Materials., 2009).

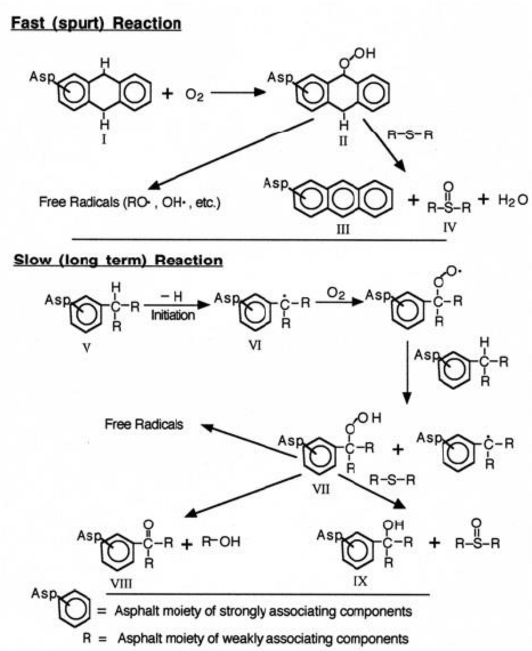


Figure 5 Proposed reaction routes for the bitumen oxidation mechanism (Petersen J.C. 2011)

Saturate fraction in bitumen are nonpolar hydrocarbons that exhibits weak interaction forces. Similarly, unoxidized sulfur atoms interact with weak forces in bitumen. On the other hand, condensed aromatic ring structured components and chemical groups containing nitrogen and oxygen interact strongly with each other and are highly polar (Petersen, J. Claine., National Research Council (U.S.)., Transportation Research Board.,Committee on Characteristics of Bituminous Materials., 2009). Moreover, saturates in bitumen with weak interaction forces show fluid nature characteristics with minimum viscosity of 10 Pa-s (Petersen, J. Claine., National Research Council (U.S.)., Transportation Research Board.,Committee on Characteristics of Bituminous Materials., 2009). Components having high interaction forces, such as aromatics and resins, show more viscous nature and these associated forces among molecules place bitumen close to high molecular weight polymers category. Oxidative ageing increases the concentration of polar functional groups. This causes immobility of molecules or molecular agglomerates due to increase in intermolecular interactions (Petersen, J. Claine., National Research Council (U.S.)., Transportation Research Board.,Committee on Characteristics of Bituminous Materials., 2009) This low mobility of molecules under thermal and mechanical stress, results in fracturing or cracking of bitumen pavement and resistant to healing (Petersen, J. Claine., National Research

Council (U.S.)., Transportation Research Board.,Committee on Characteristics of Bituminous Materials., 2009)

Previous research has shown that sufficient high temperature favours ketone oxidation that occurs in polar aromatics of bitumen as the asphaltene fraction is dissociated (Petersen, J. Claine., National Research Council (U.S.)., Transportation Research Board.,Committee on Characteristics of Bituminous Materials., 2009). It is understandable that temperature and bitumen composition both are major factors affecting the oxidative age hardening. Kemp and Predoehl presented in their study that temperature has greater effect on age hardening in comparison with air-void content (Kemp, Predoehl 1981). Furthermore, their reported data shows greater impact of temperature (climate) on oxidative age hardening than bitumen composition. Oxidative age hardening level of pavement is ultimately governed by maximum temperature, not the average temperature that the pavement experiences during its service life (Petersen, J. Claine., National Research Council (U.S.)., Transportation Research Board.,Committee on Characteristics of Bituminous Materials., 2009)

2.5 Rejuvenation in bitumen

In order to reduce this oxidative hardening of bitumen, rejuvenator is added during recycling of road pavement material. The purpose of rejuvenating the hard bitumen is to recover the initial properties of old bitumen by adding small amount of oil or raw bitumen. The term rejuvenator may referred to as softer grade raw bitumen or recycling agent specifically designed with viscosity reducing capability. Typically, it is diluting the apshaltenes, created as a consequence of ageing, by the addition of new maltenes. Previous literature has shown that better rejuvenation is attained when amount of resins and aromatics are higher in mixture (Yu, Zaumanis et al. 2014).

Bitumen and rejuvenator must be necessarily compatible with one another in order to create homogeneous mixture, and that mainly depends on the nature and distribution of intermolecular associations. In some cases, total stiffness of recycled bitumen mix turns out to be less than the expected. One hypothetical explanation is that the rejuvenator acts as a lubricant and creates a coating layer around old bitumen and aggregates, thus giving lubricating effect (Karlsson, Isacsson 2003c). Therefore, it is important that the added binder must diffuse into the old bitumen during mixing within giving period of time. However in the actual mixing process, blending time lasts for only 60-90 seconds (Ma, Huang et al. 2015). Although, studies have shown that 10-50% rejuvenator by weight of reclaimed asphalt pavement can take 44-144 h to completely diffuse into the bitumen pavement (Hong, Chen et al. 2010). Hung Viet Nguyen et al. found that longer mixing time contributes to better homogeneity with higher stiffness modulus in recycled mixtures (Moghaddam, Baaj 2016).

The consistency of recycled asphalt mixture depends on mechanical mixing, compatibility parameter of two materials and diffusion of rejuvenator into the aged binder (Karlsson, Isacsson 2003a). Homogeneity of final mix is related with the nature of the materials, while mechanical mixing serves in even distribution of binder and aggregates throughout the bitumen mixture and its effectiveness is influenced by mixing time, temperature, mixer type and binder viscosity (Karlsson, Isacsson 2003a). Diffusion on the other hand occurs at micro level and enables the recycled mixture to remain homogeneous.

2.6 Diffusion process in bitumen rejuvenation

Diffusion phenomena is involved in bitumen processing by several means likewise, oxidative ageing (oxygen diffusion), stripping (water diffusion), and rejuvenation in bitumen recycling (mixing of binders). It is typically the transport of matter due to Brownian motion of molecules and largely, dependent on temperature changes (Karlsson, Isacsson 2003a). Diffusion rates depends on molecular mobility, microscopic structure, intermolecular forces and temperature (Karlsson, Isacsson 2003c) The main four steps involved in diffusion of rejuvenator into bitumen are presented in L. J. Zearley at Iowa DOT and Carpenter and Wolosick at the University of Illinois work that follows:

1. Formation of very low viscous layer of modifier around aggregate, which already surrounded by highly viscous coating of aged bitumen around it.

2. The modifier softens the aged bitumen as it penetrates the old aged bitumen layer.

3. As the penetration continues, the viscosity of inner layer decreases due to the diffusion of modifier into the aged layer and consistency of outer and inner layer varies with time.

4. Finally, consistency in viscosities of two layers achieved and equilibrium approached over the shell of the bitumen cement.

Complexity of bitumen composition makes it difficult to study diffusion process. Bituminous binder is composed of various substances and all substances diffuse at different rates depending on the molecular shape, size and polarity. Very few molecules can be considered as arising from the given binder. During the process, composition of the media in which diffusion takes place changes (Blomberg, Makowska et al. 2016). A research showed that even in properly recycled bitumen pavement, premature distresses, such as cracking and potholes are identified in early service life. The reason to explain this fact is associated with existence of the localized higher viscosity binder films even though the recycled mixture appeared to be well rejuvenated (Blomberg, Makowska et al. 2016). The diffusion phenomena in bituminous binders may follow two phase mechanism. Firstly, the diffusion of oil into the maltenes phase of bitumen then secondly, the migration of asphaltenes of bitumen into the rejuvenated maltenes (Lesueur, Gerard et al. 1996). Karlsson et al. described in his work that ageing did not significantly affect diffusion and it appeared to turn some maltenes into viscosity builders, while most of the maltenes remain in same molecular distribution (Karlsson, Isacsson 2003e)

3 Technique used to measure rejuvenation in bitumen

Fourier transform infrared spectroscopy (FTIR) is an extremely reliable and well recognized technique in identification and quantification of substances. The principle of FTIR was based on the fact the most of the molecules absorbed light in infrared region. When this infrared radiation incident on a sample, some radiations was absorbed by the sample and some passes through. The detector attached formed the resulting spectrum of this absorption change. The resulting spectrum thus showed a molecular "fingerprint" of the sample. By using this principle, one can measure the change in spectrum of a substance when its composition is changes. (Markovich, Pidgeon 1991)

Attenuated total reflectance (ATR) exploits the attenuation of internally reflected light due to energy absorption of an analyte in contact with the reflecting surface of non-absorbing prism (Karlsson, Isacsson 2003c). Multiple internal reflections enhances the quality of measured absorption spectra. FTIR-ATR offers two major advantages in comparison to transmittance FTIR that includes the measurement of whole spectrum without solvent blankout, and prevention of chemical influence caused by use of solvents (Karlsson, Isacsson et al. 2007a).

FTIR has been vastly utilized in measurements of bitumen characteristics. This technique has been applied in the analysis of oxygen diffusion into bitumen (Davison, Bullin et al. 1994), functional group analysis of bitumen (Jemison, Burr et al. 1992) and diffusion through thin film polymers by quantifying the change in absorbance at wavenumbers characteristic of the diffusive substances (Adlinge, Gupta 2013). Similarly, major factors influencing diffusion process, such as temperature, viscosity, molecular size, shape and polarity, has been investigated by using FTIR-ATR methods (Karlsson, Isacsson et al. 2007a). Ageing effects in bitumen was also studied by using FITR-ATR method by monitoring the increase in carbonyl content in bitumen films (Karlsson, Isacsson et al. 2007a).

In measurement of FTIR-ATR, penetration depth of absorption is an important factor to consider when examining the diffusion of substances. Penetration depth of evanescent wave is a function of the wavenumber or wavelength, angle of incident of beam and the refractive index of both the ATR prism and the sample (Nishikida, Nishio et al. 1995).

$$d_p = \frac{\lambda_1}{2\pi\,(sin^2\theta - \eta_{21}^2)^{\frac{1}{2}}} \tag{1}$$

Where,

d_p = depth of penetration
θ = phase angle
λ = wavelength
η = ratio of refractive index of lighter to denser medium

In equation 1, the angle of incidence is constant, as set by the manufacturer of the FT-IR-ATR equipment. η_{21} is a relationship between the refractive index of the rarer and denser medium. The refractive index of the prism is a function of the material, and as the prism in our equipment is diamond, this value can also be considered a constant. Unfortunately, as the material changes composition during the rejuvenation, the refractive index of the rare medium is unknown at each point in time during the diffusion and exact depth of penetration cannot be easily determined. However, when a point in time is considered a refractive index of the rare medium is constant and therefore the depth of penetration is dependant on the wavelength of the incident light.

As a result, then we simplify the equation we can see that $d_p = f(\lambda)$ and therefore for large wavelength the penetration of the wave into the material should be deeper. If the diffusion is therefore not instantaneous, the level of diffusion as determined at different wavelength should be different and obtained values should not be averaged, but rather considered as indicative of various thickness of lamelle investigated with the technique.

In evaluating the results, this fact was taken under consideration to analyze the variations in spectrum obtained.

To evaluate the level of blending in bitumen, a method was developed where concentration profile was created by using linear correlation with reference concentrations. This procedure was based on Beer-Lambert law which provides a relationship between absorbance, molar absorptivity, path length and molar concentration at a certain frequency or wavelength (Jon H. Hardesty, Bassam Attili 2010).

$$A = \varepsilon l c \tag{2}$$

Where,

A = Absorbance
ε= molar absorptivity
l = path length (cm)
c = concentration of solution (mol dm-1)

From equation 2 it is clear that absorbency linearly correlates with the concentration, keeping molar absorptivity and path length constant. This relation was utilized in the technique and calibration curves were created of known concentrations. Assuming linear absorbency change within tested range, interpolation can be done within the calibration curves in order to determine the concentration of an unknown solution.

The absorbency at different wavelengths is of different magnitude and changes according to a different variant of equation 2. The molar absorptivity of each functional group is different. Therefore for each tested peak a separate calibration curve needs to be established.

4 Material used

4.1 Aged bitumen in use

The master's thesis is a part of an ongoing research project REMIX commissioned by Finnish Transport Agency. Bitumen samples used in this research were collected during the rehabilitation of Highway NO.1 by hot in-place recycling (HIP-RC) process for REMIX project. Detailed information about the samples collection and rehabilitation conditions of the site can be found in (Jon H. Hardesty, Bassam Attili 2010). Bitumen aged sample denoted as 1R was collected from the road segment, referred as Area 1, and extracted from the road aggregates according to standard SFS-EN 12697-1. Bitumen was then recovered from the solvent (dichloromethylene) by using rotary evaporator, following SFS-EN 12697-3 standard procedure. The other bitumen sample 70/100, denoted as B2, was tested to obtain comparable results. These bitumen were categorized on the basis of empirical properties like calculated softening point and penetration grade. The values of penetration grade were found by using SFS-EN 1426 needle penetration standard. However, it is important to mention that for the softer grade bitumen, this test was performed at lower temperature, 15°C.

Dynamic shear rheometer (DSR) measurements of G* were utilized in determining the softening point explained in (Blomberg, Makowska et al. 2016). DSR has widely been used in characterization of bitumen rheology. It is capable of quantifying elastic and viscous properties of bitumen. The DSR measures a specimen's complex modulus (G*) and phase angle (δ). The complex shear modulus (G*) is a function of stress over strain. The larger the phase angle (δ), the more viscous the material (Pavement interactive 2011). Softening temperatures for the respected bitumen were recorded when G* = 150 Pa at 0,0159 Hz, detailed calculations can be found in (Blomberg, Makowska et al. 2016). Table 1 represents the characterization parameters of bitumen.

Table 1 Specifications of bitumen used (1R and B2)

Bitumen Samples	Penetration grade (dmm)	Calculated softening point °C
Area 1 (1R)	22,0	65,0
B2	76,0	48,8

4.2 Rejuvenators used

In this experimental work, four different rejuvenators, namely R1, R2, R3 and R4 were used. Two of the rejuvenators, R1 and R4, were softer grade bitumen while R2 was bio based and R3 was oil derivative rejuvenators. The specifications of these rejuvenators are given in table 2, where binders are characterized by penetration grade and calculated softening point and oily derived rejuvenators by viscosities.

Table 2 Specifications of rejuvenators used

Rejuvenators	Penetration grade (dmm)	Calculated softening point °C	viscosity (Pa) at 60°C
R1	279	26,5	6,196448
R2	-	-	0,0216
R3	-	-	0,0333
R4	-	-	1,2092

5 Methodology

In this section a method used to measure the rejuvenation process in bitumen layer at different temperatures is described. Four types of rejuvenators have been used during this work that includes softer grade bitumen and oil derivatives. Bitumen containing different ageing level and softening points were examined through series of experiments at particular temperatures. The experimental work was designed on the same method describes in (Karlsson, Isacsson 2003c) and carried out in an open atmosphere therefore certain unwanted signals have been recorded in the spectra. Since bitumen shows visco-elastic behavior that is highly influenced by temperature therefore, three different temperatures near and above the softening point of bitumen were set during analysis of diffusion process. Each experiment was monitored for 2 hours of total time scale and scans were recorded at time interval of 4 minutes per spectra. A sequence of experimental arrangement is mentioned in table 3

Table 3 Experimental sequence of materials used

S.No:	Bitumen samples	Rejuvenators				Temperatures applied (°C)	Monitoring time at each temp (hours)
1	Bitumen from area 1 (1R)	R1 (650/900)	R2 (Bio based Product 1)	R3 (Oil based Product 2)	R4 (V1500)	40, 60, 90	2
2	Bitumen 70/100 (B2)	R1 (650/900)	R2 (Bio based Product 1)	R3 (Oil based Product 2)	R4 (V1500)	40, 60, 90	2

5.1 Sample preparation

To determine the influence and level of rejuvenation, samples were prepared by gluing two brass frames, denoted as (a) and (b), of different slot widths in a way that frame (a) was fixed above the top of the frame (b). Layers of bitumen and rejuvenator (in case of softer grade bitumen) were created by scraping the materials into the slots of frame (a) and frame (b), respectively. The method however limits that bottom layer must not be deformed during the application of upper layer. This frame was placed in absolute contact over the top of the ATR prism and the two slots are adjusted over each other in a manner that no air is trapped in between the layers. An experimental image and schematic representation of steps involved in sample preparation were presented in figure 6 and 7, respectively. In case of oil based liquid rejuvenators, layers cannot be produced. Therefore, micro pipettes were used to drop small amount of rejuvenator on top of the bitumen layer so that it covered the complete layer.

The instrument used in this method was ThermoFisher spectrophotometer fitted with ATR, heatable to 200°C. The scans were recorded at a time interval of every 4 min with resolution of 4000 cm^{-1} to 400 cm^{-1} up to 2 hours. Scans were recorded at given temperatures of 40°C, 60°C and 90°C for each bitumen with four different rejuvenators.

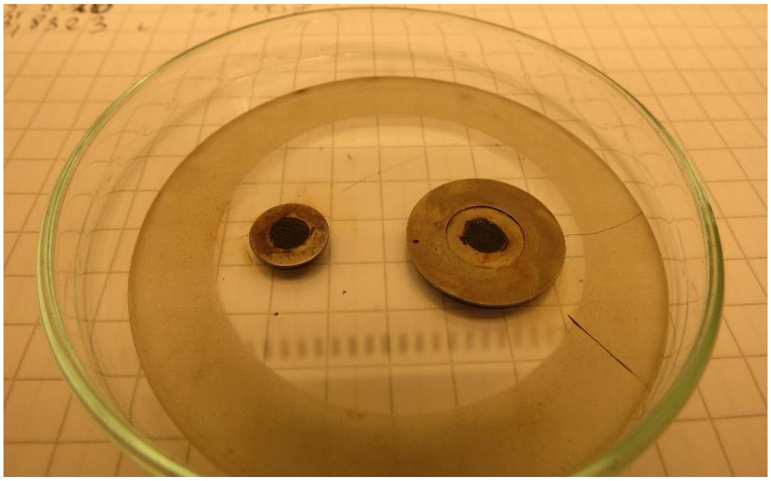


Figure 6 Samples layers of bitumen (right frame) and rejuvenator (left frame)

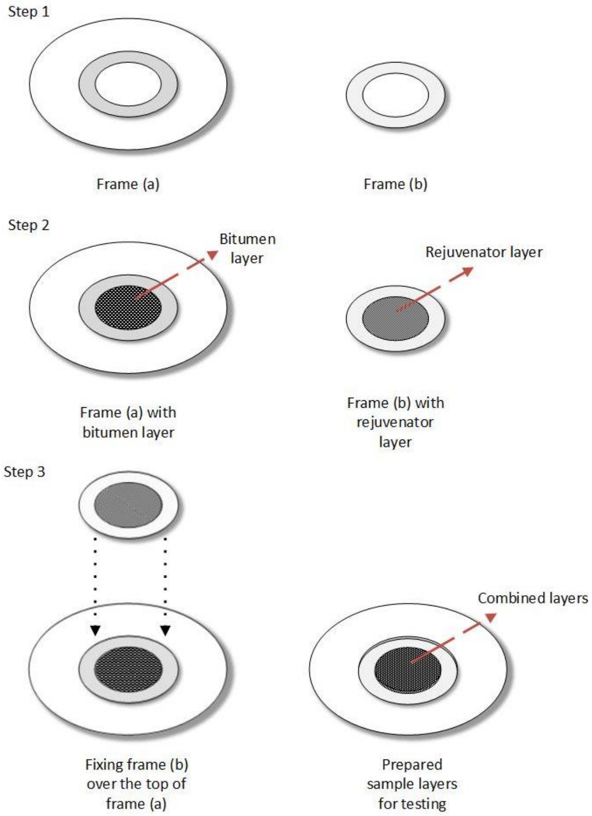


Figure 7 Schematic representation of sample preparation

5.2 Data collection

Diffusion of rejuvenator through bitumen film is previously studied using FTIR-ATR spectroscopy (Karlsson, Isacsson 2003c) considering different parameters such as temperature, binder film thickness, type of bitumen, and, to some extent, chemical properties of binder. Karlsson et al. determined rates of diffusion by analyzing the diffusion of selected well-defined substances through the binder film (Karlsson, Isacsson 2003a). The technique used in this thesis to determine the level of rejuvenation is similar to the method applied in (Karlsson, Isacsson 2003a) work. In addition, the variations in the corresponding spectra of aged bitumen upon rejuvenation were recorded at different temperatures.

