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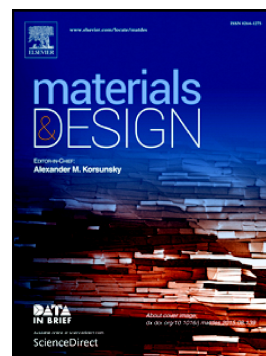
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Physical and rheological characterization of carbonated bitumen for paving applications

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ABSTRACT

In the paving industry, current attempts aimed at reducing greenhouse gas emissions have focused on the development of technologies that decrease bitumen viscosity so that asphalt mixtures can be produced at temperatures that are lower than conventional mixing temperature for hot-mix asphalt. This study focuses on the feasibility of producing new lower energy asphalt mixtures using CO_2-modified bitumen. Gravimetric sorption techniques were used to establish the kinetics of CO_2 diffusion in bitumen at multiple pressures. The rheological properties of the carbonated bitumen were characterized at multiple temperatures and loading frequencies using a dynamic shear rheometer.

The results showed that CO_2, at concentrations of up to about 0.3% w/w, caused significant (up to 3-folds) reduction in bitumen viscosity. A 10-fold increase in equilibrium CO_2 uptake was observed when binders were conditioned in CO_2 at 300 psi versus at 40 psi. The carbonated bitumen developed in this study has potential application in the production of lower energy asphalt mixtures. The work presents a novel application of CO_2 at subcritical conditions, to reducing bitumen viscosity so that asphalt can be produced at lower temperature for paving applications. The work represents the first time such as attempt has been in the asphalt paving industry.

1. Introduction

Bituminous mixtures used for pavement construction such as hot-mix asphalt (HMA), warm-mix asphalt (WMA), and cold-mix asphalt (CMA) are all produced by coating mineral aggregates with fluidized low-viscosity bitumen (usually in very thin films) in a mixing plant , and then compacting the resulting mixture in the field to achieve the final product. At ordinary temperatures, paving grade bitumen is a highly viscous material with viscosity at 60°C on the order of 100-1000 Pa.s, depending on type, compared with the recommended asphalt mixing and compaction viscosities of 0.17±0.02 Pa.s and 0.28±0.03 Pa.s, respectively. Thus in practice, substantial effort in terms of energy (HMA), additives and/or expensive processes (WMA), and solvents and/or expensive processes (CMA) are required to reduce bitumen viscosity in order to achieve the recommended mixing and compaction viscosities for asphalt mixture production. Of the existing methods, the most commonly used (and also the least sustainable) is the reduction of bitumen viscosity using fossil fuel-powered plants (that generate substantial amount of greenhouse gases) to heat (130°C -160°C for HMA) the bitumen and thereby decrease its viscosity. The current method of asphalt mixture production that utilizes high temperature mixing and compaction temperatures are considered not sustainable in the long-term because of its dependence on fossil fuels for generating the required heating energy and its release of substantial greenhouse gasses. The increasing levels of greenhouse gases in the atmosphere have been linked with global warming that can lead to climate change (Meehl et al., 2007).

Recent attempts at reducing greenhouse gas emissions have been in the development of viscosity-modifying technologies such as foaming with water (eg Advera), waxes (eg Sasobit), foaming and emulsification (low-energy asphalt) that decrease viscosity of bitumen so that asphalt mixtures can be produced at temperatures that are lower than conventional mixing temperature (~150°C) HMA [Koenders et al., 2000; Romier et al. 2006; Prowell and Hurley, 2007; Jones et al., 2010; Kvasnak et al. 2010; Visscher et al., 2010; Zelelew et al., 2013]. A reduction in mixing temperature of about 10-20°C can be achieved using this so-called warm-mix asphalt (WMA) technology. However, the savings obtained by reducing mixing temperatures used in WMA production are offset by the higher production cost (WMA may cost up to 40% more than HMA) because of additives/processes required to produce WMA and the comparatively large amount of greenhouse gasses that are still produced. Another attempt at reducing the greenhouse footprint of asphalt pavements has been the gradual phasing out of volatile organic solvents for reducing bitumen viscosity. Because of obvious environmental concerns, conventional solvents (such as Naphthalene, gasoline, kerosene, white spirit) are rarely used nowadays to reduce bitumen viscosity for

paving applications even though there are currently limited or no apparent environmentally acceptable replacements. Thus, there is a major need for improvement in asphalt mixture production in terms of 1) reducing bitumen viscosity for lower temperature applications, 2) more environmentally sustainable solvents, and 3) reducing CO_2 emission footprint of the paving industry. This study targets how current asphalt production technologies could be made even more sustainable by exploiting the unique properties of CO_2 at or near its critical conditions (Figure 1) to act as an effective viscosity-reducing solvent in paving grade bitumen. Carbon dioxide at or above its critical temperature of 31.1°C (304.25°K) and pressure of 7.39 MPa (73.9 bar) can exist as a dense gas or liquid with dual gas (high diffusivity) and liquid (good solvent) properties in most polymeric materials.
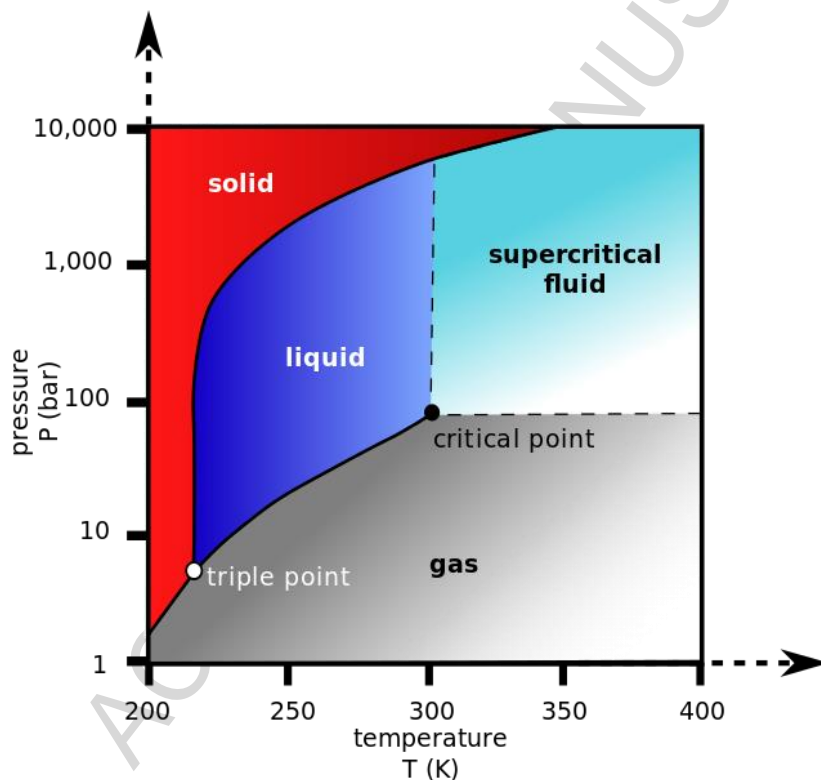
Figure 1. *CO_2 pressure-temperature phase diagrams (after Jacobs, 2005).*

The critical properties of CO_2 are important because under critical conditions CO_2 has the density of a liquid but the diffusional properties of a gas which may explain the high solubility of CO_2 in bitumen and other polymers. For instance, diffusion of CO_2 in bitumen can be extremely high (~280x10-^{12}m^2/s [Tharanivasan et al., 2006; Upretit and Mehrotra, 2002; Zhang et al., 2000; Mehrotra and Svrcek, 1988;

Saboorian-Jooybari et al. 2014] compared to moisture in bituminous materials (~$1 \times 10^{-12} m^2/s$ [Apeagyei et al. 2014]). The ability of pressurized CO2 to dissolve profusely in bitumen could be accompanied by significant reduction in viscosity. These unique properties of bitumen have been exploited in the recovery of bitumen from oil fields [Seright, 2016; Saboorian-Jooybari et al. (2015); Saboorian-Jooybari et al. (2016); Seright 2017]. The ability of pressurized CO_2 to dissolve profusely in bitumen could be accompanied by significant reduction in viscosity. It was anticipated that understanding how CO_2 (near its critical temperature of 31°C) interacts with bitumen can lead to new approaches for producing asphalt mixtures at reduced temperatures using more eco-friendly and sustainable techniques.