Because of the fact that rejuvenator R2 expresses the peaks within the regimes characteristic for aged bitumen, the change in the signal intensity during diffusion was not linear. As a result the Lambert-Beer law could not be applied in that region. Therefore, three different spectral ranges were considered to monitor the diffusion of rejuvenator R2 and assigned as marker Peak A, Peak B and Peak C. The level of rejuvenation of Peak B is the closest to comparable to Sulfoxide regime. Approximated wavenumbers in FTIR spectra where selected functional groups were generally detected is presented in below table 4.

Table 4 Selected wavenumbers for functional group regimes

Rejuvenators used	Aprox. Carbonyl regime	Approx. Aromatics regime	Approx. Sulfoxide regime
	cm^{-1}	cm^{-1}	cm^{-1}
R1, R3, R4	1696	1598	1027
	Other selected peaks		
	Peak A	Peak B	Peak C
R2	1598	867	806

The change in concentrations of these functional groups regime was expected when the rejuvenator diffuses into the bitumen. Since absorption is the function of concentration therefore, any major variation in the absorption band of carbonyl, sulfoxide and aromatics range was observed as a result of rejuvenation, defined as diffusion of less viscous liquid into the denser liquid. An example of spectrum recorded during rejuvenation of 1R with R1 is presented in figure 8

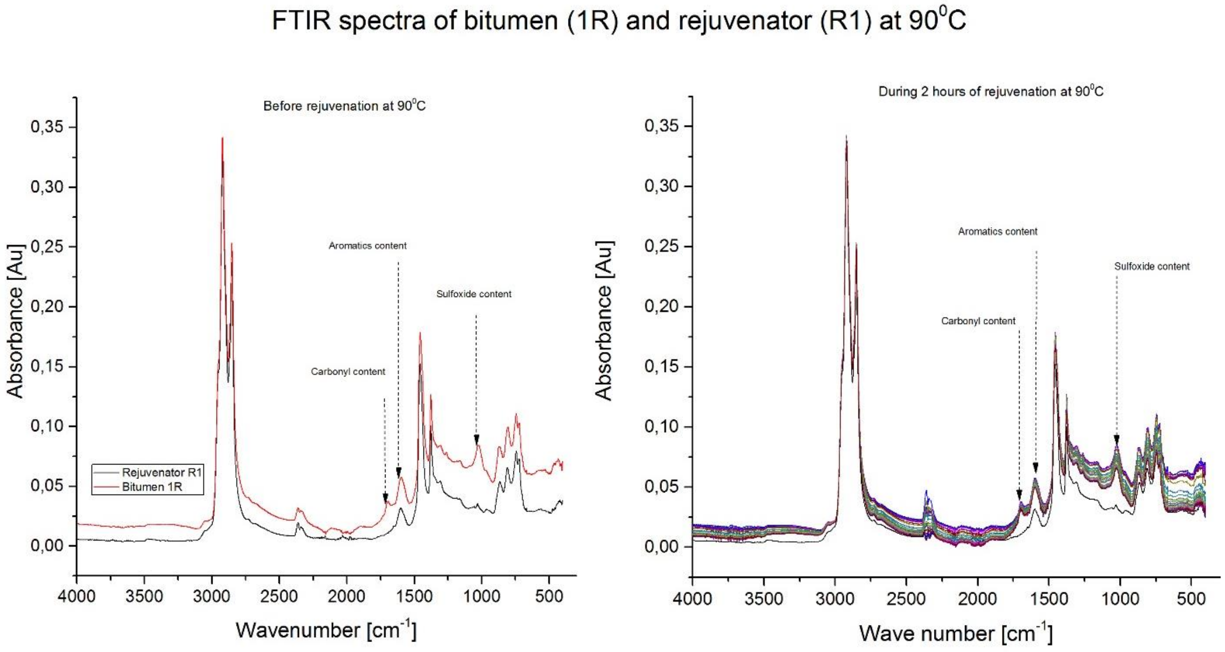


Figure 8 Spectrum obtained before and after rejuvenation

Figure 9 shows change in spectrum of bitumen (1R) when rejuvenator (R1) is applied at 90°C before and during rejuvenation and figure 10 shows similar comparison but for bitumen (1R) and rejuvenator (R2). It illustrates an example spectrum of marker peaks obtained during the rejuvenation of bitumen (1R) with rejuvenator (R2) performed at 90°C for 2 hours.

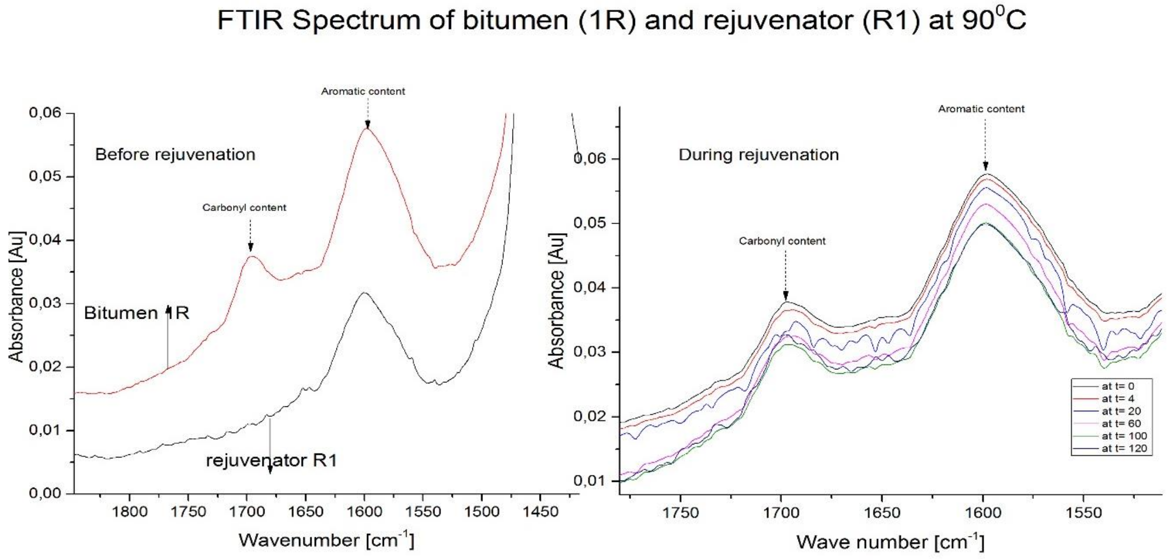


Figure 9 Spectral variations during rejuvenation (following Beer-Lambert law)

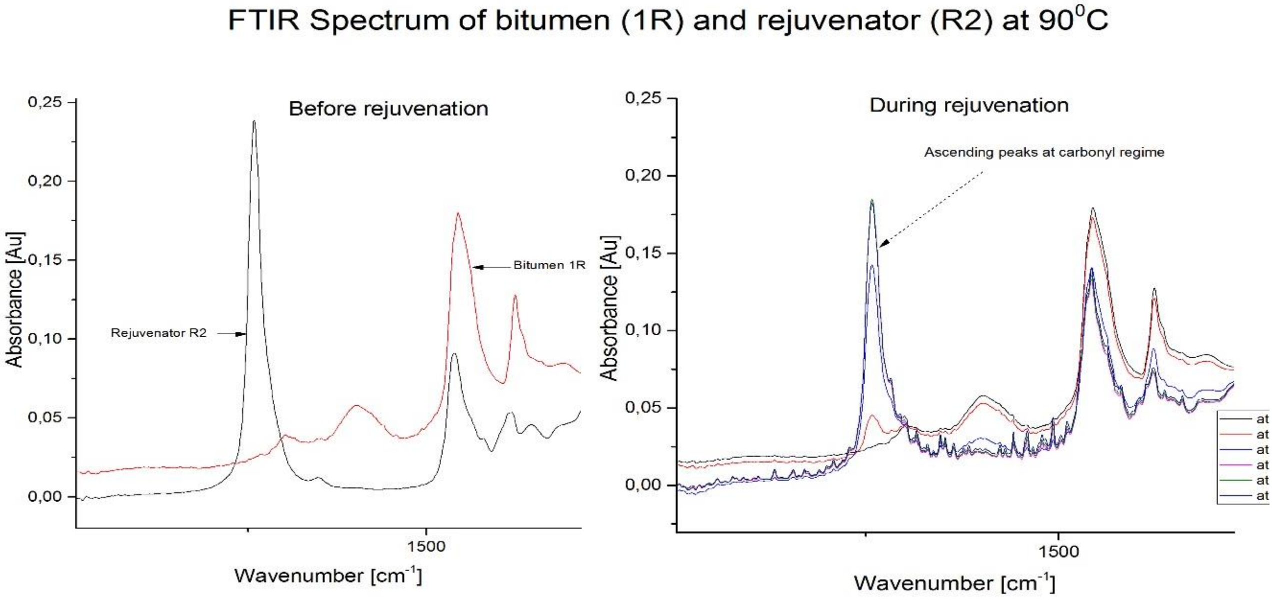


Figure 10 Spectral variations during rejuvenation (Beer-Lambert law not followed)

In order to make reference spectrum of given concentrations, aged bitumen was taken as 100% concentration of functional groups under consideration while rejuvenator with no ageing was assume to have 0% concentration of respected functional groups. A blend of aged bitumen and rejuvenator was made with the ratio of 50:50 and referred to have 50% concentration of the same functional groups. The blend was made by measuring equal amounts by weight of both bitumen and rejuvenator then mixed at low heat to produce homogeneous blend. Figure 11 represents reference spectrum of 50:50 blend of bitumen (1R) and rejuvenator (R1) along with reference spectrum of bitumen and rejuvenator at concentration of 100 and 0%, respectively.

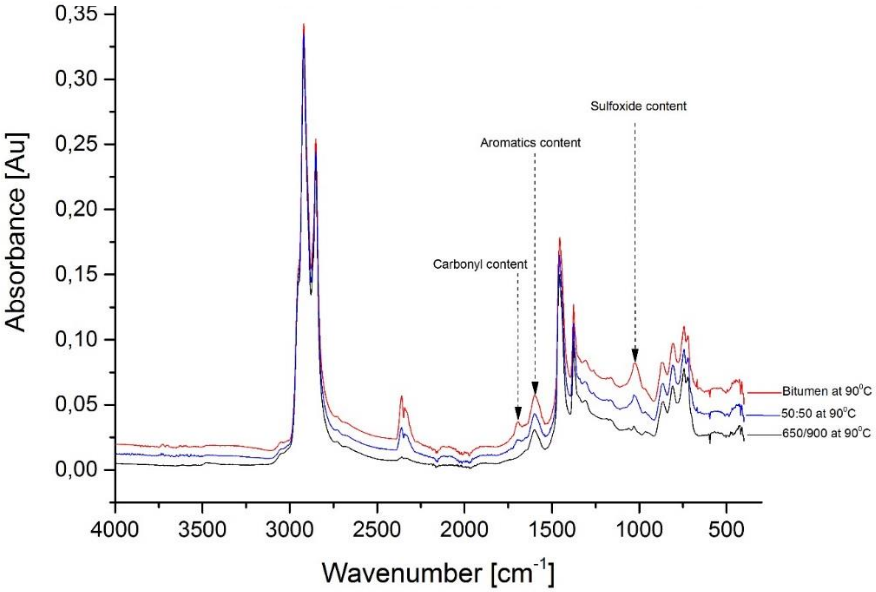


Figure 11 FTIR spectra of bitumen and rejuvenator at 90°C

These reference curves of known concentrations were plotted against the corresponding absorbance values measured by FTIR. Data sets obtained from experimental spectrum were plotted over the reference curves to compute the corresponding concentration values.

6 Data processing

ThermoScientific Nicolet iS50 spectrometer was used to generate FTIR measurements, synchronized with OMNIC data collection, processing and analysing software. Nicolet iS50 Spectrometer was equipped with GladiATR sample heating accessory that can operate with maximum temperature to 210°C or 300°C. It utilizes a monolithic diamond crystal attached with 45° angle of incidence to obtain attenuated total reflectance. GladiATR is accessed by TempPRO software capable of setting and monitoring isothermal or multi-ramped temperature profile.

The spectrum obtained during rejuvenation were converted into absorbance scale and saved in a format of OriginPro software. OriginPro allows to identify the exact absorbance values from the plotted curves therefore, it was used to pick the absorbance point from the maximum of selected peak of each curve. All the absorbance values of every experiment were noted in a similar manner and a set of absorbance values was obtained at every required time interval. Vertical drifts and shifting of peaks with the base line was observed during the measurements. These factors may interfere in recording the maximum height of peak at the same wavenumber each time, therefore these variations were also taken into account during the test. In some cases, there were rippled signals observed in the spectrum during the measurements, shown in figure 12.

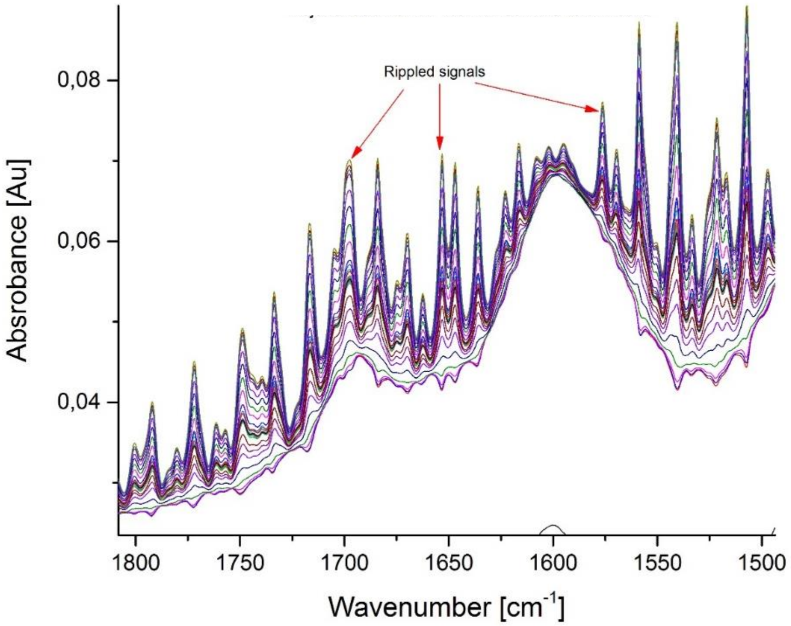


Figure 12 Rippled signals in spectrum

Smoothing of these rippled curves was performed, as is demonstrated in figure 13, using OriginPro functional tool and the maximum absorbance values of smooth curves were compared. The compatibility of curves obtained before and after the application of smoothing function was matched and the difference in values was negligible. Therefore, absorbance values were noted from the smooth curves, in case where smoothing function was applied over spectra.

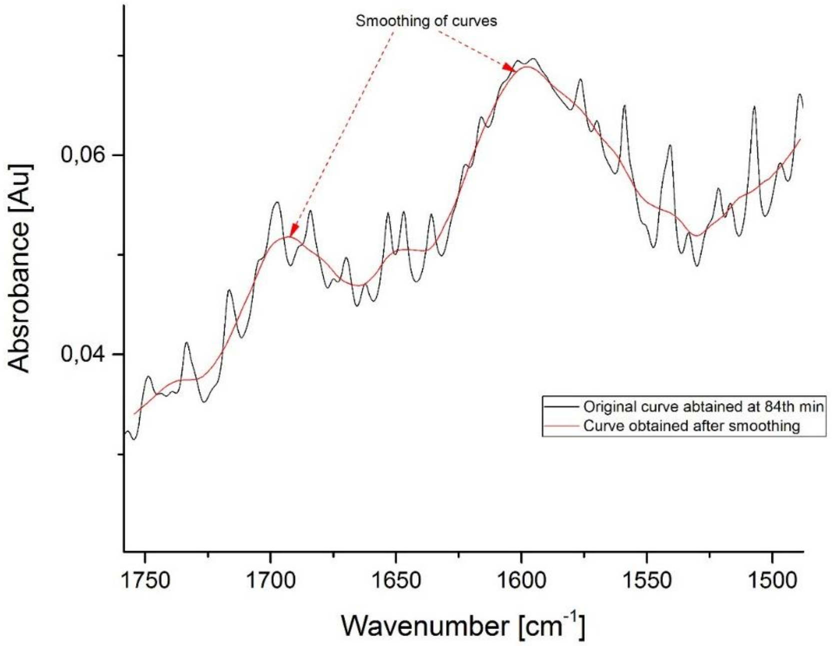


Figure 13 Smoothing of rippled signals

It was mentioned earlier that only three functional groups were chosen for consideration. Because polarity and aromaticity influence the rheology of the binder, we followed the changes in the signals in the region characteristic for this type of compounds in order to determine the level of blending. As mentioned before, on the basis of equation 1, they are also potentially representative of a concentration change/blending level in a slightly different thickness of the lamelle.

Similarly, the absorbance values of corresponding reference spectrum were also recorded and plotted against the respected 0, 50 and 100% concentration values. An example of such calibration curve can be seen in figure 14, where standard concentration in percent were plotted against the corresponding absorbance values.

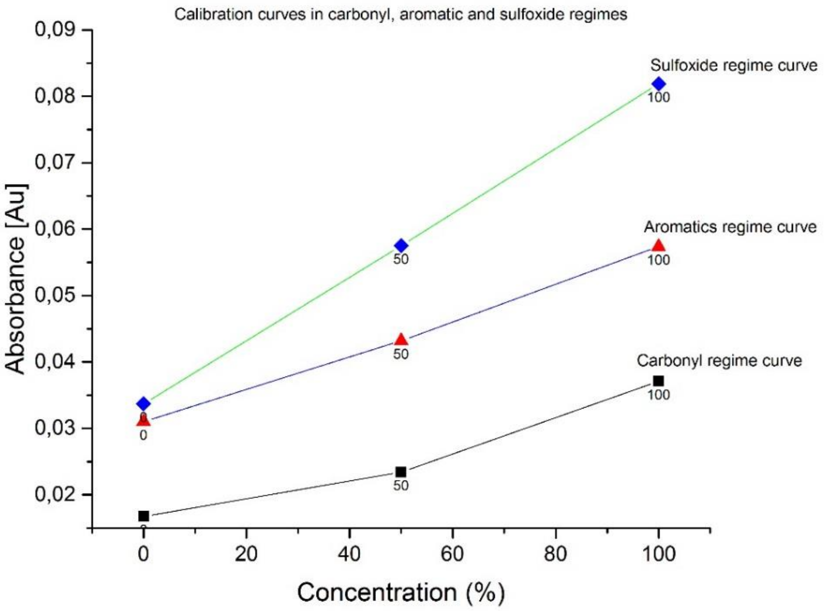


Figure 14 Calibration curves at standard concentrations

Linear correlation was developed in between the three concentration values and line equation was computed to calculate the unknown concentrations at every interval of time. There were three reference points altogether at every concentration value therefore, a linear relationship was made in between the two points in each case. This provides two linear equations for reference graph of each functional groups regime. A choice of equation depends upon the best fit of experimental data with the equation. A simple linear equation fitted with the data is mentioned below:

$$y = a + b^{*}x \tag{3}$$

$$=> x = [\frac{y - a}{b^{*}}] \tag{4}$$

Where;

x = concentration (%)
y = Absorbance (Au)
b = Slope
a = Intercept

The above derived equation 4 was used to calculate the concentration (x) by putting the values of other remaining parameters in an equation. Absorbance points from experimental data set were then placed in a best fitted equation and the concentration percent was computed for each absorbance value. These calculated concentration values with corresponding absorbance were then plotted over the reference curves to analyze the coherence of experimental data with reference curves. An example of such experimental data consistency with calibration curves can be seen in figure 15.

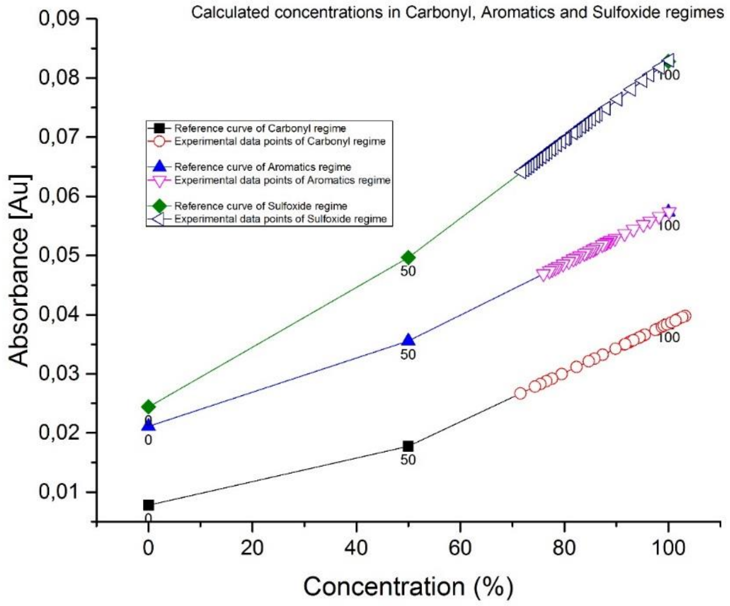


Figure 15 Experimental data points with corresponding calibration curves

7 Result and analysis

To evaluate the level of rejuvenation in aged bitumen, series of experiments were performed according to the method described in methodology section. All four rejuvenators were used in the rejuvenation of both bitumen at required temperatures of 40°C, 60°C, and 90°C and experimental data was established. Analysis of experimental data shows a number of areas of interest that mainly includes interpolation of experimental data points in calibration curves and calculations of percent concentration from these fitted data points. This section only deals with the analytical and statistical data whereas, the calculated concentration tables of each experiment can be found in Appendix A and graphical representation in Appendix B

7.1 Concentration calculations

To evaluate the level of rejuvenation, concentration values were calculated for each experiment by the method described in methodology section. Concentration values were essentially presented as the remaining percent amount of selected functional group after the dilution in fresh binder due to rejuvenation. The percent amount of these designated functional group regimes was calculated by using calibration curves and linearly correlated with them. A tabular and graphical representation of these calculated percent concentrations of every experiment is attached in the Appendix. Few examples of these representation were given below from table 5-9 and figure 16-20.

As shown in table 5, concentration values were higher than the maximum concentration of 100% as the absorbance 1R bitumen increases with time. This manner of change in absorbance might arises as a result of short-term ageing and in addition no rejuvenation was detected

Table 5 Calculated concentration levels in bitumen 1R rejuvenated by R1 at 40°C

Bitumen 1R rejuvenated by R1 at 40°C

Time	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime	Calculated Concentration
Min	[Au]	%	[Au]	%	[Au]	%
0	0,05655	100,93645	0,0795	101,22521	0,11096	100,81595
4	0,05665	100,78468	0,07959	102,21661	0,11113	101,07171
8	0,05694	101,69492	0,07974	102,63749	0,11108	101,18899
12	0,05725	102,66792	0,0798	102,80584	0,11113	101,45494
16	0,05731	102,85625	0,07984	102,91807	0,11116	101,37672
20	0,05768	104,01758	0,08001	103,39506	0,11119	101,45494
24	0,05797	104,92781	0,08023	104,01235	0,11134	101,50188
28	0,05792	104,77087	0,08022	103,98429	0,11138	101,54881
32	0,0581	105,33584	0,08029	104,1807	0,11139	101,78348
36	0,05773	104,17451	0,08016	103,81594	0,11118	101,84606
40	0,05777	104,30006	0,08021	103,95623	0,11118	101,8617
44	0,05776	104,26868	0,08022	103,98429	0,11123	101,53317
48	0,05775	104,23729	0,08032	104,26487	0,11122	101,53317
52	0,05781	104,42561	0,08036	104,3771	0,11128	101,61139
56	0,05775	104,23729	0,08032	104,26487	0,11125	101,59574
60	0,05784	104,51977	0,08035	104,34905	0,11117	101,68961
64	0,05784	104,51977	0,08029	104,1807	0,11112	101,64268
68	0,05792	104,77087	0,08036	104,3771	0,11114	101,51752
72	0,05806	105,2103	0,08033	104,29293	0,11108	101,4393
76	0,05808	105,27307	0,08035	104,34905	0,11101	101,47059
80	0,05825	105,80665	0,08035	104,34905	0,11109	101,37672
84	0,05822	105,71249	0,08039	104,46128	0,1111	101,26721
88	0,05836	106,15191	0,08034	104,32099	0,11104	101,39237
92	0,05868	107,15631	0,08046	104,65769	0,11112	101,40801
96	0,05898	108,09793	0,0805	104,76992	0,11123	101,31414
100	0,05909	108,44319	0,08049	104,74186	0,11118	101,4393
104	0,05938	109,35342	0,08065	105,1908	0,11137	101,61139
108	0,05915	108,63151	0,0806	105,05051	0,11132	101,53317
112	0,05904	108,28625	0,08046	104,65769	0,11137	101,83041
116	0,05655	100,46738	0,0795	101,97043	0,11132	101,75219
120	0,05665	100,78468	0,07959	102,21661	0,1112	101,56446

It can also be observed from figure 16, all the experimental data points were beyond the range of exclusive functional group in calibrated curves

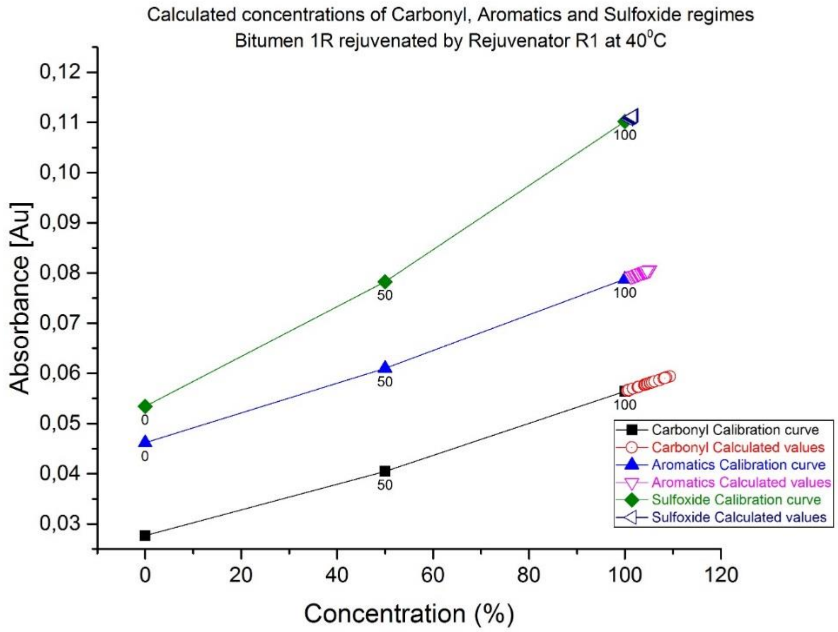


Figure 16 Concentration profile of bitumen 1R rejuvenation by R1 at 40^{0}C

From the data obtained for rejuvenation of 1R at 60°C by R1, calculated concentration values follows the coherency within the range of calibrated curves. Table 6 presents the change in concentration of selective functional group regimes during 2 hours of rejuvenation process. Although, there were some fluctuations in the concentration values however, a fair occurrence of rejuvenation is observable.

Table 6 Calculated concentration levels in bitumen 1R rejuvenated by R1 at 60°C

Bitumen 1R rejuvenated by R1 at 60°C

Time	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime	Calculated Concentration
Min	[Au]	%	[Au]	%	[Au]	%
0	0,04763	99,75047	0,06888	99,71787	0,10023	99,7273
4	0,04758	99,59451	0,06879	99,43574	0,10008	99,48669
8	0,04755	99,50094	0,06874	99,279	0,10012	99,55085
12	0,04731	98,75234	0,0686	98,84013	0,1001	99,51877
16	0,04767	99,87523	0,06881	99,49843	0,10014	99,58293
20	0,04768	99,90643	0,06877	99,37304	0,10025	99,75938
24	0,04781	100,31192	0,06878	99,40439	0,10017	99,63106
28	0,04778	100,21834	0,06876	99,34169	0,10013	99,56689
32	0,04739	99,00187	0,06867	99,05956	0,10016	99,61501
36	0,04714	98,22208	0,06858	98,77743	0,10007	99,47064
40	0,04718	98,34685	0,06854	98,65204	0,10002	99,39044
44	0,04732	98,78353	0,06857	98,74608	0,1002	99,67918
48	0,04738	98,97068	0,06844	98,33856	0,10021	99,69522
52	0,04766	99,84404	0,0685	98,52665	0,10011	99,53481
56	0,04784	100,40549	0,06858	98,77743	0,10019	99,66314
60	0,048	100,90455	0,06859	98,80878	0,10021	99,69522
64	0,04797	100,81098	0,06858	98,77743	0,10016	99,61501
68	0,04773	100,06238	0,06841	98,24451	0,09995	99,27815
72	0,04771	100	0,06844	98,33856	0,09988	99,16586
76	0,04744	99,15783	0,06836	98,08777	0,09999	99,34232
80	0,04699	97,75421	0,06821	97,61755	0,09983	99,08566
84	0,04715	98,25328	0,06836	98,08777	0,09991	99,21399
88	0,04676	97,03681	0,06823	97,68025	0,09975	98,95733
92	0,04684	97,28634	0,06827	97,80564	0,0999	99,19795
96	0,0469	97,47349	0,06817	97,49216	0,09966	98,81296
100	0,04712	98,1597	0,0682	97,58621	0,0998	99,03754
104	0,04709	98,06613	0,06823	97,68025	0,09968	98,84504
108	0,04697	97,69183	0,0682	97,58621	0,09962	98,7488
112	0,04685	97,31753	0,06809	97,24138	0,09968	98,84504
116	0,0468	97,16157	0,06815	97,42947	0,09968	98,84504
120	0,04687	97,37991	0,06813	97,36677	0,0997	98,87713

In addition, it is obvious to conclude that at most higher temperature is favorable to provide better rejuvenating results. However, the data shows that sufficient requirement of time for interaction between the materials is necessary as well. A graphical representation of data can be found in figure 17.

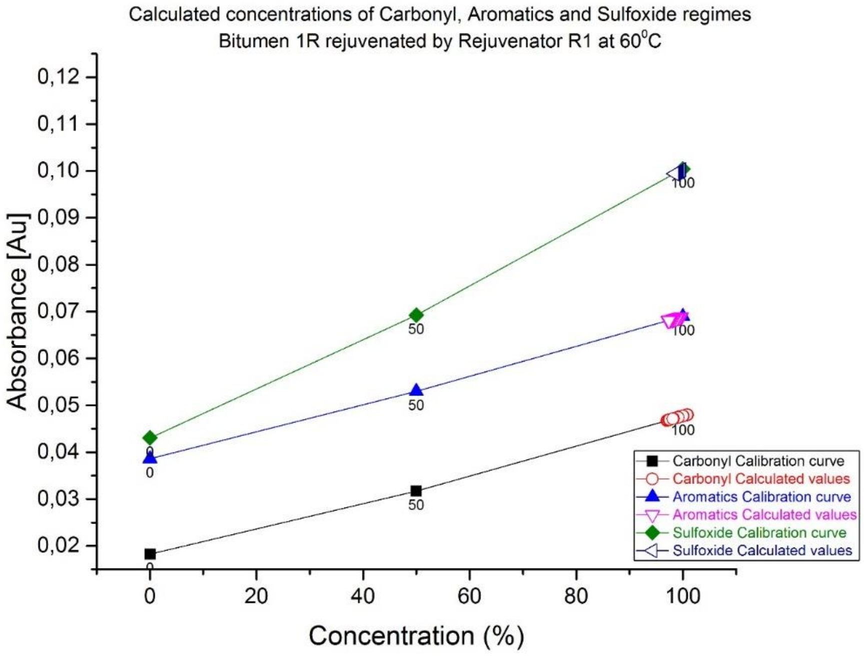


Figure 17 Concentration profile of bitumen 1R rejuvenation by R1 at 60^{0}C

At higher temperature, i.e. 90^0C, the level of rejuvenation is much higher. The change in concentration of selected regimes is presented in table 7 where concentration of carbonyl regime decrease almost from 100% to 83%. This decrease in concentration level follows in aromatic and sulfoxide regime from 100% to 73% and from 100% to 65%, respectively.

Table 7 Calculated concentration levels in bitumen 1R rejuvenated by R1 at 90°C

Bitumen 1R rejuvenated by R1 at 90°C

Time	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime	Calculated Concentration
Min	[Au]	%	[Au]	%	[Au]	%
0	0,0374	100,09489	0,05675	97,71127	0,0841	100,5082
4	0,0365	97,81022	0,0568	97,88732	0,0829	102,04918
8	0,0354	93,79562	0,0561	95,42254	0,0814	98,97541
12	0,0348	91,60584	0,0557	94,01408	0,0808	97,7459
16	0,0339	88,32117	0,0555	93,30986	0,0808	97,7459
20	0,0336	87,22628	0,055	91,5493	0,0806	97,33607
24	0,0339	88,32117	0,0556	93,66197	0,0808	97,7459
28	0,0351	92,70073	0,0557	94,01408	0,0805	97,13115
32	0,0346	90,87591	0,0549	91,19718	0,0778	91,59836
36	0,0341	89,05109	0,0546	90,14085	0,0767	89,34426
40	0,0334	86,49635	0,0541	88,38028	0,0753	86,47541
44	0,0332	85,76642	0,054	88,02817	0,0743	84,42623
48	0,033	85,0365	0,0538	87,32394	0,0731	81,96721
52	0,0326	83,57664	0,0534	85,91549	0,0718	79,30328
56	0,0326	83,57664	0,0532	85,21127	0,0714	78,48361
60	0,0323	82,48175	0,0529	84,15493	0,0708	77,2541
64	0,0314	79,19708	0,0516	79,57746	0,0686	72,7459
68	0,0311	78,10219	0,0512	78,16901	0,0679	71,31148
72	0,0306	76,27737	0,0506	76,05634	0,0669	69,2623
76	0,0302	74,81752	0,0505	75,70423	0,0666	68,64754
80	0,03	74,08759	0,0502	74,64789	0,0662	67,82787
84	0,03	74,08759	0,0501	74,29577	0,066	67,41803
88	0,0302	74,81752	0,0501	74,29577	0,066	67,41803
92	0,0305	75,91241	0,05	73,94366	0,0658	67,0082
96	0,031	77,73723	0,0502	74,64789	0,0658	67,0082
100	0,0311	78,10219	0,05	73,94366	0,0656	66,59836
104	0,0318	80,65693	0,0499	73,59155	0,0655	66,39344
108	0,032	81,38686	0,0498	73,23944	0,0653	65,98361
112	0,032	81,38686	0,0497	72,88732	0,065	65,36885
116	0,0325	83,21168	0,0498	73,23944	0,0651	65,57377

It is notable in data tables initially, concentration percent of carbonyl, aromatic, and sulfoxide regime was higher than 100%. Most likely it is because that some short term ageing effect the bitumen layer in the start of the experiment and absorbance increases slightly higher than the absorbance noted for 100% concentration curve.

Table 7 showed that diffusion of rejuvenator follows the calibration curve and shows blending towards 50% concentration at 90°C. The fact of higher temperature and sufficient time to achieve proper blending seems to be valid from the data. This indicate that during mixing of bitumen and rejuvenator, temperature and sufficient time of blending are necessary and requires special attention. Graphical representation of concentration values are presented below in figure 18.

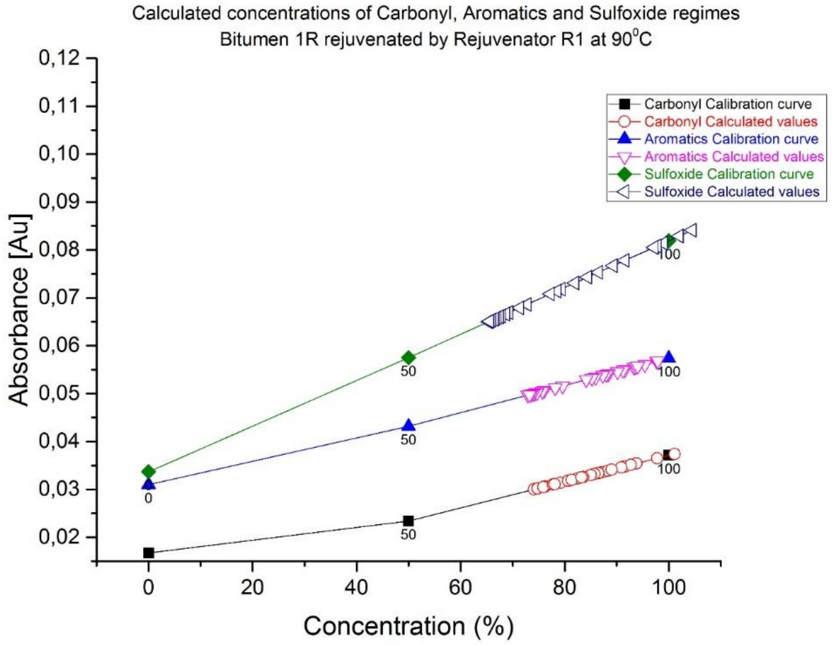


Figure 18 Concentration profile of bitumen 1R rejuvenation by R1 at 90°C

In case of oil derivative rejuvenator R2, other marker peaks at specific frequencies were recorded to monitor the change in spectrum upon rejuvenation. The reason for selecting peaks other than carbonyl, aromatics and sulfoxide regimes was describes earlier in data processing section.

It was observed that no rejuvenation was found at 40°C and 60°C. Table 8 shows the level of concentration calculated for 1R bitumen at 60°C when rejuvenator R2 was applied. At the end of experiment there was no significant decrease in the level of concentration.