The overall aim of this research was to investigate the feasibility of reducing bitumen viscosity by CO_2 modification of paving grade bitumen as a technique for producing lower energy, more environmentally sustainable asphalt mixture. Two grades of bitumen with different viscosities, a harder 40/60pen and a softer pen 160/220 that are commonly used in the UK were used for the experimental work. Four specific objectives to achieve the aim of the project included: a) evaluating the kinetics of CO_2 diffusion in bitumen using gravimetric sorption techniques at multiple temperatures and pressures; b) evaluating the desorption kinetics of CO_2-modified bitumen under ambient conditions to establish its storage stability, c) undertaking laboratory measurement of the viscosity-temperature relationships of the modified bitumen at multiple loading frequencies using a dynamic shear rheometer in order to characterize the viscoelastic response of CO_2-modified bitumen. The results were used to determine the feasibility of using CO_2 as a solvent for producing eco-friendly sustainable bitumen for paving application by relating the diffusivity of CO_2 in bitumen to rheological changes in bitumen modified by CO_2. A novel feature of the current study, compared to previous studies, is the use of CO_2 at subcritical conditions (20-25°C and pressures 0.4 – 2MPa). Another innovation is the application of CO_2-modified bitumen for paving applications.

2. Background

2.1 Interactions of CO_2 and bitumen mixtures

Bitumen is a complex mixture of polymers that can interact with CO_2 through physical diffusion. This ability of CO_2 is due to the unique property of CO_2 to exist as a supercritical fluid at temperatures close to ambient (Figure 1). The relatively high diffusivity of CO_2 results in substantial solubility in bitumen with reported values ranging from 0.5 to 11% depending on prevailing temperature and pressure as well as

physical interaction between bitumen and CO_2. It has also been established that near critical or super-critical conditions, CO_2 can cause significant changes in bitumen. One of the most important effects of CO_2 dissolution in bitumen is viscosity reduction or plasticization characterized by changes in mechanical and physical properties such as the significant reduction in glass transition temperature. The plasticizing effect of CO_2, especially supercritical CO_2, has been exploited in the enhanced crude oil recovery, where CO_2 under in-situ crude oil pressures (2-20 MPa) are often used as solvents in bitumen recovery and also in CO_2 sequestration in depleted oil reservoirs. Other important physical property changes caused by CO_2 interaction with bitumen include diffusivity modification, viscosity reduction, glass transition suppression, and melting pointers. These properties are important in many industrial applications where polymer melts need to be processed into useful products. In these applications, CO_2 has several advantages over existing solvents and other extraction techniques. For example, CO_2 is economical, environmentally friendly, and sustainable. For these and other novel applications, as presented in this paper, certain fundamental properties of CO_2-bitumen mixtures need to be quantified. These properties include diffusivity (diffusion coefficient) and temperature and time dependent rheological properties.

2.2 Diffusion of CO_2 in Bitumen

Diffusion can be defined as the movement of molecules from a region of high concentration to a region of low concentration. Previous studies have shown that the diffusional ability of (supercritical) CO_2 in bitumen, as in many other polymers, could be substantial with reported values of up to 10 wt%. The mechanism by which CO_2 diffuses in bitumen has been extensively investigated especially in the chemical and petroleum industries where both theoretical and experimental approaches have been used (Sheikha et al. 2005; Tharanivasan et al. 2006; Ratnakar and Dindoruk, 2015; Civan and Rasmussen, 2006). Of these, the pressure-decay method in which the pressure of the CO_2 gas is monitored over time, while the molecules of the gas diffuse into the bitumen until equilibrium pressure is reached is the most commonly used, especially in the enhanced crude oil recovery area. As shown in Table 1, different equilibrium pressures have been used by different authors resulting if different CO_2 diffusivities being reported. According to Zhang et al. 2000, diffusivity is highly sensitive to the estimated value of the equilibrium pressure. Therefore, a major drawback of the pressure-decay method is the difficulty in precisely determining the equilibrium pressure and its effects on the estimated diffusivity as illustrated by Behzadfar and Hatzikiriakos 2014. Therefore, the pressure decay approach was not adopted in the current. Also, the majority of previous studies have focused on the diffusion of supercritical CO_2 to better

simulate typical conditions used during crude oil extraction. For paving applications, which is the focus of this paper, CO_2 near or below supercritical conditions (low pressures and moderate temperatures) are to be preferred for obvious reasons.

Table 1. *Selected list of CO2 diffusivity studies using the pressure-decay method*

Material	T (°C)	P_0 (MPa)	P_{eq} (MPa)	D (x10^{-9}m^2/s)	Reference
Heavy oil	21	3.4	2.9	4.76	Zhang et al., 2000
[1]Bitumen	25-90	4.0	3.1-3.5	0.16-0.47	Upreti & Mehrotra, 2002
[1]Bitumen	50-90	8.0	N/A	0.40-0.93	Upreti & Mehrotra, 2002
Bitumen	75, 90	4.0	3.1-3.2	0.51-0.79	Sheikha et al., 2005

NOTE: [1] Athabasca bitumen; P_0 = initial pressure, Peq = equilibrium pressure.

2.3 Modeling of CO₂ Diffusion in Bitumen

For experimental expediency and to circumvent some of the aforementioned problems, a gravimetric sorption technique in which pressured CO_2 is allowed to diffuse freely into a planar sample of bitumen held in an impervious metal container such that diffusion occurs through a process as shown in Figure 2 was used. By maintaining the pressure of the CO_2 in the pressure vessel at a constant level, the gravimetric approach we used ensured that the concentration at the bitumen-CO_2 interface was independent of time. As shown in Figure 2, the nature of experimental set-up sample container (aluminum can with only the top open to the pressurized CO_2), the assumption of 1-D diffusion appears valid. A brief discussion of the diffusion models for this CO_2-bitumen is described below.

For the situation illustrated in Figure 2 (assuming one-dimensional diffusion in a thin medium (bitumen) bounded on two parallel planes (at x=0 and x= l) such that the diffusing CO_2 gas enters through the plane where x=0, that the surface at x= l is impermeable, and that a negligible amount of diffusion occurs through edges between the aluminum container and the bitumen) it has been shown by Crank (1975) that Eq. 1, which is a solution to Fick's diffusion model is applicable for $0 < x < l$, where l is specimen thickness.

For this study only the first 19 terms in the series expansion in Eq. 1 were used for estimating the diffusion coefficient as suggested by Tutuncu and Labuza (1996). Using the CO_2 uptake data and Eq. 1, CO_2 diffusion coefficient values for the two bitumen samples were estimated.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{\frac{-D(2n+1)^2 \pi^2 t}{4l^2}} \tag{1}$$

where M_t = CO_2 uptake at time t; M_∞ = equilibrium moisture uptake; l = specimen thickness; and n = an integer and n takes the values 0, 1, 2, … 19.
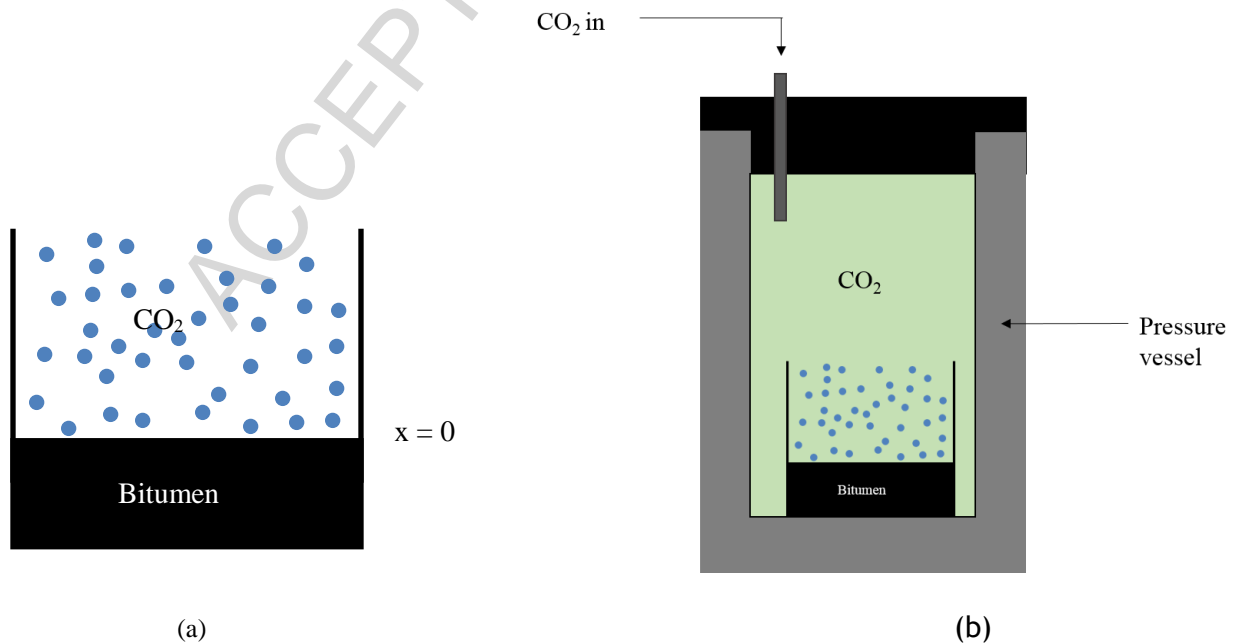
(a)

(b)

Figure 2. *Schematic of bitumen specimen in an impermeable aluminum can that was used for CO_2 diffusion experiments.The tests were conducted in a pressured vessel (b) maintained at a constant pressure so that the concentration of CO2 at the bitumen-CO2 interface remained constant throughout the test and thus ensuring a one-dimensional diffusion.*

2.4 *CO_2 Uptake Profiles*

A CO_2 uptake profile describes the relationship between the amount of CO_2 (M_t) a material exchanges (absorbs or desorbs), at a given gas pressure and temperature, with time. If w_0 is the initial (dry) mass of a given material and w_t is the mass after time t, then the CO_2 uptake can be computed as the ratio of the amount of CO_2 absorbed at a given time to the initial dry mass of the sample at the of beginning the test (Eq. 2). For a material at a given temperature and gas pressure, CO_2 uptake by bitumen increases until it reaches a thermodynamic equilibrium at which point no further changes in CO_2 uptake occurs. The uptake at thermodynamic equilibrium (M_∞) is called equilibrium CO_2 uptake.

The data (mass uptake and conditioning time) were fitted to a two-parameter non-exponential empirical model proposed by Peleg (1988) for moisture diffusion in foods. The Peleg model shown in Eq. 3 enables prediction of moisture uptake after long exposure from experimental data obtained in relatively short time. The model has been found to model moisture diffusion of bituminous mixtures very well (Apeagyei et al. 2013). The model parameter C_1 represents the rate of CO_2 uptake while C_2 is a measure of the equilibrium CO_2 content (reciprocal of the maximum CO_2 uptake).

$$Mass\,uptake\,(\%) = M_t = \frac{w_t - w_0}{w_0} \tag{2}$$

$$M_t = \frac{t}{C_1 + t * C_2} \tag{3}$$

3. MATERIALS AND METHODS

3.1 Bitumen

Two different bituminous binders, one 50 Pen (40/60 penetration paving grade) and one 190 Pen (160/220 penetration paving grade) were used as base binders to produce the CO_2-modified binders (carbonated bitumen). The two binders were different in terms of their consistencies as well as their crude source and therefore, were expected to display different physical and chemical properties in both the modified and unmodified state. The physical properties of the binders were characterized using standard bitumen empirical tests by their penetration, ring and ball softening point, and mass loss, as presented in Table 2. One important difference between the two binders was the amount of volatile components they contain. The mass loss in the softer 190 Pen bitumen was more almost three times that of 50 Pen bitumen which suggests the former has significantly higher amounts of volatile organic content than the later. The mass loss for 160/220 paving grade binders is limited to 0.5% since excessive amounts of volatile components could lead to excessive hardening during bitumen storage, application or in service (Whiteoak, 1991).

Table 2. *Physical properties of for base binders.*

Bitumen	Penetration (dmm)	Softening point (˚C)	Mass loss (wt%)
190 Pen	187	38	0.44
50 Pen	53	50	0.16

NOTES: Physical properties determined according to BS 3690 Part 1: Specification for penetration grade bitumen; dmm = decimillimetre

3.2 Carbon dioxide (CO_2)

The 99.99% high purity carbon dioxide used for modifying the bitumens was supplied by BOC Industrial Gasses in 150 cm tall by 23cm diameter stainless steel containers. The critical properties of the CO_2 were respectively, 31.1°C and 7.38 MPa for critical temperature and critical pressure. Density of CO_2 was assumed to be 0.001977 g/cc. Figure 1 depicts additional physical properties CO_2 in the form a temperature-pressure phase diagram commonly reported in the literature.

3.3 Preparation of carbonated bitumen

The experimental test set-up for producing the carbonated bitumen is presented in Figure 3 which shows compressed CO_2 at room temperature designed to diffuse into bitumen at room temperature. The set-up used was a modified version of the Saturation Ageing Tensile Stiffness (SATS) developed at the University of Nottingham (Collop et al. 2004) with the air and steam supplies replaced with bone-dry CO_2 (Figure 4). It consists of a compressed CO_2 gas cylinder connected, via high capacity pressure transducers and associated pressure valves, to a Paar high capacity pressure vessel capable of handling pressure ranging from 0-20 bar at temperatures ranging from 20-80°C. The pressure vessel is equipped with sample holders capable of holding six separate specimens on vertical stainless steel racks as depicted in Figure 3. Bitumen samples each weighing approximately 10 g were placed in steel cans to form a nominal thickness of about 5 mm. CO_2 at two different pressures, 40 psi and 300 psi, and at temperatures (22-25°C) close to the critical temperature of CO_2 was employed for the carbonation process. One reason for selecting the conditioning temperature close to the critical temperature was that CO_2 behaves as a dense liquid but with diffusivity of a gas. Two penetration grade bitumens (50 Pen and 190 Pen) were used to produce the CO_2-modified binders (carbonated bitumen). The two bitumens were different in terms of their consistencies as well as their crude source and therefore, were expected to display diverse physical and chemical properties in both the modified and unmodified state.
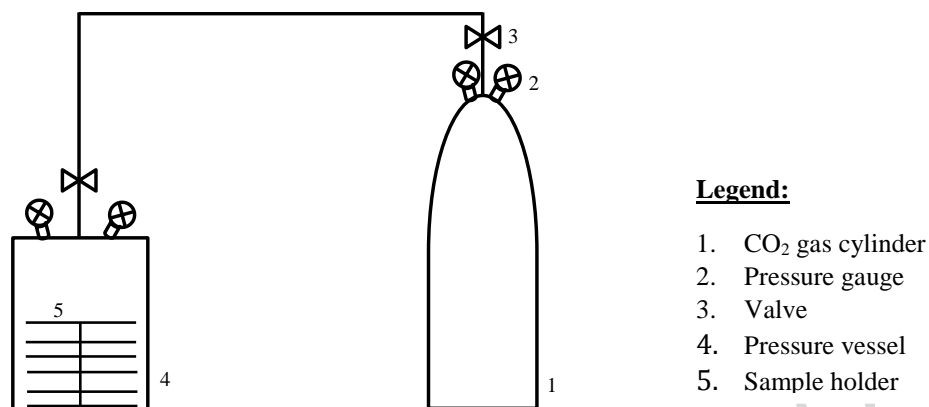
Legend:

1. CO_2 gas cylinder
2. Pressure gauge
3. Valve
4. Pressure vessel
5. Sample holder

Figure 3. *Schematic of the CO2 system used for modifying bitumen.*

Figure 4. *Modified SATS test set-up consisting of pressure vessel, pressure and temperature controllers, and bitumen sample holder for producing CO_2-modified bitumen.*

3.4 Kinetics of CO_2 Diffusion in Bitumen

The kinetics of CO_2 diffusion in bitumen was measured using gravimetric analysis at multiple temperatures. Similar techniques have been used successfully to study the diffusion moisture in bituminous mixtures (Apeagyei et al. 2013). The amount of CO_2 absorption by bitumen as a function of time and pressure under isothermal conditions were determined and the results used to develop kinetic models for diffusion of CO_2 in bitumen.

3.5 Storage Stability of CO_2-Bitumen Mixture

For paving applications, it was deemed important to establish the time frame over which the viscosity-reducing effects of CO_2 lasts under anticipated conditions for low-energy highly sustainable asphalt mixture production (referred to as storage stability in this paper). It was assumed that storage stability of the CO_2-modified binder frame could be related to the CO_2 content of the modified binder that remains in solution after a given time at ambient conditions. The storage stability could be considered as analogous to the half-life (measured in tens of seconds) that is commonly used to determine the stability of foamed bitumen for asphalt mixtures. Therefore, in order to establish this time frame, samples of CO_2-modified bitumen were stored under ambient temperature and pressure and the mass loss with time monitored with a sensitive micro-balance. The results were used to generate "desorption" kinetics of the CO_2-modified bitumen. Another reason for determining the desorption profile was to determine if the interactions between CO_2 and bitumen were purely physical, chemical or some combination of both.

3.6 Rheological Characterization of CO_2-Bitumen Mixture

Experiments to establish the rheological properties of the CO_2-modified binders were undertaken by regularly taking samples used for the kinetics studies previously described and performing dynamic mechanical analysis (DMA) on them using a dynamic shear rheometer (DSR). A DMA is an extensively used technique to characterize a material's properties as a function of temperature, time, frequency, stress, atmosphere or a combination of these parameters. In strain-controlled DMA, a sinusoidal strain is applied to a specimen and the resulting stress is monitored as a function of frequency. The DSR tests were conducted in the strain-controlled mode. With the DSR it was possible to measure the linear viscoelastic properties of bituminous binders such as stiffness and viscosity at different temperatures, stress and strain levels, and test frequencies. The following DSR testing conditions were used:

a) mode of loading: controlled strain
b) testing temperatures: 20°C, 5°C, and 0°C
c) testing frequencies: 0.1-10 Hz
d) plate geometry: 8 mm diameter parallel plate with 3 mm gap
e) strain amplitude: 0.1%

One of the key analytical techniques used in evaluating DMA data involves the construction of master curves and the associated temperature shift-factors. Master curves are constructed using the time-

temperature superposition principle by shifting the modulus data at various temperatures with respect to frequency until the curves merged into a single function of modulus versus reduced frequency. The amount of shifting required at each temperature to form the master curve is called the shift factor, a(T). A plot of log a(T) versus temperature can be considered as the viscosity changes with respect to the reference temperature. Thus the master curve and shift-factor versus temperature curve provide complete characterization of the viscoelastic behavior of bituminous binders. In general, a master curve can be modeled as a sigmoidal function (Eq. 4) and the model parameters estimated using numerical optimization techniques: where: f_r is the reduced frequency at the reference temperature (equal to a(T) times test frequency); and δ, α, β, and γ are model parameters.

$$\log G^* = \delta + \frac{\alpha}{1 + e^{\beta + \gamma \log f_r}} \qquad (4)$$

The viscosity-reducing effect of CO_2 in bitumen was evaluated by means of a softening index, SI, defined as:

$$SI = \frac{RP_{modified}}{RP_{unmodified}} \qquad (5)$$

where: $RP_{unmodified}$ represents some rheological property measured on the unmodified binder (such as modulus, viscosity, etc); $RP_{modified}$ represents the same rheological property as measured on the unmodified binder but performed after modification. Thus SI can take values in the range 0 to 1. For example, a modified binder with a smaller SI would indicate a larger effect of CO_2 than a binder with a higher SI.

4. Results and Discussion

4.1 Kinetics of CO_2 diffusion in bitumen

Kinetics of CO_2 diffusion in bitumen at 20°C were determined using gravimetric sorption techniques by placing 5 mm thin films of bitumen in a pressure vessel kept at 40 psi (0.28 MPa) for periods of up to 170 hours and monitoring the weight gain with conditioning time using an ultra-sensitive weighing balance (0.1μg). The amount of CO_2 absorbed by each binder was computed using Eq. 2. Figure 5 shows the kinetics of CO_2 diffusion for the two bitumen samples plotted as a function CO_2 conditioning time. The data represent the average CO_2 uptake for at least three different bitumen samples measuring about 50 mm diameter by 5 mm thick and weighing about 10 g. The error bars shown in Figure 5 represent one standard deviation of the mean CO_2 uptake. The equilibrium uptake values for the two binders were 0.41±0.0306wt % and 0.3324±0.0277 wt % for 160 pen and 50 pen, respectively. This suggests the amount of CO_2 absorbed by the two binders were of the same order of magnitude and that the differences in equilibrium CO_2 uptake by the two types of bitumen were not statistically significant. However, the data also shows that high-viscosity 50 Pen bitumen absorbed relatively lower amounts of CO_2. The equilibrium CO_2 uptake obtained in this study is comparatively lower than reported values of CO_2 diffusion in bitumen that have been reported by previous researchers. This could be attributed to the fact that majority of the reported CO_2 diffusion studies were conducted at or near supercritical conditions as exemplified by the data presented in Table 1.
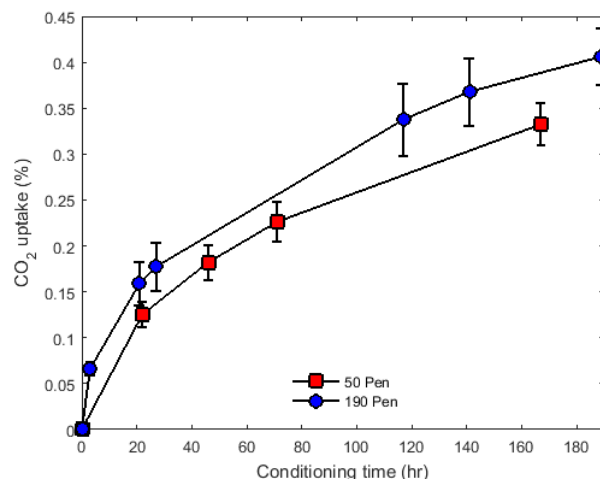
Figure 5. *CO_2 diffusion kinetics in bitumen at 20°C and 40 psi. Error bars represent one standard deviation of the mean. CO_2 uptake was observed to be higher in the softer 160-220 pen bitumen than in the harder 40-60 pen bitumen.*