Table 8 Calculated concentration levels in bitumen 1R rejuvenated by R2 at 60°C

Bitumen 1R rejuvenated by R2 at 60°C

Time	Absorbance Peak A	Calculated Concentration	Absorbance Peak B	Calculated Concentration	Absorbance Peak C	Calculated Concentration
Min	[Au]	%	[Au]	%	[Au]	%
0	0,06916	101,32202	0,09514	101,22426	0,11192	101,17219
4	0,06798	100,03824	0,09394	99,93089	0,11068	100,21394
8	0,06815	100,22979	0,09435	100,37015	0,11103	100,48368
12	0,06819	100,27293	0,09426	100,28211	0,11119	100,60926
16	0,06829	100,37759	0,09428	100,3019	0,11117	100,58971
20	0,06836	100,44906	0,09456	100,60273	0,11108	100,52689
24	0,06841	100,50372	0,09466	100,71245	0,11127	100,67163
28	0,06838	100,47247	0,09445	100,47809	0,11122	100,62787
32	0,06834	100,43363	0,09456	100,60411	0,11124	100,6495
36	0,06836	100,45154	0,0945	100,53266	0,11134	100,72132
40	0,06832	100,41014	0,0944	100,42876	0,11119	100,60949
44	0,06823	100,31633	0,09446	100,4928	0,11113	100,56153
48	0,06824	100,32837	0,09457	100,60918	0,11136	100,73739
52	0,06823	100,31356	0,09462	100,66128	0,1112	100,61657
56	0,06819	100,27381	0,09455	100,58956	0,11122	100,62809
60	0,06823	100,31041	0,09472	100,77516	0,11117	100,59132
64	0,0683	100,38343	0,09457	100,60713	0,11132	100,70799
68	0,06826	100,34652	0,09467	100,72095	0,1114	100,76971
72	0,06837	100,46018	0,09481	100,87014	0,11147	100,82262
76	0,06836	100,45368	0,09493	101,00562	0,11157	100,89972
80	0,06857	100,67897	0,09507	101,15094	0,11155	100,88364
84	0,06862	100,72904	0,095	101,08057	0,11171	101,00601
88	0,06862	100,72958	0,09508	101,16176	0,11185	101,11771
92	0,06862	100,72909	0,09488	100,94449	0,11164	100,9541
96	0,06872	100,84233	0,09508	101,16791	0,11177	101,05216
100	0,06881	100,93855	0,09491	100,97606	0,11148	100,82779
104	0,06878	100,90929	0,09499	101,06899	0,11169	100,99348
108	0,06878	100,90631	0,09515	101,2382	0,11147	100,82038
112	0,06877	100,89703	0,09525	101,34883	0,11166	100,97104
116	0,0692	101,35782	0,09529	101,39326	0,11176	101,04425
120	0,06874	100,86768	0,09497	101,03991	0,11159	100,91893

Calculated value was over 100% showing that there was no diffusion of R2 in the bitumen layer. A graphical representation can be found in figure 19

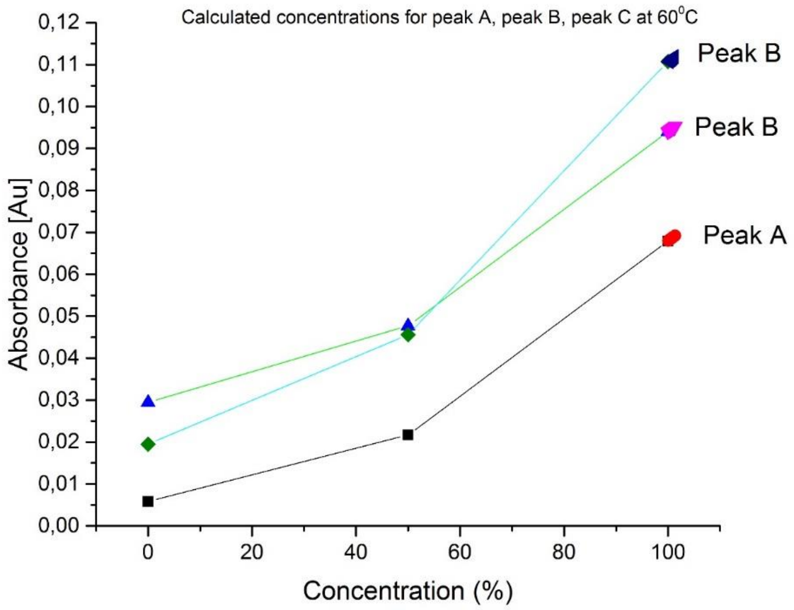


Figure 19 Concentration profile of bitumen 1R rejuvenation by R2 at 60°C

Only reduction of concentration level for R2 was noticed at temperature 90°C. The results can be found in table 9. Even that the rejuvenator has the lowest viscosity, still the rejuvenation was observed at higher temperature. Figure 20 shows the plotted data points with the calibration curves for concentration at 90°C.

Table 9 Calculated concentration levels in bitumen 1R rejuvenated by R2 at 90°C

Bitumen 1R rejuvenated by R2 at 90°C

Time	Absorbance Peak A	Calculated Concentration	Absorbance Peak B	Calculated Concentration	Absorbance Peak C	Calculated Concentration
Min	[Au]	%	[Au]	%	[Au]	%
0	0,05787	99,9083	0,08293	99,48708	0,10049	100,23532
4	0,0529	93,52658	0,07895	94,60621	0,09352	94,37818
8	0,04647	85,27169	0,07322	87,56499	0,08434	86,66598
12	0,04015	77,14709	0,06723	80,20511	0,07484	78,67734
16	0,03445	69,81981	0,06154	73,22374	0,06596	71,21875
20	0,03005	64,16536	0,05683	67,44183	0,05884	65,23311
24	0,02603	59,00187	0,05212	61,65822	0,0518	59,32
28	0,02356	55,83319	0,04902	57,84439	0,04742	55,64231
32	0,02122	52,82281	0,04583	53,9299	0,04338	52,24626
36	0,01974	50,91654	0,04592	54,04652	0,04124	50,4453
40	0,01903	50,01417	0,04405	51,74714	0,04029	49,64751
44	0,01867	49,54744	0,04349	51,06384	0,03977	49,2073
48	0,0187	49,58482	0,0431	50,57521	0,03972	49,17173
52	0,01873	49,62412	0,04336	50,89239	0,04007	49,4642
56	0,019	49,96996	0,04351	51,07689	0,04074	50,02556
60	0,01916	50,17375	0,0441	51,81082	0,04128	50,47757
64	0,01941	50,4914	0,04435	52,11729	0,04185	50,95788
68	0,0196	50,74722	0,04483	52,69782	0,04216	51,21739
72	0,01996	51,20359	0,04491	52,80596	0,04295	51,88399
76	0,02016	51,45684	0,04553	53,56722	0,04343	52,28279
80	0,02037	51,73532	0,04589	54,00221	0,04364	52,4659
84	0,02039	51,75063	0,04612	54,28265	0,04386	52,64826
88	0,02085	52,34636	0,04676	55,07054	0,04474	53,38914
92	0,02077	52,2498	0,04685	55,18968	0,04492	53,53566
96	0,021	52,54374	0,04708	55,47206	0,04519	53,76339
100	0,02103	52,57872	0,04739	55,84476	0,04568	54,17656
104	0,02135	52,98784	0,04762	56,12854	0,04635	54,73944
108	0,02147	53,14908	0,04797	56,56389	0,04662	54,96972
112	0,02165	53,37722	0,04808	56,69654	0,04722	55,46669
116	0,02197	53,78576	0,04846	57,16666	0,0479	56,04577
120	0,02248	54,43948	0,04908	57,92124	0,04878	56,77844

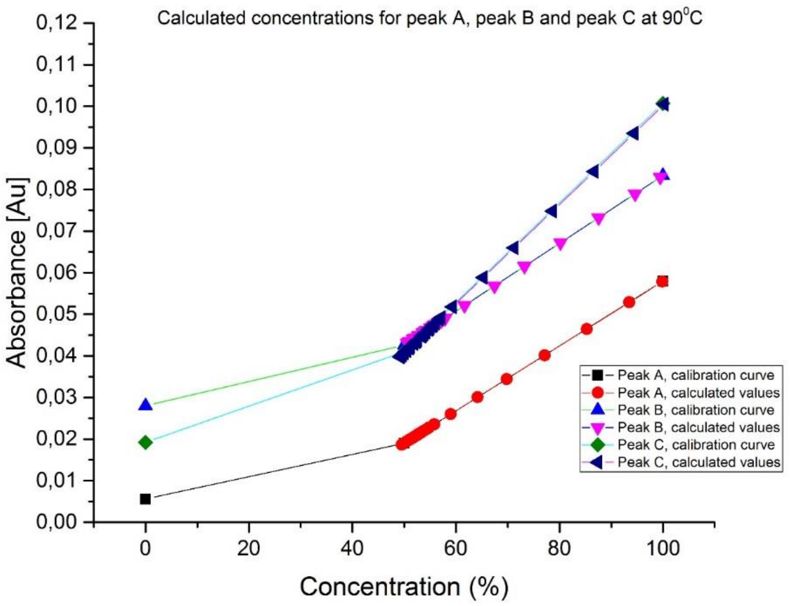


Figure 20 Concentration profile of bitumen 1R rejuvenation by R2 at 90^0C

7.2 Rejuvenation analysis

In this research, rejuvenation was examined on the basis of variations in signals of FTIR spectra and the level of diffusant in bitumen media was calculated by percent concentration. The level of blending is defined at 0% when spectra of bitumen is not reached and 50% when the spectra of final bitumen is consistent with the spectra of a 50:50 blend. Temperature and properties of bitumen as well as rejuvenator appeared to be the key parameters while examining rejuvenation process in the bitumen. The influence of these factors is discussed below.

7.2.1 Influence of temperature

Since diffusion is directly proportional to the absolute temperature according to Stoke-Einstein's equation therefore, any rise in temperature determines the increase in diffusivity of the material through diffusion media (Miller 1924). Therefore the level of rejuvenation should increase with increasing temperature. However, one must consider the state of the matter into which a diffuser penetrates. Bitumen and tars are considered as liquids. However, depending on the temperature the bitumen can be considered as solid, semisolid or liquid.

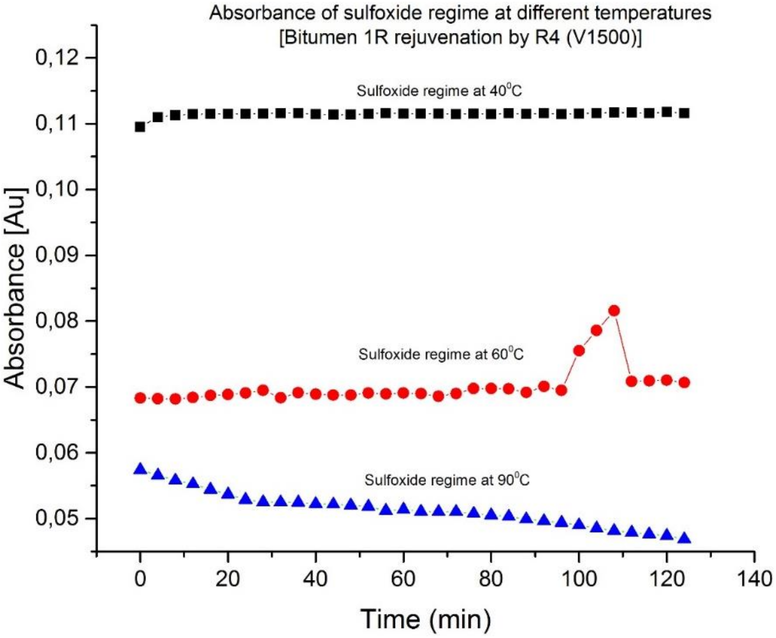


Figure 21 Comparison of absorbance of sulfoxide regime at given temperatures

It can be seen form figure 21 that initial values of absorbance for all three temperatures starts from different points. Further, the changes in absorbance of sulfoxide regime at 40°C and 60°C are very less as compare to 90°C. This shows higher temperature favors the diffusion of rejuvenator within a given time frame. Similar influence of temperature was found in other experiments of this research that can be seen from spectrum attached in the Appendix A. Therefore, it can be stated that higher temperature must be provided, around 90°C, for better blending options during recycling of aged bitumen. It also clears that after the compaction of recycled material, temperature of the mix starts to decline therefore, decrease in rejuvenation can be expected. If the temperature drops drastically in cold weather, diffusion of rejuvenators eventually slows down as the viscosity parameter becomes higher.

The bitumen rheological behavior can be characterized by multiple techniques, but in the scope of below analysis the softening point was considered to be the most likely affecting the diffusion. During the test (SFS-EN 1427) below that temperature the bitumen behaves like a solid and is able to support a steel ball. Above that softening point temperature, the steel ball penetrates into the bitumen and the film visibly flows just like a liquid would. It was hypothesized therefore, that the diffusion of rejuvenator into the bitumen can be hindered if the bitumen is in the solid/semisolid state (below the softening point temperature).

Table 10 Level of concentration witnessed be sulfoxide or Peak B in bitumen due to all four rejuvenators

	R1	R2	R3	R4	Temperature
Bitumen	Concentration				
	%	%	%	%	°C
1R	102	102	110	110	40
1R	97	101	104	105	60
1R	**73**	**62**	**67**	**77**	90
B2	94	98	105	119	40
B2	97	**49**	99	98	60
B2	**50**	**47**	**32**	**24**	90

Table 10 presents that the signal of bitumen in the lamelle after 2 h of rejuvenation at particular temperature as witnessed by peak B or Sulfoxyl regime. The values in bold indicate that a concentration has significantly changed at higher temperature, i.e. 90°C, for all four rejuvenators.

7.2.2 Influence of type of bitumen

Effect of Rejuvenators through two bitumen of different penetration grade was monitored. Bitumen from area 1, referred as 1R, has penetration grade of 22 dmm whereas; the other bitumen 70/100, referred as B2, holds penetration grade of 76dmm. Calculated softening point, 65°C for 1R and 48°C for B2, obtained from interpolation of DSR parameter G* also show the difference in softening of bitumen samples. It is noticeable that B2 bitumen is of much softer grade than bitumen 1R. According to Stoke-Einstein's equation the stiffness or viscosity of diffusion media is proportional to resist the diffusion of molecules through material (Karlsson, Isacsson 2003e). Therefore, it can be assumed that the diffusion of each rejuvenator in bitumen at specific temperature will be different according to stiffness of bitumen used. In addition, temperatures above softening point, such as 60°C and 90°C for B2 and 1R respectively, the lower layer of bitumen becomes softer, thus allowing faster diffusion of rejuvenator molecules. Table 11 shows a comparison of concentration level of sulfoxide regime of the two bitumen at 60°C and 90°C when rejuvenated by R4

Table 11 Concentration level of sulfoxide regime in 1R and B2

Bitumen	Avg. concentration level in sulfoxide regime (%)	
	At 60°C	At 90°C
1R	98	99
B2	25	72

It was observed that absorbance of sulfoxide regime in both the bitumen 1R and B2 rejuvenated by R4 at 60°C is nearly unchanged during the process. At 90°C sulfoxide regime indicates the decrease in intensity for both bitumen 1R and B2. It was observed that at 90°C absorbance in B2, softer grade bitumen, altered significantly at initial measurements as compared to absorbance of 1R, relatively stiffer bitumen. This concludes the assumption that softening of bitumen influence the rejuvenation process by means of lowering the viscosity and allows faster movement of diffusive molecules. It also suggests that stiffer bitumen must be exposed to temperature higher than the softening point during mixing of materials for better blending with rejuvenators.

7.2.3 Influence of rejuvenator properties

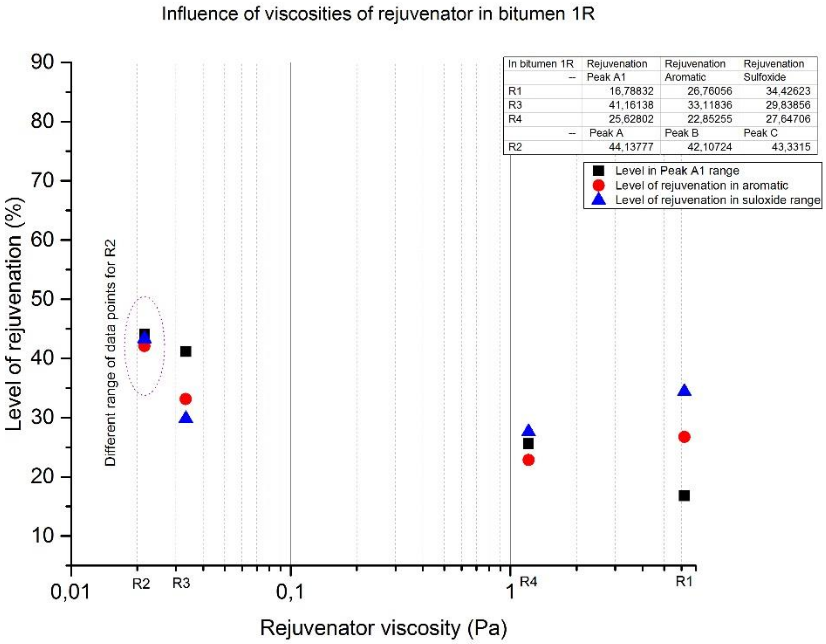
Four different types of rejuvenators were used in the analysis of rejuvenation of bitumen 1R and B2. Rejuvenators were separated on the basis of viscosity measurements. R1 and R4 were softer grade bitumen that were relatively more viscous than other two rejuvenators. R2 and R3 were oily liquids having relatively much lesser viscosities. Viscosity specifications were given in section 3.2

In a series of experiments, rejuvenators were compared on the basis of maximum rejuvenation level achieved at the end of experiment. Since maximum rejuvenation was observed at higher temperature therefore, rejuvenators were also compared at maximum temperature of 90°C.

Three of the rejuvenators; namely R1, R3, and R4; were tested in similar regimes of significant peaks. In case of soft bitumen B2, it was difficult to identify the absorbance of carbonyl regime. The reason was associated with the noise of rippled signals (Figure 12.) that appeared during the rejuvenation process. These vibratory signals overlaps with the peaks of carbonyl regime and made it difficult to note the exact absorbance of maximum peak height. At some frequencies, spectrum showed signals below than minimum level of 0% thus, giving negative values. Therefore, another range for peak in the spectrum was selected near 3052,3 cm^{-1} wavenumber, referred as Peak A1, to analyze the influence of viscosity.

Note: Important to mention that this selected peak A1 was used only for viscosity case. Calculations for concentration of carbonyl regime in bitumen B2 was not processed due to low confidence in the result of calculations.

Figure 22 illustrates different levels of rejuvenation achieved in bitumen 1R by each rejuvenator when applied at 90°C.

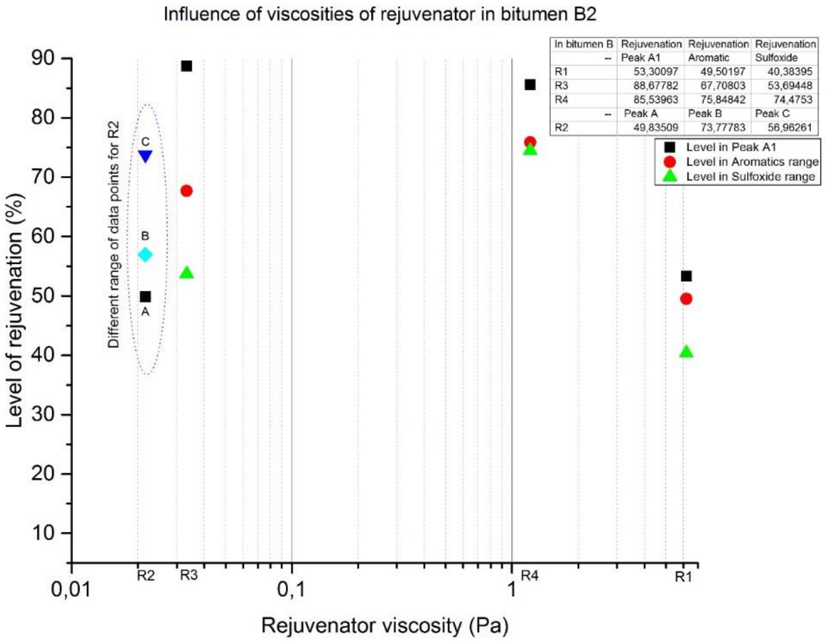


In bitumen 1R	Rejuvenation	Rejuvenation	Rejuvenation
--	Peak A1	Aromatic	Sulfoxide
R1	16,78832	26,76056	34,42623
R3	41,16138	33,11836	29,83856
R4	25,62802	22,85255	27,64706
--	Peak A	Peak B	Peak C
R2	44,13777	42,10724	43,3315

Figure 22 Level of rejuvenation in 1R at given viscosities of rejuvenators at 90^0C

Typically, higher viscosity renders the diffusion of molecules and it can be expected that more viscous rejuvenator will diffuse lesser. Figure 22 shows that R1 being relatively viscous rejuvenator than R4, diffuses in bitumen 1R more than R4 in aromatics and sulfoxide range. Peak A1 has higher rejuvenation level with R4 in comparison to R1. This can be explained by the importance of size and shape of diffusing molecules. As described in (Karlsson, Isacsson 2003e), shape and size contribute in the mean radius of molecule. Substances with low viscosity might experience hindrance while diffusing through media due to the presence of molecular shape as well as intermolecular interactions (Karlsson, Isacsson 2003e). In case of R2 and R3, similar trend of rejuvenation level was observed. R3 was slightly more viscous than R2 yet it shows more rejuvenation in the Peak A1 range as compare to R2. On the other hand, aromatic and sulfoxide ranges showed higher level of rejuvenation by R2.

The influence of these rejuvenator on bitumen B2 is presented in figure 23. It is important to mention that B2 itself is less viscous than 1R bitumen therefore, the influence of rejuvenators on B2 differs from the 1R observations.