4.2 Diffusivity and Equilibrium Uptake of CO_2 in bitumen

The changes in CO_2 concentration in bitumen over time were predicted using Eq. 3 (Pelleg model). The purpose of the model was used to quantify the relationship between CO_2 uptake over time in order to smooth the measured data for analysis, provide a theoretical estimate of equilibrium CO_2 uptake and ensure accurate determination of the diffusion coefficient or the diffusivity of CO_2 in bitumen. A least square regression analysis was used to estimate the model parameters C_1 and C_2 in Eq. 3. The results of the regression analysis showing a good fit of the CO_2 uptake data by Pelleg model are shown in Figure 6. The model parameters were utilized in three ways in order to characterize the diffusion of CO_2 in bitumen. First, the model parameters C_1 and C_2 were used to generate cumulative CO_2 uptake as a function of time (Figure 7) from which Fick's second law (Eq. 1) was applied to estimate the diffusion coefficient of CO_2 in bitumen at 20°C and 40 psi as 40.2×10^{-12} m^2/s for the 190 Pen bitumen and 36.3×10^{-12} m^2/s for the 50 pen bitumen. The diffusion coefficient values obtained for the binders used in this study appear reasonable when compared to D obtained for supercritical bitumen (Table 1). As previously stated, the model parameter C_1 represents the rate of CO_2 uptake while C_2 is a measure of the equilibrium moisture content (reciprocal of the maximum water uptake). The C_1 data suggest that the rate of CO_2 uptake is relatively higher in 50 Pen (140.45) compared with 190 Pen bitumen (90.6612). The data also suggest, based on the reciprocal of C_2, that the theoretical equilibrium CO_2 uptake under the experimental conditions of 20°C and pressure of 40 psi in 160 Pen 160 (0.48%) was comparable to that in 50 Pen bitumen (0.45%). These results appear reasonable when compared with CO_2 diffusivity in bitumen obtained by other researchers using supercritical CO_2 and higher temperatures.
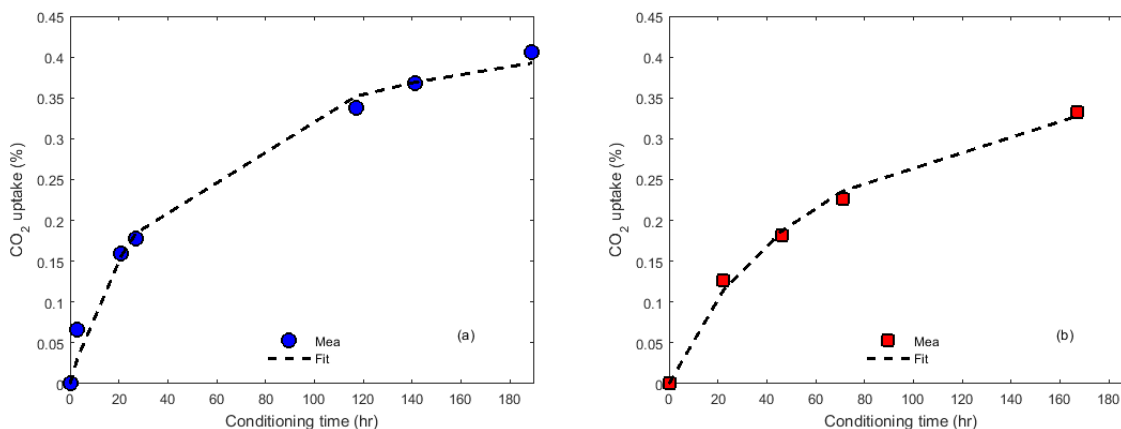
Figure 6. *Pelleg model fit to CO_2 uptake by bitumen at 25°C and 40 psi. a) 190 Pen, model parameters were: C_1=90.6612 and C_2 = 2.0666, b) 50 Pen, model parameters were: C_1=146.4474 and C_2 = 2.1763.*
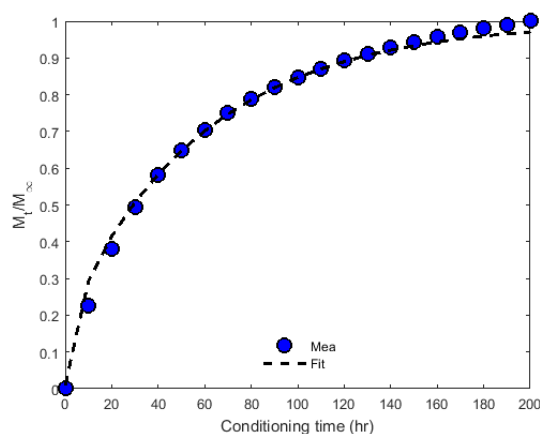

Figure 7. *Fick's law fit to CO_2 uptake showing a good fit. Data for 190 pen at 25°C and 40 psi.*

4.3 Storage Stability of CO_2-Bitumen Mixtures

The stability of the CO_2-bitumen mixtures (carbonated bitumen) was evaluated by comparing the kinetics of pressurized CO_2 diffusion in bitumen with CO_2 desorption from bitumen under ambient conditions (20°C and 1 atmosphere). This information was deemed important to establish because there has been

very little published data on the kinetics of CO_2 absorption and desorption (degassing) from bitumen, especially paving grade bitumen. It would be impossible to fully exploit the full viscosity reducing effect of CO_2 in bitumen without establishing the timeframe over which the carbonated bitumen remains softer than the unmodified base binder. Another reason was that in order to understand the release of CO_2 from bitumen, it is essential that CO_2 diffusional kinetics should be established in order to determine the time frame for optimal concentration of CO_2 for bitumen modification and estimate the room temperature storage stability of carbonated bitumen.

Figure 8 shows a graph of desorption (at ambient temperatures and atmospheric pressure) for the two different binders used. Samples of bitumen were conditioned in CO_2 at 40 psi for almost 200 hours prior to the desorption measurements. The weights of the bitumen samples used for the desorption experiments were measured periodically using the same sensitive balanced that was used during the sorption measurements. The results are displayed in Figure 8. As shown in Figure 8, the rate of CO_2 diffusion at 40 psi was relatively lower than rate of CO_2 desorption during degassing at ambient conditions for both binders. In a similar fashion to the diffusion experiments, desorption coefficients were computed using the data in Figure 8 and a modified form of Eq. 1. The coefficient of desorption results (50 Pen, 55.86E-12 m2/s and 190 Pen, 42.46E-12) indicate that the rate of CO_2 desorption out of a carbonated bitumen was about 30% higher in the stiffer binder than the softer binder. The results also indicate that the rate of desorption of CO_2 from bitumen was higher than diffusion which could be attributed to the fact that diffusion occurred under elevated pressure conditions. Another important observation that could be made from the trends in Figure 8 and which may have important implications for CO_2-modified bitumen is that the time scale required for CO_2 desorption from bitumen is on the order of days. For paving application, this finding is significant as it suggests carbonated bitumen appears to be stable under ambient condition for durations far in excess of typical mixing times for bituminous mixtures. It is interesting to note that even after almost 200 hours storage under ambient conditions, the carbonated bitumen retained residual CO_2 concentration of about 0.065±0.009% which was more than twice the CO_2 concentration of approximately 0.027-0.037% in air. Thus it may be possible to sequestrate CO_2 in bitumen long enough for the mixture to be useful for paving purposes.
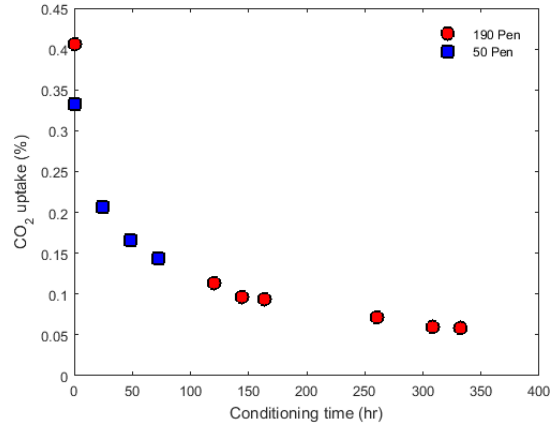
Figure 8. *Desorption rates of CO_2 from modified bitumen under ambient conditions. Bitumen samples were previously conditioned in CO_2 at 40 psi for up to 200 hours prior to desorption experiments.*

4.4 Rheological Characterization of carbonated bitumen

A series of CO_2 sorption tests were conducted using two different types of bituminous binders – 50 Pen and 190 Pen. The sorption tests consisted of exposing thin films (approximately 5 mm) of binders to CO_2 gas at a temperature of 20°C and a pressure of 40 psi and measuring the concentration and rheological response periodically. The rheological measurements were conducted at three temperatures (20°C, 5°C and 0°C) using a DSR programed to perform frequency sweeps from 0.1 Hz to 10 Hz to determine the complex shear modulus and phase angle as a function of conditioning time and also as a function of CO_2 concentration.

Figure 9 shows a graph of complex shear modulus obtained at 20°C plotted against loading frequency as a function of CO_2 conditioning time for 50 Pen and 190 Pen binders. The viscosity-reducing effect of CO_2 on bitumen stiffness is apparent from the graph. Similar results have been obtained at the two other testing temperatures (0°C and 5°C) for all the other binders and are not shown for brevity. It should be noted that in Figure 9, the apparent non-monotonous variation of shear modulus with conditioning time can be attributed to the viscoelastic nature of bitumen. For bitumen, complex shear modulus is very sensitive to or loading frequency and the relationship between loading frequency and complex shear modulus can be highly non-linear. Therefore, a plot of shear modulus versus frequency appears non-monotonous. The point of the figure 9 is to show the softening effect of CO2 under each loading condition. For example, in Fig. 9a, complex shear modulus at 4 Hz and 10 Hz are respectively 1.3E7 Pa

and 2.4E7 Pa for the unmodified bitumen containing no CO2, (i.e. conditioning time = 0 hours). The corresponding values for bitumen conditioned in CO2 for 70 hours containing (i.e. 0.298% of CO2) are about 0.3E7 Pa and 0.7E7 Pa, for 4 Hz and 10 Hz, respectively. Thus, the softening effect of CO2 can be clearly seen irrespective of loading frequency.
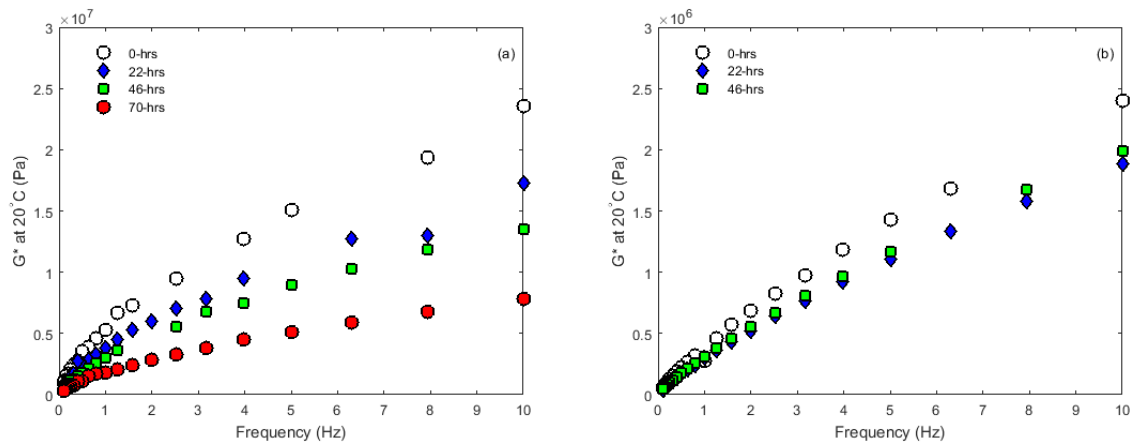

Figure 9. *Complex shear modulus for CO2-modified bitumen showing the viscosity-reducing (softening) effects of pressurized (40 psi) CO_2 dissolved in bitumen. a) 50 Pen bitumen. b) 190 Pen bitumen.*

Differences in the ability of CO_2 to plasticized bitumen appear to be bitumen type dependent. For example, from Figure 9 (b), and comparing stiffness changes at 20°C, after 46 hours of conditioning, the modified binder was only 70% of the base binder. On the other hand, from Figure 9 (a) the stiffness of CO_2-modified 50 Pen binder at 20°C was as low as 50% that of the base bitumen. It should be noted that the 190 Pen binder also contained about three times more the amount of volatiles than the 50 Pen binder. Therefore, the lower softening effect of CO_2 observed could be due to the loss of volatiles that could result from the pressurized CO_2 used displacing some of the volatiles. This observation is significant and requires additional studies. The differences in the softening effect of CO_2 in bitumen also appear to be time dependent. As can be seen in Figure 9, the longer bitumen is conditioned, the softer the binder becomes.

The amount of CO_2 absorbed by bitumen depends on the length of conditioning time. Therefore, the changes in rheological properties could be related not only to conditioning time as presented in Figure 9

but also to the amount of CO_2 uptake. Figures 10 and 11 are sample plots which depict complex modulus data plotted as a function of loading frequencies, testing temperature, and CO_2 concentration for 190 Pen and 50 Pen, respectively. The results show that the presence of dissolved CO_2 caused substantial reduction in binder stiffness for most of the testing conditions considered. Reduction in bitumen stiffness appears to be greater at lower temperatures and/or higher frequencies than at higher temperatures or lower loading frequency. This effect is counter to the effect of most traditional asphalt modifiers that cause the opposite effect. The effect of CO_2 on bitumen viscosity was more pronounced in the 50 Pen bitumen than in the 190 Pen bitumen. This can be clearly seen in Figure 10 where stiffness reduction of 3 or more times of the base binder could be observed. Similar to the 190 Pen data, the results for 50 Pen also suggest the effect of CO_2 on bitumen stiffness may be more pronounced at higher frequencies and /or lower temperatures. The data suggest that the effect of CO_2 of bitumen rheology is complicated and appears to depend on multiple factors including bitumen type, conditioning time and testing temperature.
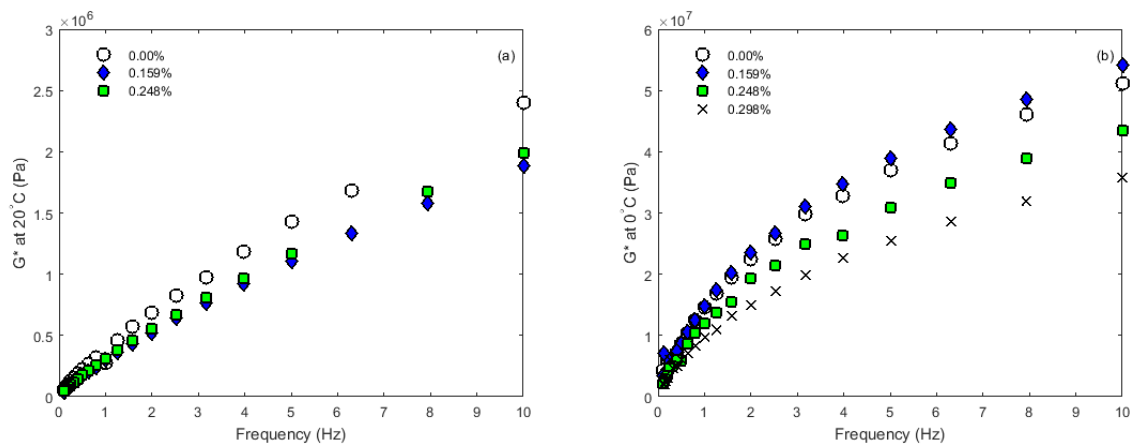