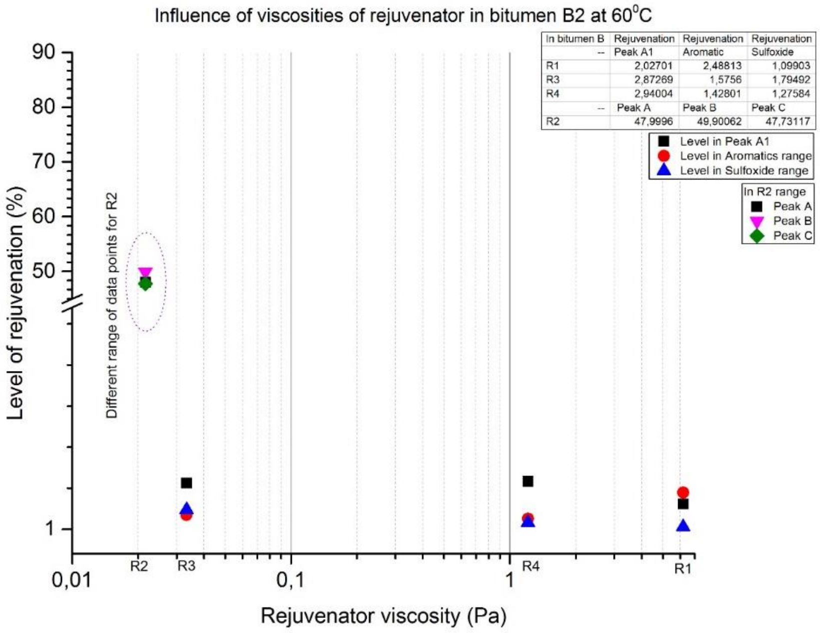
In bitumen B	Rejuvenation	Rejuvenation	Rejuvenation
--	Peak A1	Aromatic	Sulfoxide
R1	53,30097	49,50197	40,38395
R3	88,67782	67,70803	53,69448
R4	85,53963	75,84842	74,4753
--	Peak A	Peak B	Peak C
R2	49,83509	73,77783	56,96261

Figure 23 Level of rejuvenation in B2 at given viscosities of rejuvenators at 90^{0}C

In case of B2, rejuvenators were applied and the maximum level of rejuvenation at the end of experiment was calculated from calibration curves.

As can be seen from figure 19, all rejuvenators showed more than 50% of rejuvenation which seems to be incorrect for the applied procedure. It was observed during the experiment that thin film of bitumen was broken when exposed to higher temperature of 90°C. Since calculated softening point of B2 was 48,8°C; it can be concluded that the thin film might deformed and flowed away from the frame at higher temperature of 90°C after few minutes. As a result, the rejuvenator reaches the surface of ATR prism without diffusing through the bitumen film thus, recorded intensities were more likely of rejuvenator instead of bitumen- rejuvenator blend.

Since the rejuvenators were tested at 60°C as well, which was still above the softening point of B2 rejuvenator. Therefore, results obtained from experiment at 60°C were analyzed in a similar manner. The level of rejuvenation attained in B2 at 60°C was plotted against the viscosities of each rejuvenator. A graphical representation is presented in figure 24



In bitumen B	Rejuvenation	Rejuvenation	Rejuvenation
--	Peak A1	Aromatic	Sulfoxide
R1	2,02701	2,48813	1,09903
R3	2,87269	1,5756	1,79492
R4	2,94004	1,42801	1,27584
--	Peak A	Peak B	Peak C
R2	47,9996	49,90062	47,73117

Figure 24 Level of rejuvenation in 1R at given viscosities of rejuvenators at 60°C

Much lower rejuvenation was observed at 60°C however, it shows that rejuvenation occurs above softening point. R2 showed maximum rejuvenation at this temperature since it has the minimum viscosity that favors more blending with bitumen B2. For the record, the low softening point of B2 bitumen contributes in more blending of bitumen and rejuvenators as compare to relatively stiffer bitumen 1R.

7.3 Depth of penetration of IR beam in measurements

As mentioned earlier in section (techniques used section) that equation 1 showed dependence of penetration depth of evanescent wave (d_p) on wavenumber and angle of incidence in absorbing rare medium. Considering wavenumber parameter in the equation 1 and assuming all other factors to be constant, it can be concluded that penetration of IR beam must have different depths at corresponding wavenumbers. Therefore, waves at lower frequencies are expected to penetrate faster and deeper. The reason was described earlier in the technique section. This fact can possibly interfere in the FTIR measurements when collecting the change in absorbance and level of blending in bitumen due to the penetration of rejuvenator. The targeted range of functional groups lies at different wave numbers. Therefore, IR beam at lower frequencies collects level of diffusion of rejuvenator at more depth. In addition, the change in absorbance of one constituent at specific wavenumber was expected to appear earlier than the other constituent at different wavenumber. The calculated level of concentration obtained at the end of experiment carried out at 90^0C in aromatic and sulfoxide range is shown in table 12. These groups were fairly at different wavenumbers, at approximate range of 1600 cm^{-1} and 1030 cm^{-1} respectively. The level of concentration at sulfoxide range was detected lower that aromatics range showing the more penetration of evanescent wave at sulfoxide range.

Table 12 concentration level detected at different wavenumbers

Rejuvenation samples	Concentration level %	
	Aromatics range approx. 1600cm^{-1}	Sulfoxide range approx. 1030cm^{-1}
1R with R1	73,23	65,57
1R with R4	75,97	71,82

8 Conclusions

The diffusion of rejuvenator into bitumen is a complex process to monitor. Several researches have covered the diffusion studies of bitumen. Based on the previous researches, this work utilizes the methodology of monitoring the diffusion of rejuvenators in bitumen. However, diffusion coefficients were not computed. The work described in this thesis was based on the principle of Beer-Lambert law where intensity was correlated with the concentration of substance. This research determined the rejuvenation level in bitumen by applying FTIR-ATR technique and factors affecting the rejuvenation process. Based on the results presented in this research, following conclusions can be drawn:

1. Softening point of bitumen was observed to have greater impact on rejuvenation process. Two bitumen of different penetration grade were examined under the application of four different rejuvenators. Rejuvenation was found to proceed within the 2 hour testing time at temperatures above softening point.

2. Rejuvenation was highly influenced by the individual viscosities of rejuvenators used. In this work, viscosity seems to soften the bitumen film. However, due to nature of rejuvenator the level of softening in terms of diffusion through the bitumen media varies between the rejuvenating agents.

3. Temperature remains key parameters in the studies of diffusion and it also shows similar importance during this study. Rejuvenation was observed in all combinations only at higher temperatures (most likely at 90°C) thus, reflecting the dependence of process on suitable temperature range. It is important to consider that maximum interaction between bitumen and rejuvenator requires sufficiently high temperatures. As the temperature starts to decline, the diffusion of molecules decreases as well and the temperature below the softening point shows no significant impact on diffusion according to the results of this work.

4. The use of FTIR-ATR in this work was found suitable to monitor the variation in spectra of bituminous materials due to diffusion of rejuvenating substances. Linear correlation of absorbance with concentration yields good fit in analyzing the concentration level of diffusing substance. However, the concentration reflects only the level of selected functional group regime as whole. The exact concentration of functional groups was not calculated.

9 Recommendations

Based on the findings from this research work, following are reasonable recommendations to consider during the field applications and further research purposes

1. Ageing was found to proceed even at lower temperatures in bitumen binder when exposed to open atmosphere. Therefore, attention should be paid in handling and storage of binders used as rejuvenators. When storing at manufacturers recommended temperature, care must be taken to minimize the exposure of air. Excessive period of storage and exposure above the elevated temperatures cause reduction in quality of binder.

2. Rejuvenation does not progress below the softening point. To ensure proper rejuvenation during interaction of bitumen and rejuvenator at different stages of recycling, temperature must be provided above softening point. Even at 90°C, the level of rejuvenation was below the targeted 50% level for most of the cases during the 2 hours monitoring. Therefore, appropriate rejuvenation requires sufficiently high temperature and maximum interaction of materials.

3. Bitumen materials must not be over heated during the application. This causes the volatilization of lighter components, resulting short term ageing. In few cases of this work, it was observed that rejuvenation was started to decrease again after reaching at certain degree at higher temperature. It interprets that excessive temperature after some time also initiate ageing therefore, long term exposure at elevated temperature should be avoided. Generally, only the quantity required for immediate use should be heated to the application temperature and reheating avoided, where practicable.

4. Bitumen after ageing becomes stiffer and highly viscous material. Softer rejuvenators appear to be more effective in reducing the stiffness of aged bitumen and desirable to use to achieve better mechanical properties in bitumen.

5. Rejuvenation proceeds slowly in terms of diffusion of molecules and found to be influenced by viscosity, temperature and softening of bitumen. It is therefore be the point of interest to evaluate the optimum level of rejuvenation required for particular pavement application and how the pavement performance is affected during the service life of road.

6. There is need for further research in application of FTIR-ATR in bitumen characterization. The depth of penetration might influence the resulting spectra as it is a function of wavenumber and refractive index of material. The change in absorbance of sample was detected earlier at few frequencies. Thus, depth of penetrating beam seems to be influenced by wavenumber and changing refractive index due to diffusion of rejuvenator. It obviously

be the point of interest to evaluate the depth of IR beam during diffusion at particular wavenumber.

7. In analyzing diffusion of oily liquids, where air and moisture are important factors, special design for sample place in FTIR-ATR is required to avoid any surrounding interference. Moreover, when analyzing the thin film of low softening point materials, keeping the film consistent and smooth at higher temperature was found difficult. Special frames with holders are required to keep the layer in perfect contact with prism and not to allow any flow of the material layer.

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11 List of appendices

Appendix 1 Calculated concentration tables of bitumen 1R and B2 at 40°C, 60°C, and 90°C

Appendix 2 Calibration graphs

Appendix 1 Calculated concentration tables of bitumen 1R and B2 at 40°C, 60°C, and 90°C

This appendix presents the calculated concentration values from recorded absorbance at each time interval of 4 minutes. The values were computed by using equation 2 as describe in section 3. Tables contain concentration columns in terms of percent and corresponding absorbance values for both bitumen 1R and R2 at given temperatures of 40°C, 60°C, and 90°C.

TABLE A1. BITUMEN 1R REJUVENATED BY R3 AT 40^{0}C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0	100,66275	0,04972	101,02488	0,06751	101,3591	0,09472
4	100,50779	0,04961	102,12227	0,06837	102,59749	0,09596
8	102,01596	0,05065	102,89714	0,06898	103,41809	0,09678
12	103,22988	0,05148	103,58234	0,06952	104,09892	0,09746
16	104,11035	0,05209	104,29405	0,07008	104,81775	0,09818
20	105,85146	0,05328	104,81603	0,07049	105,38721	0,09875
24	107,1017	0,05414	105,20837	0,0708	105,75304	0,09911
28	108,01527	0,05476	105,73786	0,07122	106,53099	0,09989
32	109,51398	0,05579	105,93881	0,07138	106,64137	0,1
36	111,04504	0,05684	106,24845	0,07162	106,90063	0,10026
40	111,91242	0,05744	106,56129	0,07187	107,33885	0,1007
44	112,77939	0,05803	106,9231	0,07215	107,55062	0,10091
48	115,60505	0,05997	107,35739	0,07249	107,93563	0,1013
52	116,58269	0,06064	107,66821	0,07274	108,10965	0,10147
56	115,84914	0,06014	107,80599	0,07285	108,42118	0,10178
60	118,40906	0,06189	108,16788	0,07313	108,5803	0,10194
64	118,69876	0,06209	108,55719	0,07344	108,87767	0,10224
68	117,76544	0,06145	108,61112	0,07348	108,9571	0,10232
72	120,05721	0,06302	108,76964	0,0736	109,09909	0,10246
76	121,08325	0,06373	109,09948	0,07386	109,3309	0,10269
80	119,51654	0,06265	109,28763	0,07401	109,6108	0,10297
84	121,05288	0,06371	109,29942	0,07402	109,80624	0,10317
88	122,08872	0,06442	109,59495	0,07425	109,96823	0,10333
92	120,25267	0,06316	109,67397	0,07432	110,12354	0,10348
96	121,05975	0,06371	109,77903	0,0744	110,12308	0,10348
100	122,21307	0,0645	110,00726	0,07458	110,39377	0,10376
104	121,33097	0,0639	110,09518	0,07465	110,45441	0,10382
108	121,38907	0,06394	110,03405	0,0746	110,70505	0,10407
112	122,86325	0,06495	110,12883	0,07467	110,59963	0,10396
116	120,99554	0,06367	110,17292	0,07471	110,77496	0,10414

TABLE A2. BITUMEN 1R REJUVENATED BY R3 AT 60^0C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0	103,35873	0,04834	102,83687	0,06767	102,55379	0,09775
4	102,18302	0,04753	101,94824	0,06693	101,87445	0,09696
8	101,79706	0,04727	102,16617	0,06711	102,31418	0,09747
12	102,07105	0,04745	102,44212	0,06734	102,46687	0,09765
16	102,2734	0,04759	102,6751	0,06753	102,6491	0,09786
20	101,91557	0,04735	102,74592	0,06759	102,83064	0,09807
24	102,45486	0,04772	103,32799	0,06807	103,15886	0,09845
28	102,50688	0,04775	103,39003	0,06812	103,2563	0,09857
32	103,315	0,04831	103,57609	0,06828	103,24848	0,09856
36	103,5433	0,04846	103,56305	0,06827	103,15958	0,09846
40	104,7473	0,04929	103,81737	0,06848	103,28236	0,0986
44	105,60617	0,04988	103,82902	0,06849	103,33369	0,09866
48	106,17059	0,05027	103,98118	0,06861	103,39539	0,09873
52	106,92399	0,05078	104,07136	0,06869	103,42583	0,09876
56	107,5911	0,05124	104,08493	0,0687	103,33713	0,09866
60	108,0925	0,05158	104,22285	0,06882	103,46743	0,09881
64	105,66258	0,04992	104,07089	0,06869	103,49773	0,09885
68	105,31874	0,04968	104,16371	0,06877	103,54683	0,0989
72	105,46309	0,04978	104,11014	0,06872	103,56448	0,09892
76	105,72209	0,04996	104,27381	0,06886	103,56685	0,09893
80	106,07525	0,0502	104,28223	0,06886	103,5766	0,09894
84	105,81536	0,05002	104,309	0,06889	103,50106	0,09885
88	105,76793	0,04999	104,2645	0,06885	103,66715	0,09904
92	106,10112	0,05022	104,36535	0,06893	103,68772	0,09907
96	106,35478	0,05039	104,39857	0,06896	103,72472	0,09911
100	106,65164	0,0506	104,38987	0,06895	103,76092	0,09915
104	106,89228	0,05076	104,3887	0,06895	103,73975	0,09913
108	107,69955	0,05132	104,35145	0,06892	103,73655	0,09912
112	107,91111	0,05146	104,43621	0,06899	103,87364	0,09928
116	108,49625	0,05186	104,62924	0,06915	103,77514	0,09917

TABLE A3. BITUMEN 1R REJUVENATED BY R3 AT 90^0C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0	102,00912	0,0368	101,39431	0,05741	100,92187	0,08252
4	98,8999	0,03528	99,64965	0,05617	99,90578	0,08151
8	96,41108	0,03406	97,64937	0,05474	98,04304	0,07965
12	90,46341	0,03114	92,67554	0,05119	93,45827	0,07508
16	84,04184	0,02799	86,99963	0,04714	88,02869	0,06967
20	77,26538	0,02466	81,89701	0,0435	83,34899	0,06501
24	74,0411	0,02308	78,97865	0,04142	80,3726	0,06204
28	71,75109	0,02196	76,8395	0,03989	78,23932	0,05991
32	71,00387	0,02159	76,06578	0,03934	77,53732	0,05921
36	70,58673	0,02138	75,74819	0,03911	77,24711	0,05893
40	72,15798	0,02216	77,02025	0,04002	78,37953	0,06005
44	73,66217	0,02289	78,37995	0,04099	79,87327	0,06154
48	74,00621	0,02306	78,70713	0,04123	80,46876	0,06214
52	73,89477	0,02301	78,83164	0,04131	80,53808	0,06221
56	73,05006	0,02259	78,35897	0,04098	80,18383	0,06185
60	72,37681	0,02226	77,9623	0,04069	79,84466	0,06151
64	71,38464	0,02178	77,28705	0,04021	79,27864	0,06095
68	70,48303	0,02133	76,79842	0,03986	78,82906	0,0605
72	69,02224	0,02062	75,99933	0,03929	78,30432	0,05998
76	67,6511	0,01994	75,04083	0,03861	77,61136	0,05929
80	66,08565	0,01918	74,12736	0,03796	76,80285	0,05848
84	64,78106	0,01854	74,12736	0,03796	75,74801	0,05743
88	63,79836	0,01805	72,25229	0,03662	75,12639	0,05681
92	63,05184	0,01769	71,45077	0,03605	74,3707	0,05606
96	62,4764	0,0174	70,84586	0,03562	73,86672	0,05556
100	61,93687	0,01714	70,15494	0,03512	73,22879	0,05492
104	61,48151	0,01692	69,62209	0,03474	72,53759	0,05423
108	60,90989	0,01664	68,82738	0,03418	71,93734	0,05363
112	59,6272	0,01601	67,93302	0,03354	71,09363	0,05279
116	59,47937	0,01593	67,41796	0,03317	70,7068	0,05241

TABLE A4. BITUMEN 1R REJUVENATED BY R4 AT 40^{0}C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0	103,74557	0,05396	105,81093	0,07583	104,92255	0,10951
4	104,60993	0,05435	108,32611	0,07699	106,87845	0,111
8	105,09752	0,05457	109,17173	0,07738	107,27225	0,1113
12	105,05319	0,05455	109,62706	0,07759	107,49541	0,11147
16	104,85372	0,05446	109,60538	0,07758	107,52166	0,11149
20	104,74291	0,05441	109,71379	0,07763	107,50853	0,11148
24	104,10018	0,05412	109,38855	0,07748	107,54791	0,11151
28	103,67908	0,05393	109,10668	0,07735	107,61355	0,11156
32	103,65691	0,05392	109,12836	0,07736	107,66605	0,1116
36	103,52394	0,05386	109,36687	0,07747	107,70543	0,11163
40	102,79255	0,05353	108,86817	0,07724	107,49541	0,11147
44	102,34929	0,05333	108,78144	0,0772	107,36414	0,11137
48	102,43794	0,05337	108,71639	0,07717	107,37726	0,11138
52	102,17199	0,05325	108,73807	0,07718	107,53479	0,1115
56	102,41578	0,05336	108,71639	0,07717	107,73169	0,11165
60	102,63741	0,05346	109,01995	0,07731	107,57417	0,11153
64	102,74823	0,05351	109,01995	0,07731	107,58729	0,11154
68	102,79255	0,05353	109,06331	0,07733	107,57417	0,11153
72	102,72606	0,0535	108,91154	0,07726	107,48228	0,11146
76	103,19149	0,05371	109,21509	0,0774	107,58729	0,11154
80	103,19149	0,05371	109,25846	0,07742	107,48228	0,11146
84	103,63475	0,05391	109,36687	0,07747	107,62667	0,11157
88	103,16933	0,0537	109,34519	0,07746	107,52166	0,11149
92	103,56826	0,05388	109,62706	0,07759	107,67918	0,11161
96	103,85638	0,05401	109,41023	0,07749	107,46915	0,11145
100	105,14184	0,05459	109,84389	0,07769	107,61355	0,11156
104	106,18351	0,05506	110,27754	0,07789	107,73169	0,11165
108	108,02305	0,05589	110,451	0,07797	107,75794	0,11167
112	109,41933	0,05652	110,53773	0,07801	107,75794	0,11167
116	110,85993	0,05717	110,8196	0,07814	107,69231	0,11162

TABLE A5. BITUMEN 1R REJUVENATED BY R4 AT 60^{0}C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0	100,2624	0,04584	100,08061	0,06832	99,79864	0,09912
4	100,31011	0,04586	99,91939	0,06824	99,5847	0,09895
8	101,02576	0,04616	99,77832	0,06817	99,39592	0,0988
12	104,60401	0,04766	100,22168	0,06839	99,59728	0,09896
16	110,23378	0,05002	100,84643	0,0687	99,64762	0,099
20	114,02672	0,05161	101,16888	0,06886	99,50919	0,09889
24	117,93893	0,05325	101,57195	0,06906	99,35817	0,09877
28	122,37595	0,05511	102,47884	0,06951	99,54694	0,09892
32	116,29294	0,05256	100,14107	0,06835	99,69796	0,09904
36	116,60305	0,05269	101,69287	0,06912	99,82381	0,09914
40	114,76622	0,05192	101,26965	0,06891	99,77347	0,0991
44	113,78817	0,05151	100,9472	0,06875	99,50919	0,09889
48	114,50382	0,05181	100,98751	0,06877	99,8364	0,09915
52	115,50573	0,05223	101,65256	0,0691	99,77347	0,0991
56	114,21756	0,05169	101,35026	0,06895	99,98742	0,09927
60	114,45611	0,05179	101,61225	0,06908	100,05034	0,09932
64	113,90744	0,05156	101,43087	0,06899	100,01258	0,09929
68	113,95515	0,05158	100,62475	0,06859	99,92449	0,09922
72	114,74237	0,05191	101,47118	0,06901	99,98742	0,09927
76	115,02863	0,05203	102,94236	0,06974	99,88674	0,09919
80	114,31298	0,05173	102,94236	0,06974	100,05034	0,09932
84	122,8292	0,0553	102,90206	0,06972	100,05034	0,09932
88	125,14313	0,05627	101,75333	0,06915	99,91191	0,09921
92	118,77385	0,0536	103,62757	0,07008	99,94966	0,09924
96	121,70802	0,05483	102,39823	0,06947	100,07551	0,09934
100	139,05057	0,0621	114,57074	0,07551	99,84898	0,09916
104	129,74714	0,0582	120,77791	0,07859	100,07551	0,09934
108	133,20611	0,05965	126,78356	0,08157	100,02517	0,0993
112	138,69275	0,06195	105,19952	0,07086	100,11326	0,09937
116	139,81393	0,06242	105,40105	0,07096	99,97483	0,09926

TABLE A6. BITUMEN 1R REJUVENATED BY R4 AT 90^{0}C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0	101,42512	0,03904	100,16077	0,05742	100,24133	0,08298
4	101,52174	0,03908	98,20854	0,05657	98,43137	0,08178
8	101,8599	0,03922	96,44006	0,0558	96,45551	0,08047
12	103,23671	0,03979	95,17685	0,05525	95,08296	0,07956
16	102,70531	0,03957	93,24759	0,05441	92,88084	0,0781
20	97,85024	0,03756	91,59394	0,05369	90,31674	0,0764
24	95,14493	0,03644	89,73358	0,05288	87,99397	0,07486
28	95,48309	0,03658	88,90675	0,05252	86,50075	0,07387
32	97,53623	0,03743	88,83785	0,05249	86,06335	0,07358
36	98,79227	0,03795	88,79192	0,05247	85,2187	0,07302
40	99,17874	0,03811	88,2407	0,05223	84,49472	0,07254
44	99,7343	0,03834	88,12586	0,05218	83,93665	0,07217
48	100,55556	0,03868	87,78135	0,05203	83,31825	0,07176
52	101,37681	0,03902	87,322	0,05183	82,57919	0,07127
56	94,27536	0,03608	85,89802	0,05121	82,27753	0,07107
60	92,41546	0,03531	86,31144	0,05139	81,74962	0,07072
64	91,61836	0,03498	85,55351	0,05106	80,58824	0,06995
68	92,92271	0,03552	85,53055	0,05105	80,22624	0,06971
72	94,51691	0,03618	85,50758	0,05104	79,48718	0,06922
76	93,30918	0,03568	84,88746	0,05077	78,6727	0,06868
80	91,69082	0,03501	84,31328	0,05052	77,94872	0,0682
84	89,85507	0,03425	83,87689	0,05033	77,51131	0,06791
88	87,3913	0,03323	82,93523	0,04992	76,84766	0,06747
92	85,77295	0,03256	82,29215	0,04964	76,28959	0,0671
96	84,71014	0,03212	81,71796	0,04939	75,68627	0,0667
100	82,36715	0,03115	80,82223	0,049	75,05279	0,06628
104	79,49275	0,02996	79,76573	0,04854	74,46456	0,06589
108	77,63285	0,02919	78,84704	0,04814	73,96682	0,06556
112	76,57005	0,02875	78,27285	0,04789	73,34842	0,06515
116	75,41063	0,02827	77,65273	0,04762	72,85068	0,06482

TABLE A7. BITUMEN B2 REJUVENATED BY R1 AT 40^{0}C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0	99,7445	0,04398	99,99632	0,07577	100,06656	0,08947
4	97,89999	0,04346	99,05484	0,07544	99,62764	0,08926
8	97,38282	0,04331	99,25533	0,07551	99,71772	0,0893
12	96,47557	0,04305	98,93154	0,07539	99,71131	0,0893
16	93,25758	0,04213	98,35241	0,07519	100,0963	0,08949
20	92,61011	0,04195	97,96519	0,07505	100,07757	0,08948
24	92,60729	0,04195	98,3202	0,07518	100,36181	0,08962
28	92,74571	0,04199	98,45733	0,07522	100,1108	0,08949
32	92,95571	0,04205	98,786	0,07534	100,43656	0,08965
36	93,63433	0,04224	99,22064	0,0755	100,53605	0,0897
40	93,77104	0,04228	99,46587	0,07558	100,67883	0,08977
44	93,07828	0,04208	99,33307	0,07554	100,81321	0,08984
48	92,6457	0,04196	99,55107	0,07561	101,13722	0,09
52	90,27671	0,04128	99,09576	0,07545	101,51631	0,09018
56	91,2441	0,04156	99,56097	0,07562	101,45016	0,09015
60	85,07791	0,0398	98,24317	0,07515	101,3131	0,09008
64	79,83711	0,03831	96,94822	0,07469	101,11169	0,08998
68	73,6383	0,03654	95,64099	0,07423	101,0625	0,08996
72	69,50816	0,03536	94,87015	0,07395	100,94367	0,0899
76	67,52379	0,0348	94,24078	0,07373	100,75402	0,08981
80	76,23422	0,03728	95,81576	0,07429	101,18866	0,09002
84	79,75434	0,03828	96,51562	0,07454	101,15973	0,09001
88	76,70586	0,03741	96,07129	0,07438	101,18642	0,09002
92	70,83208	0,03574	95,10333	0,07404	101,17249	0,09001
96	66,76731	0,03458	94,09571	0,07368	101,11444	0,08998
100	63,76377	0,03373	93,21317	0,07337	100,95501	0,08991
104	70,13843	0,03554	94,30845	0,07375	101,1322	0,08999
108	76,92152	0,03748	95,65141	0,07423	101,13388	0,08999
112	75,16694	0,03698	95,16972	0,07406	101,18032	0,09002
116	70,17956	0,03555	94,22882	0,07373	101,02255	0,08994

TABLE A8. BITUMEN B2 REJUVENATED BY R1 AT 60^{0}C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0	101,268	0,03412	100,82901	0,06452	99,43478	0,07071
4	99,27401	0,0337	100,0447	0,0643	98,99265	0,07058
8	98,62555	0,03357	99,63557	0,06419	99,23335	0,07065
12	98,04886	0,03345	99,72493	0,06421	98,90097	0,07055
16	98,66549	0,03358	100,05217	0,0643	99,50483	0,07073
20	96,28845	0,03309	99,55853	0,06416	100,08081	0,0709
24	96,37964	0,0331	99,204	0,06406	99,5522	0,07075
28	96,96694	0,03323	99,49794	0,06415	100,28711	0,07096
32	96,67603	0,03317	99,29002	0,06409	99,97404	0,07087
36	96,96071	0,03323	99,64933	0,06419	100,59431	0,07105
40	97,4248	0,03332	99,74656	0,06422	100,80277	0,07111
44	97,19759	0,03327	99,51099	0,06415	101,54996	0,07134
48	96,86967	0,03321	99,54831	0,06416	101,87352	0,07143
52	97,16682	0,03327	99,65493	0,06419	102,25162	0,07154
56	96,73787	0,03318	99,45436	0,06413	101,96827	0,07146
60	95,51989	0,03293	99,58275	0,06417	102,16163	0,07152
64	94,53126	0,03272	99,11647	0,06404	102,08641	0,07149
68	94,22429	0,03266	98,81117	0,06395	102,18422	0,07152
72	94,24707	0,03266	98,65467	0,06391	101,69674	0,07138
76	94,52401	0,03272	98,51247	0,06387	101,69661	0,07138
80	95,34381	0,03289	98,73933	0,06393	102,12712	0,07151
84	96,18933	0,03307	98,55262	0,06388	101,81592	0,07141
88	95,36936	0,0329	98,46744	0,06386	101,83586	0,07142
92	95,49296	0,03292	98,42919	0,06385	102,08828	0,07149
96	94,92386	0,0328	98,30865	0,06381	101,70082	0,07138
100	94,60822	0,03274	98,22268	0,06379	101,8385	0,07142
104	93,05692	0,03242	98,14201	0,06376	102,12422	0,07151
108	91,07313	0,03201	97,51485	0,06359	102,30675	0,07156
112	90,93014	0,03198	97,55429	0,0636	101,80772	0,07141
116	91,00663	0,03199	97,4171	0,06356	101,40081	0,07129

TABLE A9. BITUMEN B2 REJUVENATED BY R1 AT 90^{0}C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0		-1)	85,8095	0,04942	83,75657	0,05273
4		-1)	78,68982	0,04769	79,29281	0,05172
8		-1)	73,09434	0,04633	76,05783	0,05099
12		-1)	68,60025	0,04523	73,48576	0,05042
16		-1)	65,55152	0,04449	71,18219	0,0499
20		-1)	62,82042	0,04383	69,35852	0,04949
24		-1)	60,14351	0,04318	67,65817	0,0491
28		-1)	57,67747	0,04258	65,95353	0,04872
32		-1)	55,71533	0,0421	65,07038	0,04852
36		-1)	53,76496	0,04163	63,17446	0,0481
40		-1)	54,52939	0,04182	62,50714	0,04795
44		-1)	55,87584	0,04214	61,40602	0,0477
48		-1)	53,9777	0,04168	60,65137	0,04753
52		-1)	52,16511	0,04124	59,70048	0,04732
56		-1)	49,76757	0,04067	59,45702	0,04726
60		-1)	47,27022	0,04018	58,3665	0,04702
64		-1)	45,65788	0,03987	57,64503	0,04685
68		-1)	46,22735	0,03998	57,21098	0,04676
72		-1)	47,08555	0,04015	57,11778	0,04673
76		-1)	48,10254	0,04035	56,93647	0,04669
80		-1)	48,64408	0,04045	56,67415	0,04663
84		-1)	49,39575	0,0406	56,75158	0,04665
88		-1)	49,60335	0,04064	56,65397	0,04663
92		-1)	50,24541	0,04076	57,23182	0,04676
96		-1)	49,25919	0,04057	57,63108	0,04685
100		-1)	49,10609	0,04054	57,88303	0,04691
104		-1)	49,25975	0,04057	58,51854	0,04705
108		-1)	49,3875	0,04059	58,15143	0,04697
112		-1)	49,49853	0,04062	58,22432	0,04698
116		-1)	50,04842	0,04073	59,05013	0,04717

1) The shape of the spectra in did not allow for determination of Carbonyl regime maximum and the confidence in the result of calculations is low and therefore we do not report them here

TABLE A10. BITUMEN B2 REJUVENATED BY R2 AT 40^{0}C

TIME	Calculated Concentration	Absorbance Peak A	Calculated Concentration	Absorbance Peak B	Calculated Concentration	Absorbance Peak C
MIN	[Au]	%	[Au]	%	[Au]	%
0	100,14156	0,07375	100,10359	0,10505	99,97163	0,12015
4	98,38694	0,07192	98,37538	0,10319	98,71461	0,11831
8	98,23861	0,07177	98,38608	0,1032	98,65331	0,11822
12	98,31555	0,07185	98,15588	0,10295	98,52362	0,11803
16	98,43556	0,07197	98,3329	0,10314	98,52526	0,11804
20	98,55621	0,0721	98,29049	0,10309	98,66232	0,11824
24	98,48591	0,07203	98,23436	0,10303	98,47177	0,11796
28	98,53669	0,07208	98,01211	0,10279	98,29459	0,1177
32	98,68317	0,07223	98,21223	0,10301	98,42648	0,11789
36	98,46091	0,072	98,38087	0,10319	98,43032	0,1179
40	98,46576	0,072	98,41164	0,10322	98,56245	0,11809
44	98,59886	0,07214	98,32718	0,10313	98,60741	0,11816
48	98,60334	0,07215	98,16953	0,10296	98,30257	0,11771
52	98,71045	0,07226	98,26918	0,10307	98,50432	0,11801
56	98,87762	0,07243	98,35729	0,10317	98,52892	0,11804
60	99,00118	0,07256	98,45892	0,10328	98,64095	0,11821
64	98,72388	0,07227	98,41651	0,10323	98,61339	0,11817
68	98,82775	0,07238	98,52022	0,10334	98,75109	0,11837
72	98,94821	0,07251	98,62886	0,10346	98,72591	0,11833
76	98,84092	0,07239	98,34079	0,10315	98,49303	0,11799
80	98,87999	0,07244	98,41051	0,10322	98,58325	0,11812
84	98,82026	0,07237	98,34818	0,10316	98,4492	0,11793
88	98,90043	0,07246	98,60597	0,10343	98,6714	0,11825
92	98,23226	0,07176	98,5361	0,10336	98,66753	0,11824
96	97,46279	0,07096	98,64393	0,10348	98,67498	0,11826
100	96,60081	0,07006	98,75382	0,10359	98,68797	0,11827
104	95,98033	0,06942	98,58647	0,10341	98,58599	0,11813
108	95,54147	0,06896	98,41413	0,10323	98,52088	0,11803
112	95,23463	0,06864	98,34168	0,10315	98,51099	0,11802
116	94,89017	0,06829	98,42028	0,10323	98,43393	0,1179
120	94,68087	0,06807	98,37651	0,10319	98,39105	0,11784

TABLE A11. BITUMEN B2 REJUVENATED BY R2 AT 60^{0}C

TIME	Calculated Concentration	Absorbance Peak A	Calculated Concentration	Absorbance Peak B	Calculated Concentration	Absorbance Peak C
MIN	[Au]	%	[Au]	%	[Au]	%
0	100,27458	0,06489	100,00198	0,09419	100,19805	0,10807
4	96,08316	0,06116	96,36908	0,09074	96,79661	0,10361
8	82,12649	0,04874	84,5661	0,07955	84,52564	0,08754
12	68,17306	0,03632	71,83122	0,06747	71,36807	0,0703
16	61,35187	0,03025	64,91844	0,06092	64,20082	0,06091
20	57,66795	0,02697	60,82172	0,05703	60,03868	0,05546
24	55,45067	0,02499	58,37569	0,05471	57,51375	0,05215
28	53,913	0,02363	56,45235	0,05289	55,72358	0,04981
32	52,98805	0,0228	55,41012	0,0519	54,64091	0,04839
36	52,24205	0,02214	54,48102	0,05102	53,85299	0,04736
40	51,75279	0,0217	53,74047	0,05032	53,1771	0,04647
44	51,23625	0,02124	53,20137	0,04981	52,68617	0,04583
48	50,76608	0,02083	52,68544	0,04932	52,21659	0,04521
52	50,47661	0,02057	52,18738	0,04885	51,79889	0,04467
56	50,30728	0,02042	51,72462	0,04841	51,57274	0,04437
60	50,18462	0,02031	51,49906	0,04819	51,33291	0,04406
64	50,06425	0,0202	51,34834	0,04805	51,14563	0,04381
68	49,88056	0,02004	50,98349	0,0477	50,90489	0,0435
72	49,74655	0,01992	50,83906	0,04757	50,75541	0,0433
76	49,82143	0,01998	50,75996	0,04749	50,69818	0,04322
80	49,51499	0,01971	50,36282	0,04712	50,3533	0,04277
84	49,31491	0,01953	50,18511	0,04695	50,15212	0,04251
88	49,24409	0,01947	49,74234	0,04653	50,10183	0,04244
92	49,42964	0,01964	49,68987	0,04648	50,0105	0,04232
96	49,45196	0,01966	49,73674	0,04652	49,88812	0,04216
100	49,56602	0,01976	49,65484	0,04644	49,96578	0,04227
104	49,51179	0,01971	49,42092	0,04622	49,93941	0,04223
108	49,5516	0,01974	49,5139	0,04631	49,85259	0,04212
112	49,51534	0,01971	49,49625	0,04629	49,81489	0,04207
116	49,34778	0,01956	49,34639	0,04615	49,96975	0,04227
120	49,13711	0,01938	49,26056	0,04607	49,74141	0,04197

TABLE A12. BITUMEN B2 REJUVENATED BY R2 AT 90^{0}C

TIME	Calculated Concentration	Absorbance Peak A	Calculated Concentration	Absorbance Peak B	Calculated Concentration	Absorbance Peak C
MIN	[Au]	%	[Au]	%	[Au]	%
0	99,70721	0,05291	99,68314	0,08077	99,20101	0,09413
4	97,6184	0,05145	98,19884	0,07959	97,99795	0,0928
8	72,23209	0,03371	73,40408	0,05999	73,21515	0,06529
12	64,39768	0,02824	62,35939	0,05126	63,34617	0,05433
16	60,99875	0,02586	57,39116	0,04733	59,18672	0,04972
20	59,38112	0,02473	54,46395	0,04501	57,02256	0,04732
24	58,32011	0,02399	53,03199	0,04388	55,68325	0,04583
28	57,86797	0,02368	52,4408	0,04341	55,13505	0,04522
32	56,50294	0,02272	50,35277	0,04176	53,62028	0,04354
36	54,87672	0,02159	48,17053	0,04004	52,10425	0,04186
40	53,68494	0,02075	46,78531	0,03894	51,17974	0,04083
44	52,9466	0,02024	46,12007	0,03842	50,5225	0,0401
48	52,43834	0,01988	45,76818	0,03814	50,3631	0,03992
52	52,3623	0,01983	45,08493	0,0376	49,92722	0,03944
56	53,04741	0,02031	44,70835	0,0373	49,67707	0,03916
60	52,97	0,02025	44,46356	0,03711	49,57745	0,03905
64	52,20394	0,01972	44,11728	0,03683	49,28777	0,03873
68	51,69068	0,01936	43,61794	0,03644	48,96205	0,03837
72	51,00959	0,01888	43,29597	0,03618	48,68977	0,03807
76	50,69697	0,01867	43,09706	0,03603	48,5018	0,03786
80	50,71746	0,01868	42,57613	0,03561	48,13089	0,03745
84	51,341	0,01912	42,23945	0,03535	48,00384	0,0373
88	51,18117	0,019	42,13954	0,03527	47,83779	0,03712
92	50,6783	0,01865	42,01893	0,03517	47,66794	0,03693
96	50,1162	0,01826	41,87581	0,03506	47,70044	0,03697
100	49,65206	0,01794	41,65244	0,03488	47,40072	0,03663
104	49,20455	0,01762	41,40982	0,03469	47,19129	0,0364
108	49,84387	0,01807	41,50261	0,03477	47,38062	0,03661
112	50,52225	0,01854	41,2572	0,03457	47,19149	0,0364
116	50,43596	0,01848	41,16259	0,0345	47,19795	0,03641
120	50,00346	0,01818	40,97978	0,03435	47,18065	0,03639