Figure 10. *Complex shear modulus data at two tests temperatures for 190 Pen bitumen modified with CO_2 gas at injection pressure of 40 psi. a) 20°C; b) 0°C. Note that CO_2 uptakes of 0.000%, 0.159%, 0.248% and 0.298% correspond to conditioning time of 0-hours, 20-hours, 50-hours and 70-hours, respectively.*
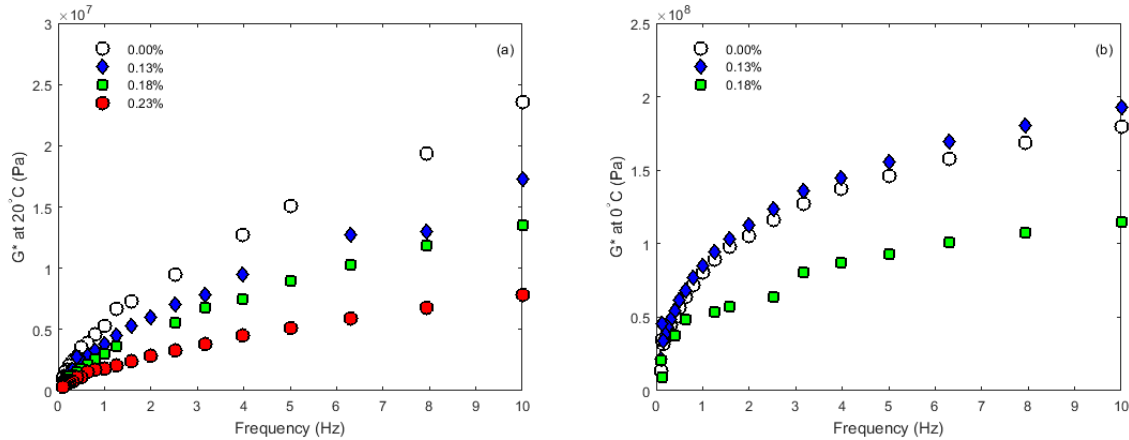
Figure 11. *Complex shear modulus data at two tests temperatures for 50 Pen bitumen modified with CO_2 gas at injection pressure of 40 psi. a)20°C; b) 0°C. Note that CO_2 uptakes of 0.000%, 0.130%, 0.180% and 0.230% correspond to conditioning time of 0-hours, 20-hours, 50-hours and 70-hours, respectively.*

4.5 *Softening Indices*

The viscosity-reducing effect of CO_2 dissolved in bitumen was evaluated by comparing stiffness of the CO_2-modified bitumen with the unmodified or base bitumen using softening indices for complex modulus computed using Eq. 5. Sample results are presented in Figure 12 for the two binders – 50 Pen and 190 Pen - modified with CO_2 at injection pressure 40 psi (0.2758 MPa). The results were obtained by using SI for complex shear modulus obtained at 20°C testing temperature and 10 Hz loading frequency. Similar results were obtained for other temperatures and loading frequencies considered but are not shown for brevity. Lower softening indices suggest higher softening effect of CO_2 on bitumen viscosity. The results suggest that the for CO_2 concentration of 0-0.25 wt% obtained using an injection pressure of 40 psi, viscosity reduction was substantial. The biggest reduction was seen in the 50 Pen bitumen where stiffness of the bitumen after modification was only about 30% of the base bitumen. In other words, there was about a threefold reduction in binder viscosity due to a CO_2 uptake of less than 0.25% when 50 Pen was modified with pressurized (40 psi) CO_2. It should be recognized that the data presented in Figure 12 are not intended to provide softening versus CO_2 uptake relationship, but simply to illustrate the potential of exploiting CO_2 as a suitable solvent for temporary modifying bitumen viscosity so that asphalt mixtures could be produced and paved in a more environmentally sustainable manner.

The data in Figure 12 showing lower SI for 50 Pen compared to 190 Pen suggest the effect of CO_2 was higher in the former than in the later. A statistical analysis was conducted using binder type, mass loss, CO_2 uptake as predictor variables for the modification indices in order to identify significant factors contributing to the viscosity reducing effect of CO_2 in bitumen. The results showed good correlation (R^2=0.76) between SI and bitumen type and CO_2 uptake. Therefore, the effect of CO_2 in bitumen appears to be bitumen type dependent: viscosity-reducing effect of CO_2 was more pronounced in 50 Pen bitumen than in 190 Pen bitumen. No chemical analysis of the bitumen used were performed, therefore deduction based on the chemical properties of the bitumen could not be ascertained. However, one major difference between the binders used was their volatile content: the softer 190 Pen binder had almost three times more volatiles than the 50 Pen bitumen (Table 2). Therefore, the bitumen dependency of SI requires further studies.
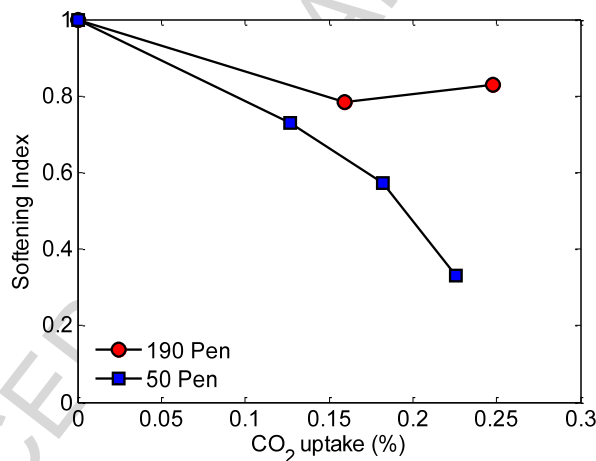

Figure 12. *Softening indices for complex shear modulus of bituminous binders showing the viscosity-reducing effect of CO_2 at 40 psi and 20°C in bitumen. Complex shear modulus data were obtained at 20°C and 10 Hz.*

4.6 *Complex shear modulus master curve*

The master curves were produced by manually shifting the complex modulus versus frequency plots at the three temperatures (20°C, 5°C and 0°C) along the frequency axis to form a single smooth curve of modulus versus reduced frequency using Eq. 4. A reference temperature of 20°C was used. The resulting master curves and the corresponding temperature shift factors are shown in Figures 13 and 14 for samples

of 50 Pen binder that were modified with CO_2 at 40 psi injection pressure. The temperature shift factors obtained for both modified and unmodified binders were similar suggesting viscosity changes in the CO_2-modified binder with respect to the reference temperature is not different from the base binder. Similar results have been obtained for different CO_2-bitumen combinations and are not presented for brevity.