TABLE A12. BITUMEN B2 REJUVENATED BY R3 AT 40^{0}C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0		-1)	107,48046	0,07275	105,98787	0,07905
4		-1)	107,29536	0,0726	105,26849	0,07841
8		-1)	107,0521	0,0724	105,37312	0,0785
12		-1)	106,60478	0,07203	105,39499	0,07852
16		-1)	106,21056	0,0717	105,36663	0,07849
20		-1)	105,72864	0,0713	105,29972	0,07843
24		-1)	105,68137	0,07126	105,29079	0,07843
28		-1)	105,62125	0,07121	105,31155	0,07844
32		-1)	106,38336	0,07184	105,20887	0,07835
36		-1)	107,08652	0,07243	105,30541	0,07844
40		-1)	106,87425	0,07225	105,38943	0,07851
44		-1)	106,3387	0,0718	105,37498	0,0785
48		-1)	105,79662	0,07135	105,41929	0,07854
52		-1)	105,42597	0,07104	105,4018	0,07853
56		-1)	105,06492	0,07074	105,42172	0,07854
60		-1)	105,69108	0,07126	105,48003	0,0786
64		-1)	107,00179	0,07236	105,60169	0,07871
68		-1)	107,10402	0,07244	105,63752	0,07874
72		-1)	106,39703	0,07185	105,76143	0,07885
76		-1)	105,56957	0,07116	105,74565	0,07883
80		-1)	105,02314	0,07071	105,74454	0,07883
84		-1)	104,62333	0,07038	105,87192	0,07895
88		-1)	105,43531	0,07105	106,02941	0,07909
92		-1)	106,0177	0,07154	106,03661	0,0791
96		-1)	106,42764	0,07188	105,97628	0,07904
100		-1)	106,07035	0,07158	105,97049	0,07904
104		-1)	105,82607	0,07138	106,0897	0,07914
108		-1)	105,4016	0,07102	105,94037	0,07901
112		-1)	105,5573	0,07115	106,02582	0,07909
116		-1)				

TABLE A13. BITUMEN B2 REJUVENATED BY R3 AT 60^{0}C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0		-1)	98,31275	0,06304	98,21679	0,07338
4		-1)	98,36015	0,06308	98,08651	0,07325
8		-1)	98,39298	0,06311	98,13641	0,0733
12		-1)	98,39813	0,06311	98,18171	0,07335
16		-1)	98,0981	0,06286	98,20508	0,07337
20		-1)	98,27037	0,06301	98,33659	0,0735
24		-1)	98,45832	0,06317	98,45157	0,07362
28		-1)	98,64594	0,06332	98,54445	0,07371
32		-1)	98,81685	0,06347	98,61698	0,07378
36		-1)	98,96292	0,06359	98,63928	0,0738
40		-1)	99,06377	0,06368	98,90606	0,07407
44		-1)	99,03588	0,06366	98,96495	0,07413
48		-1)	98,80356	0,06346	98,90014	0,07406
52		-1)	98,82621	0,06348	98,96921	0,07413
56		-1)	98,91108	0,06355	98,86879	0,07403
60		-1)	99,20783	0,0638	99,07421	0,07424
64		-1)	99,59395	0,06413	99,21317	0,07437
68		-1)	99,79035	0,0643	99,25198	0,07441
72		-1)	100,07693	0,06454	99,30712	0,07447
76		-1)	100,26478	0,0647	99,51445	0,07467
80		-1)	99,72924	0,06424	99,39005	0,07455
84		-1)	99,67882	0,0642	99,43212	0,07459
88		-1)	100,27782	0,06471	99,78771	0,07495
92		-1)	100,64017	0,06502	99,89611	0,07505
96		-1)	100,90086	0,06524	99,93937	0,0751
100		-1)	101,10504	0,06541	99,97008	0,07513
104		-1)	101,26874	0,06555	100,05698	0,07521
108		-1)	100,64335	0,06502	100,26249	0,07542
112		-1)	99,36672	0,06394	100,14193	0,0753
116		-1)				

TABLE A14. BITUMEN B2 REJUVENATED BY R3 AT 90^{0}C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0		-1)	99,58452	0,0526	99,17014	0,06015
4		-1)	97,73562	0,05134	97,44835	0,05878
8		-1)	92,65248	0,04785	93,23954	0,05543
12		-1)	81,54933	0,04025	83,58042	0,04775
16		-1)	69,90333	0,03227	74,47407	0,04051
20		-1)	53,13425	0,02079	59,05212	0,02825
24		-1)	37,12668	0,01562	52,47506	0,02302
28		-1)	30,33182	0,01401	50,77348	0,02167
32		-1)	26,7581	0,01317	49,15162	0,02088
36		-1)	24,42715	0,01262	46,96131	0,02045
40		-1)	22,67549	0,01221	44,92561	0,02005
44		-1)	21,09268	0,01183	42,67348	0,01961
48		-1)	20,54454	0,0117	41,7806	0,01944
52		-1)	19,8719	0,01155	41,36093	0,01935
56		-1)	19,83049	0,01154	41,28667	0,01934
60		-1)	21,96567	0,01204	41,1916	0,01932
64		-1)	25,61795	0,0129	42,11353	0,0195
68		-1)	25,83333	0,01295	42,83709	0,01964
72		-1)	24,34398	0,0126	42,60906	0,0196
76		-1)	23,02913	0,01229	43,13046	0,0197
80		-1)	22,35124	0,01213	43,17319	0,01971
84		-1)	21,37886	0,0119	42,20264	0,01952
88		-1)	20,89084	0,01179	42,8618	0,01965
92		-1)	19,72834	0,01151	42,49222	0,01958
96		-1)	19,67006	0,0115	42,54057	0,01959
100		-1)	21,87467	0,01202	43,06126	0,01969
104		-1)	24,53057	0,01265	43,74417	0,01982
108		-1)	27,25623	0,01329	44,58855	0,01999
112		-1)	29,44036	0,0138	45,35303	0,02014
116		-1)	31,35381	0,01425	46,47789	0,02036
120		-1)	32,29197	0,01448	46,30552	0,02032

TABLE A15. BITUMEN B2 REJUVENATED BY R4 AT 40^{0}C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0		-1)	113,53499	0,07142	109,26137	0,08433
4		-1)	114,54747	0,07179	109,89752	0,08465
8		-1)	116,40856	0,07247	111,04559	0,08522
12		-1)	116,94414	0,07266	111,46043	0,08543
16		-1)	117,66642	0,07292	111,77423	0,08559
20		-1)	118,20096	0,07312	112,0392	0,08572
24		-1)	118,6655	0,07329	112,36018	0,08588
28		-1)	118,50546	0,07323	112,53859	0,08597
32		-1)	118,92832	0,07338	112,55568	0,08598
36		-1)	119,06201	0,07343	112,73746	0,08607
40		-1)	119,23151	0,07349	112,82131	0,08611
44		-1)	119,22709	0,07349	112,94636	0,08617
48		-1)	119,45867	0,07358	113,04701	0,08622
52		-1)	119,52818	0,0736	113,11571	0,08625
56		-1)	119,71284	0,07367	113,37817	0,08639
60		-1)	119,57906	0,07362	113,29029	0,08634
64		-1)	119,66756	0,07365	113,18507	0,08629
68		-1)	119,13239	0,07346	113,18912	0,08629
72		-1)	118,95246	0,07339	113,20802	0,0863
76		-1)	119,26072	0,0735	113,67618	0,08653
80		-1)	119,41395	0,07356	113,53682	0,08646
84		-1)	119,62865	0,07364	113,47896	0,08644
88		-1)	119,77073	0,07369	113,75111	0,08657
92		-1)	120,14994	0,07383	113,82198	0,08661
96		-1)	119,96823	0,07376	113,76466	0,08658
100		-1)	120,18465	0,07384	114,00612	0,0867
104		-1)	120,24646	0,07386	113,86207	0,08663
108		-1)	119,89589	0,07374	113,79567	0,08659
112		-1)	119,85557	0,07372	113,99743	0,08669
116		-1)	119,92101	0,07374	114,07612	0,08673
120		-1)	119,78194	0,07369	114,17423	0,08678

TABLE A16. BITUMEN B2 REJUVENATED BY R4 AT 60^0C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0		-1)	99,72929	0,06522	99,92982	0,07291
4		-1)	95,63314	0,06327	96,39821	0,07105
8		-1)	95,21961	0,06307	96,37152	0,07104
12		-1)	94,83599	0,06289	96,61817	0,07117
16		-1)	94,64067	0,06279	96,57956	0,07115
20		-1)	95,02332	0,06298	96,45534	0,07108
24		-1)	96,10613	0,06349	96,49484	0,0711
28		-1)	97,40109	0,06411	96,68488	0,0712
32		-1)	98,54175	0,06465	96,70282	0,07121
36		-1)	99,50731	0,06511	96,44533	0,07108
40		-1)	100,18067	0,06543	96,86446	0,0713
44		-1)	100,79226	0,06573	97,04191	0,07139
48		-1)	101,39536	0,06601	97,29536	0,07153
52		-1)	101,54592	0,06609	97,20479	0,07148
56		-1)	101,47213	0,06605	97,89048	0,07184
60		-1)	99,79261	0,06525	98,03815	0,07192
64		-1)	98,30821	0,06454	97,5037	0,07164
68		-1)	97,62901	0,06422	97,84853	0,07182
72		-1)	96,32342	0,0636	97,54875	0,07166
76		-1)	95,57244	0,06324	97,67796	0,07173
80		-1)	95,22201	0,06307	97,68998	0,07173
84		-1)	94,64139	0,06279	97,68678	0,07173
88		-1)	94,3541	0,06266	97,71157	0,07174
92		-1)	93,75099	0,06237	97,5014	0,07163
96		-1)	93,77362	0,06238	97,43447	0,0716
100		-1)	94,95278	0,06294	97,87963	0,07183
104		-1)	95,67149	0,06328	98,15035	0,07198
108		-1)	96,67088	0,06376	98,42116	0,07212
112		-1)	97,25885	0,06404	98,73798	0,07229
116		-1)	97,92868	0,06436	98,85504	0,07235
120		-1)	98,57199	0,06467	98,72416	0,07228

TABLE A17. BITUMEN B2 REJUVENATED BY R4 AT 90⁰C

TIME	Calculated Concentration	Absorbance Carbonyl regime	Calculated Concentration	Absorbance Aromatic regime	Calculated Concentration	Absorbance Sulfoxide regime
MIN	[Au]	%	[Au]	%	[Au]	%
0		-$^{1)}$	98,03153	0,05036	98,50882	0,05441
4		-$^{1)}$	77,92214	0,04289	78,95868	0,04722
8		-$^{1)}$	70,65921	0,04019	72,73892	0,04493
12		-$^{1)}$	61,75747	0,03688	64,46505	0,04188
16		-$^{1)}$	56,04049	0,03476	59,19374	0,03994
20		-$^{1)}$	52,45688	0,03342	56,0171	0,03877
24		-$^{1)}$	50,02294	0,03252	53,93812	0,03801
28		-$^{1)}$	48,66557	0,03202	52,42643	0,03745
32		-$^{1)}$	46,80705	0,03175	51,62165	0,03715
36		-$^{1)}$	45,36236	0,0314	51,05065	0,03694
40		-$^{1)}$	44,32473	0,03115	50,36267	0,03669
44		-$^{1)}$	42,06032	0,03061	49,10642	0,03634
48		-$^{1)}$	41,15593	0,03039	47,92598	0,03605
52		-$^{1)}$	40,17687	0,03016	45,86586	0,03556
56		-$^{1)}$	39,78746	0,03007	45,18028	0,0354
60		-$^{1)}$	40,02927	0,03012	44,05515	0,03513
64		-$^{1)}$	39,10887	0,0299	42,93836	0,03486
68		-$^{1)}$	38,66431	0,0298	42,17765	0,03468
72		-$^{1)}$	36,53755	0,02929	39,61772	0,03406
76		-$^{1)}$	34,4691	0,02879	37,98013	0,03367
80		-$^{1)}$	33,45289	0,02855	36,95878	0,03343
84		-$^{1)}$	32,16414	0,02824	35,19306	0,033
88		-$^{1)}$	31,7266	0,02813	34,05546	0,03273
92		-$^{1)}$	30,483	0,02784	32,41323	0,03234
96		-$^{1)}$	29,2619	0,02754	30,53718	0,03189
100		-$^{1)}$	27,85234	0,02721	29,87522	0,03173
104		-$^{1)}$	26,96252	0,02699	28,93394	0,0315
108		-$^{1)}$	25,89846	0,02674	27,62823	0,03119
112		-$^{1)}$	25,39114	0,02662	27,21671	0,03109
116		-$^{1)}$	24,23003	0,02634	25,77582	0,03075
120		-$^{1)}$	24,15158	0,02632	25,5247	0,03069

Appendix 2 Calibration graphs

This appendix provides the graphical representation of experimental data points correlated with the calibration curves. The data points were plotted by using the same concentration and absorbance values obtained from the concentration tables. The consistency of experimental data with calibration curves of standard concentration can be classified from the graphs. Experimental description was presented with each graph.

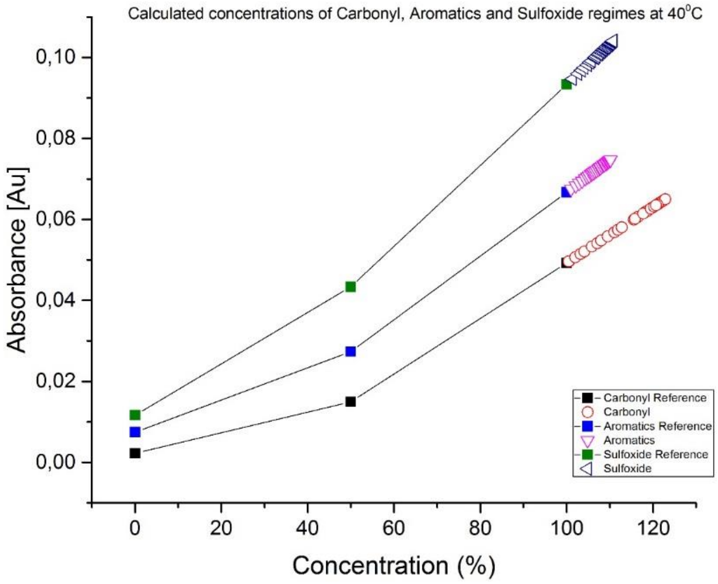

Figure A1. Calibration curve for the experiment of 1R rejuvenation by using R3 at 40^{0}C

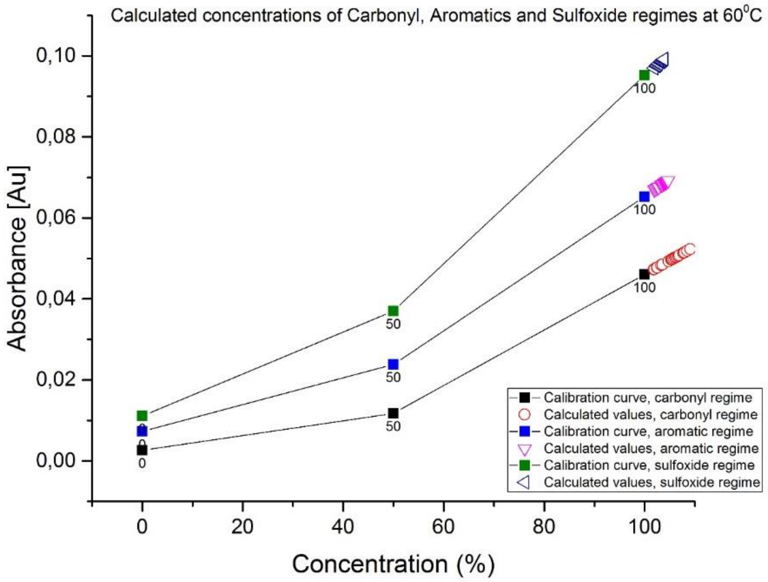

Figure A2. Calibration curve for the experiment of 1R rejuvenation by using R3 at 60^{0}C

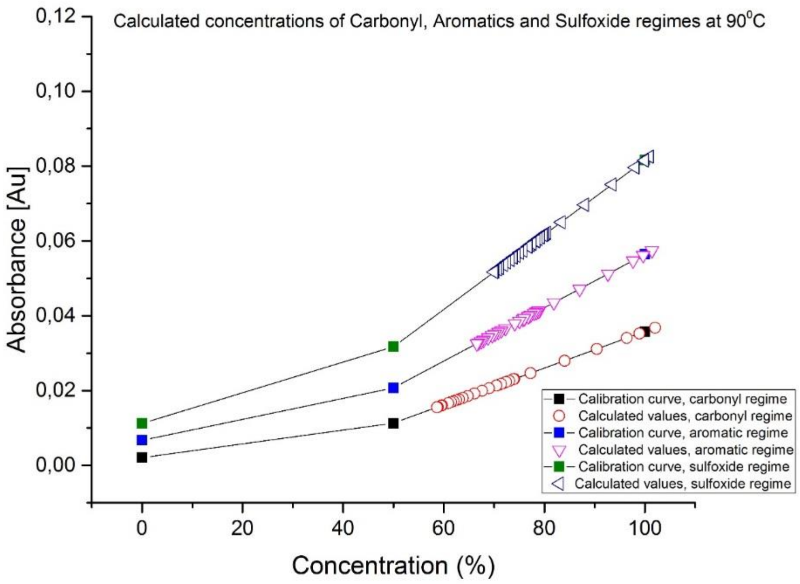

Figure A3. Calibration curve for the experiment of 1R rejuvenation by using R3 at 90^{0}C

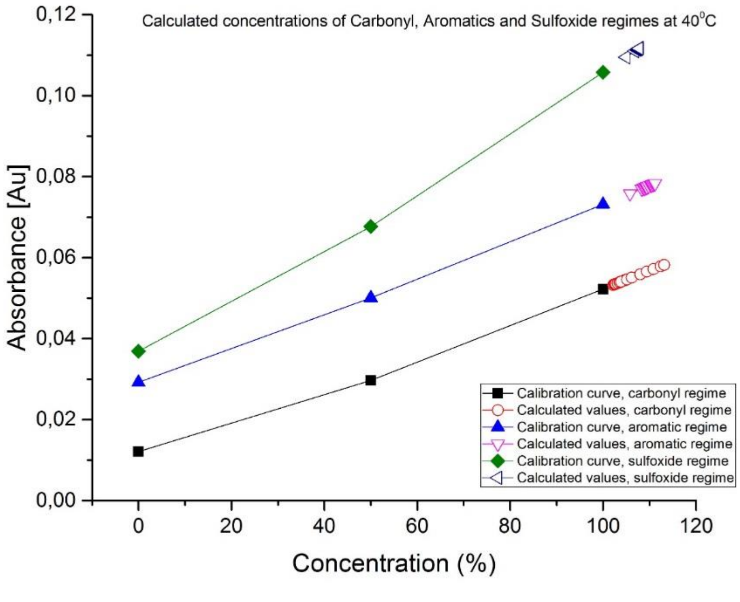

Figure A4. Calibration curve for the experiment of 1R rejuvenation by using R4 at 40^{0}C

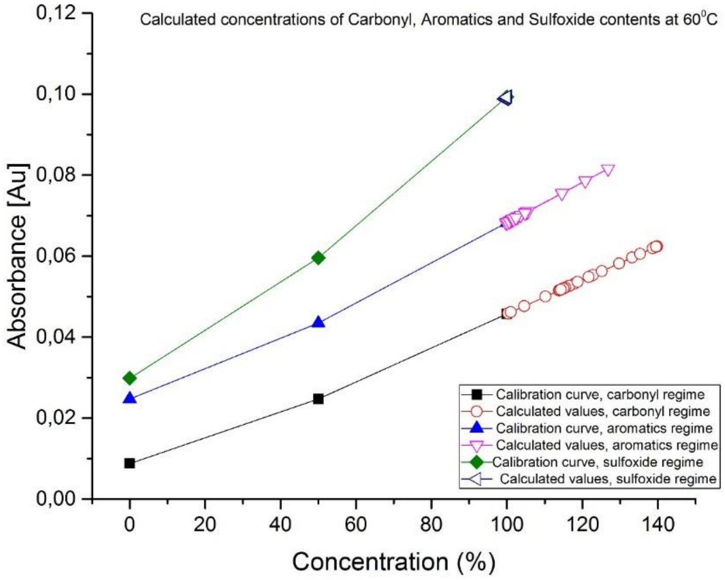

Figure A5. Calibration curve for the experiment of 1R rejuvenation by using R4 at 60^0C

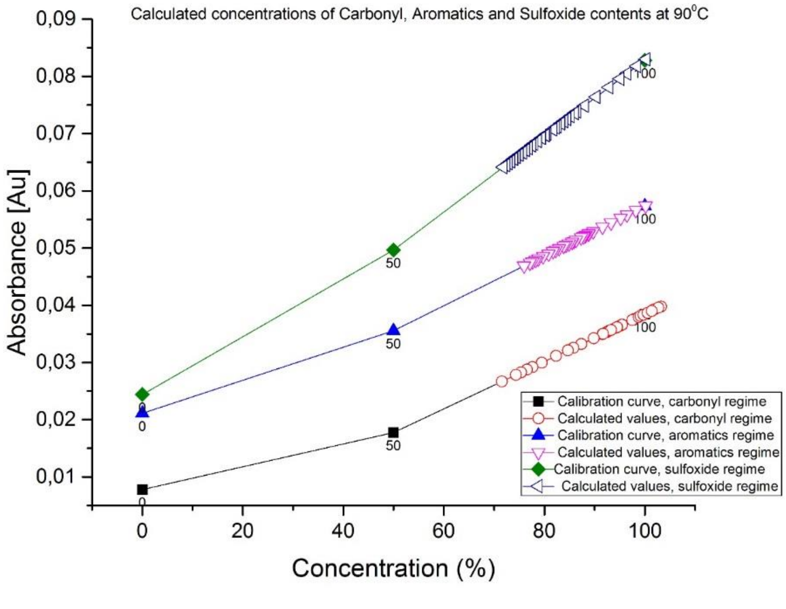

Figure A6. Calibration curve for the experiment of 1R rejuvenation by using R4 at 90^0C

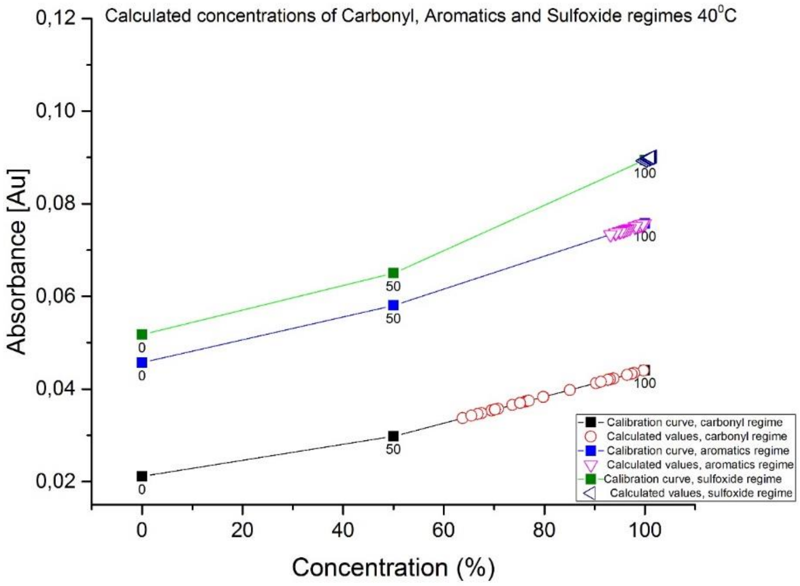

Figure A7. Calibration curve for the experiment of B2 rejuvenation by R1 at 40^0C

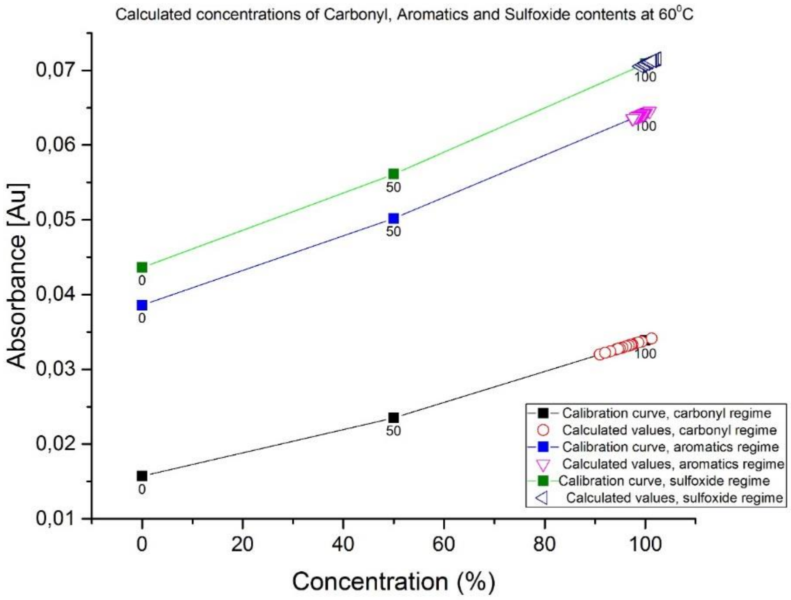

Figure A8. Calibration curve for the experiment of B2 rejuvenation by R1 at 60^0C

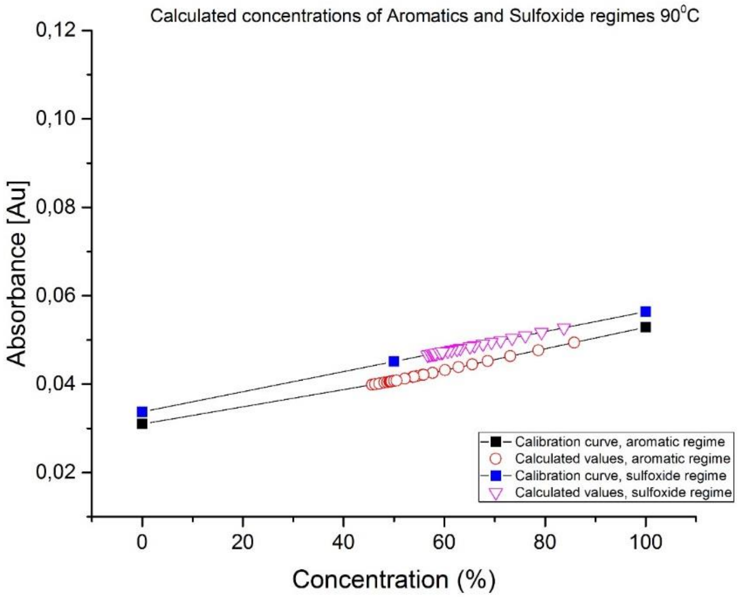

Figure A9. Calibration curve for the experiment of B2 rejuvenation by R1 at 90^{0}C

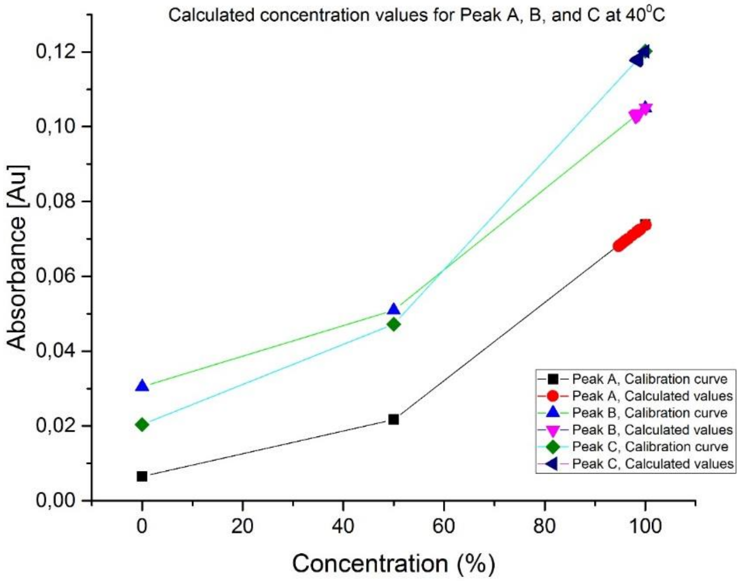

Figure A10. Calibration curve for the experiment of B2 rejuvenation by R2 at 40^{0}C

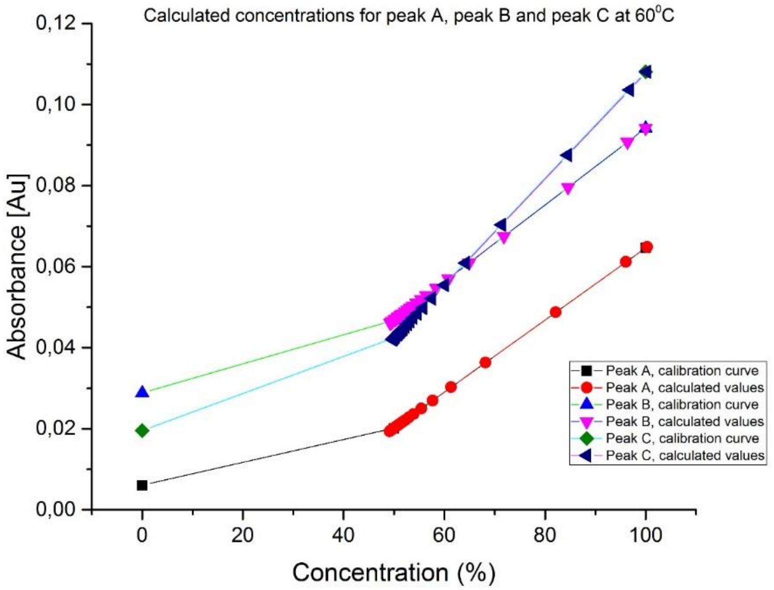

Figure A11. Calibration curve for the experiment of B2 rejuvenation by R2 at 60^0C

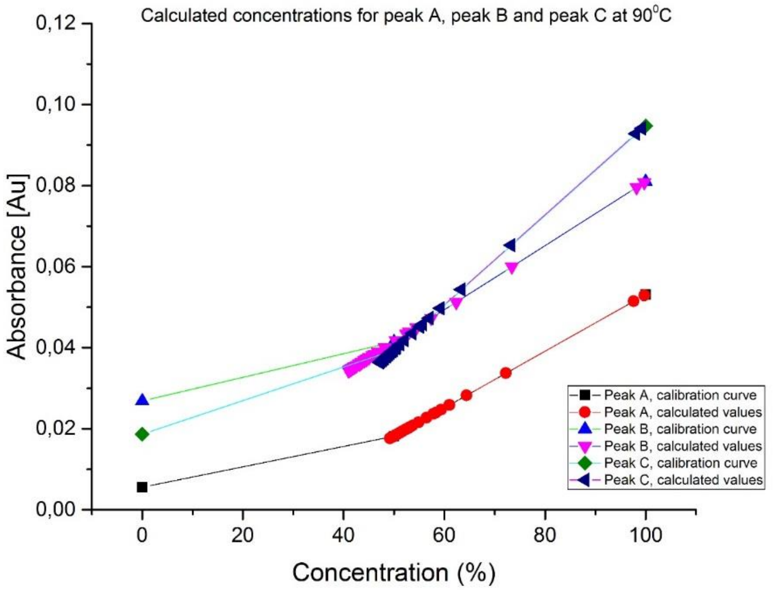

Figure A12. Calibration curve for the experiment of B2 rejuvenation by R2 at 60^0C

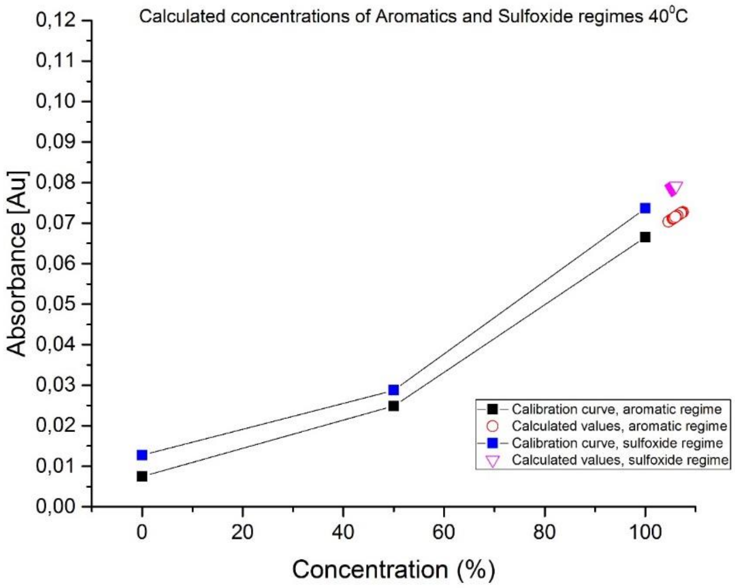

Figure A13. Calibration curve for the experiment of B2 rejuvenation by R3 at 40^0C

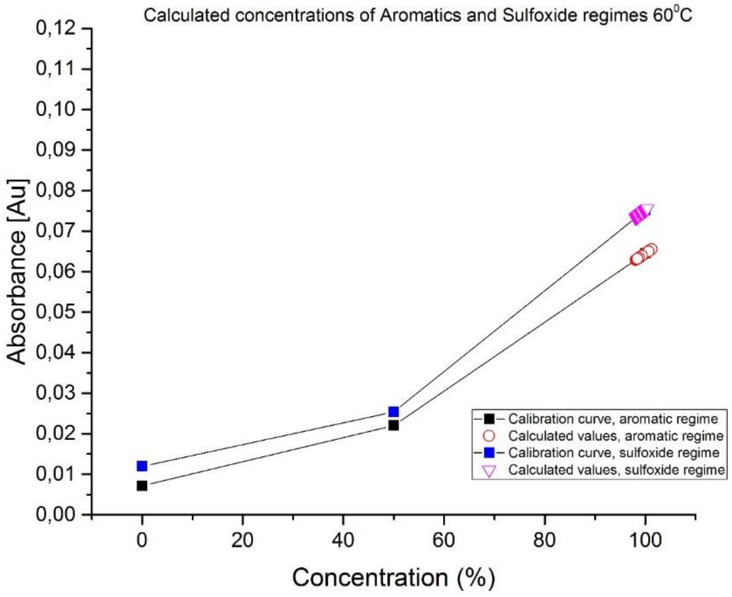

Figure A14. Calibration curve for the experiment of B2 rejuvenation by R3 at 40^0C

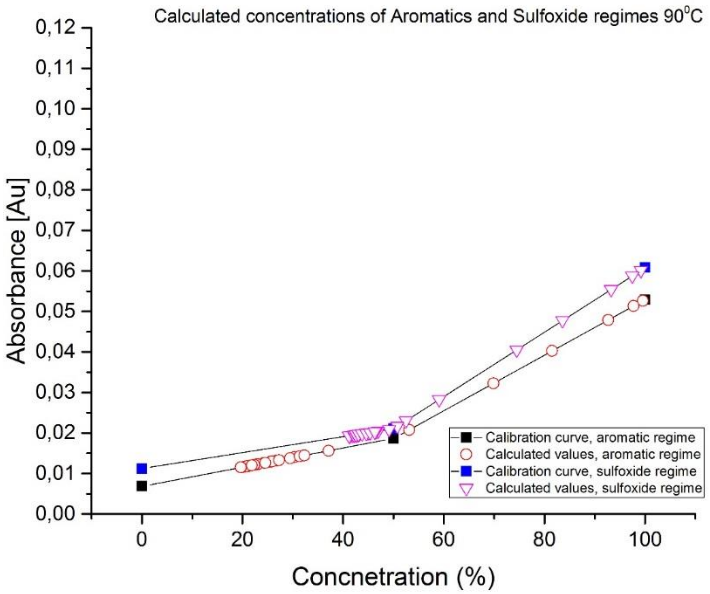

Figure A15. Calibration curve for the experiment of B2 rejuvenation by R3 at 90^0C

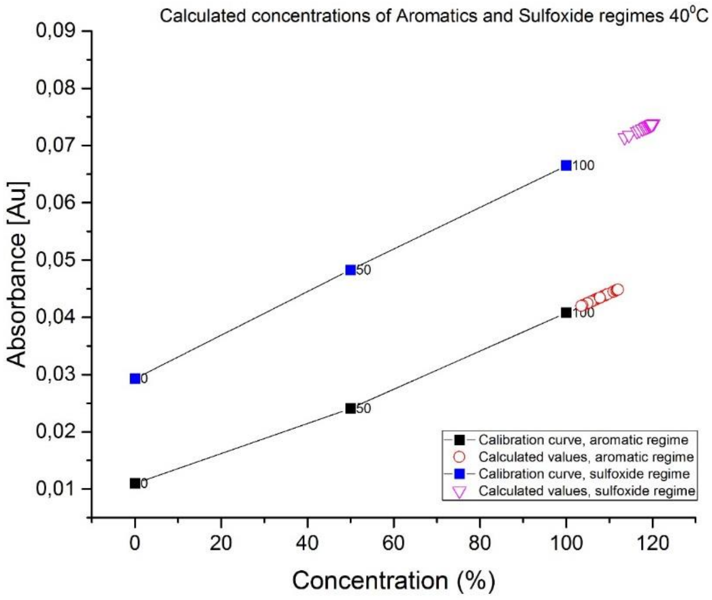

Figure A16. Calibration curve for the experiment of B2 rejuvenation by R4 at 40^0C

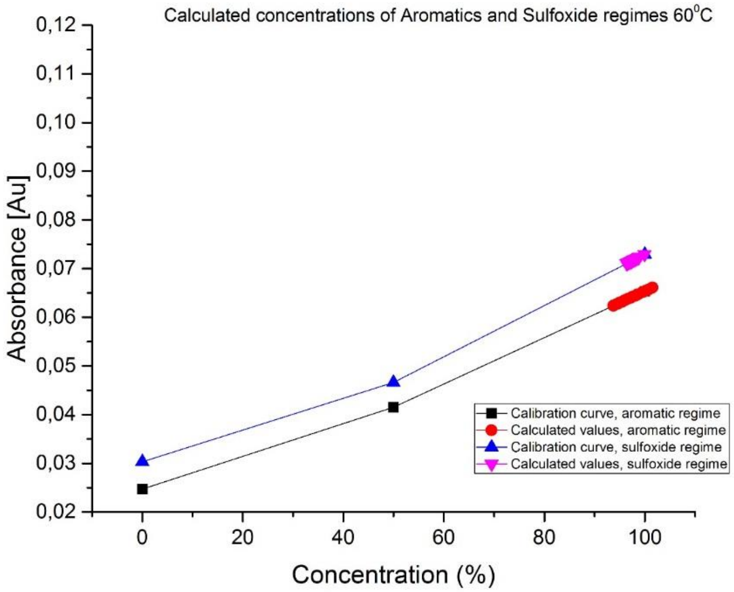

Figure A17. Calibration curve for the experiment of B2 rejuvenation by R4 at 60^0C

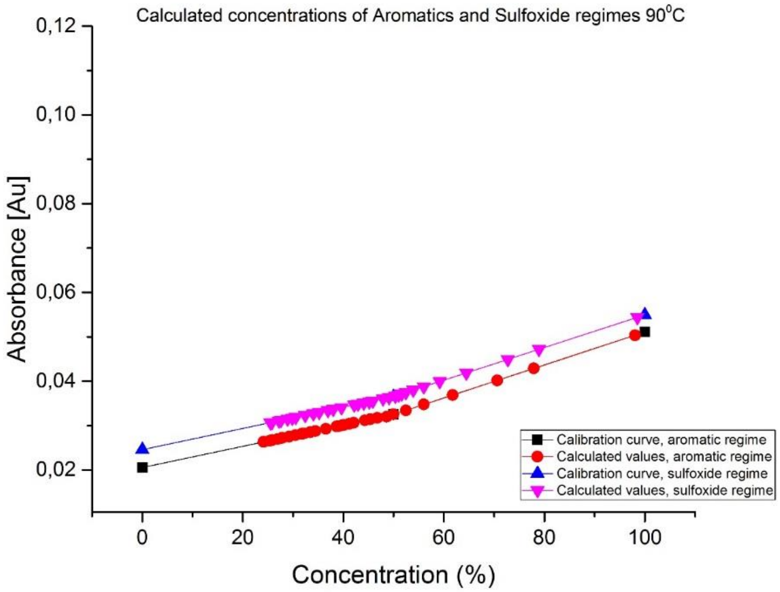

Figure A18. Calibration curve for the experiment of B2 rejuvenation by R4 at 90^0C