Since the pure binder obeys time-temperature superposition principle, it follows that CO_2-modified binder could also be considered as rheologically simple materials. The smoothness and lack of breaks in the master curves suggest lack of structural changes in the bitumen as a result of CO_2 bitumen modification. The results further suggest that the interaction of CO2 and bitumen maybe reversible. The data shows CO_2-modified binder, like the unmodified binder, obeys the time temperature superposition principle.
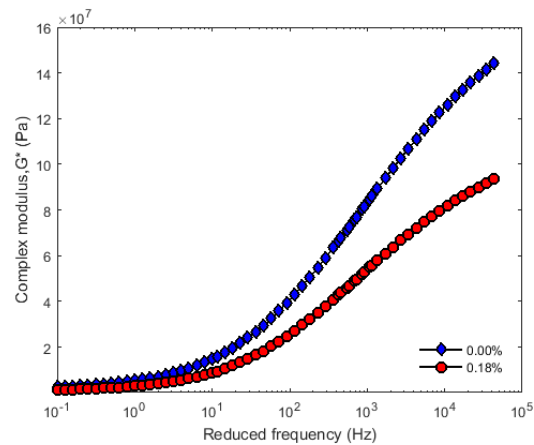

Figure 13. *Complex shear modulus master curve for 50 pen at two CO_2 concentrations. Reference temperature: 20°C.*
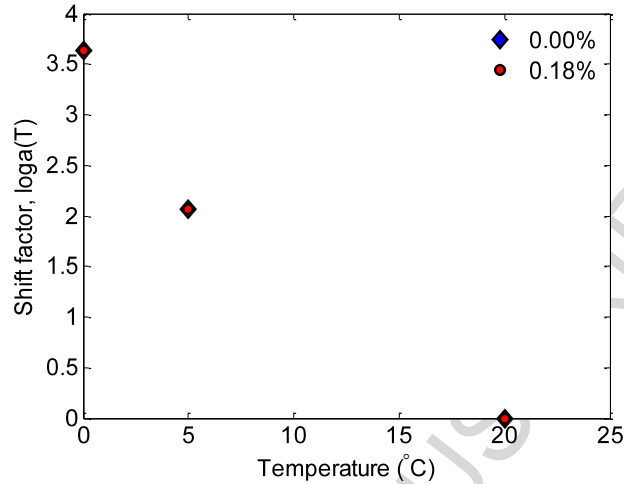
Figure 14. *Temperature shift factors for constructing master curve in Figure 13.*

4.6 *Concentration dependent shift factors*

As previously discussed, the amount of shifting required at each temperature to form the master curve is called a shift factor, a(T) which can be considered as the viscosity changes with respect to the reference temperature. Because the viscosity reducing-effect of CO_2 at 40 psi in bitumen appears to be a function of concentration (see Figures 10 and 11, for example), it was felt necessary to investigate if concentration could be used as a scaling factor in much the same way as a temperature-shift factor so that master curves in which the effects of CO_2 concentration are characterized entirely through a viscoelastic scaling factor. The basis for this presumption was that a closer inspection of the master curves obtained for the modified binders were of the similar shape as the unmodified binder. This approach was previously used by Gerhardt et al. (1998) to model polydimethylsiloxane-CO_2 systems. In this case if a scaling factor, a, defined in similar fashion as SI in Eq. 4 is used to reduce the measured rheological parameter (here complex modulus but can be any other viscoelastic parameter) and plotted as a function of reduced frequency, f_r/a. As an illustration, modulus and reduced frequency in Figure 13 were further reduced using the scaling factor, a. The results are shown in Figure 15 which demonstrates the concentration-dependent scaling factor produced master curves that are identical to the master curves of pure binders.
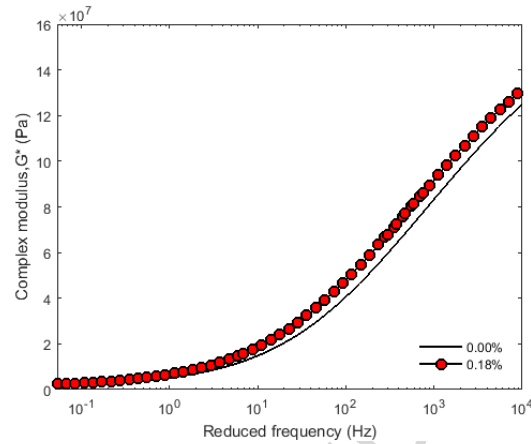
Figure 15. *Comparison of master curves for complex modulus using both temperature depended and concentration dependent scaling factors.*

4.7 *Black diagram*

An alternative technique to the master curve construction for representing the viscoelastic properties of bituminous binders involves the construction a Black diagram where the modulus data is plotted against the phase angle. One advantage of the Black diagram representation of viscoelastic data is that there is no need to determine shift factors as in the case of master curves since the Black diagram representation is independent of temperature and frequency of measurement. The diagram thus allows direct comparison of the materials examined. Like the master curve, a Black diagram with a smooth curve indicates a binder that obeys the time-temperature superposition principle. The smooth curve obtained for the CO_2-modified binder shown in Figure 16 suggests no major structural changes occurred as a result of the modification compared to the unmodified.

The Black diagram also provides a means to validate the suitability of the DSR to provide data for DMA. In this case, a plot of log G^* versus log(1+tandelta), where delta is the phase angle, yield a straight with y-axis intercept on the order of 10^9 Pa, the limiting maximum stiffness of paving grade bitumen. One such plot is shown in Figure 17 which compares unmodified Black diagram with CO_2 modified binder. From

Figure 17, the limiting stiffness values for the binders were respectively, 1.34E+09 Pa and 0.97E+09 Pa for the unmodified base binder and the CO_2-modified base binder (CO_2 at 40 psi for 46 hours).
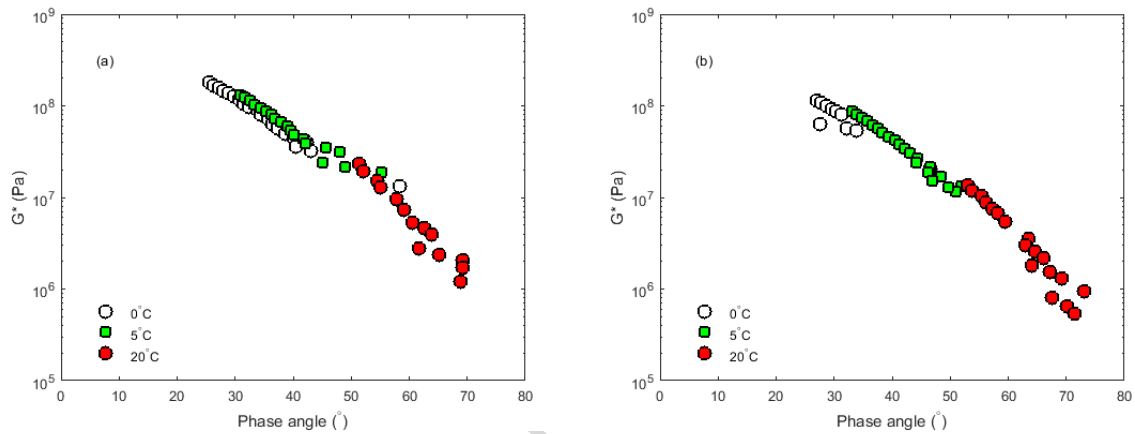

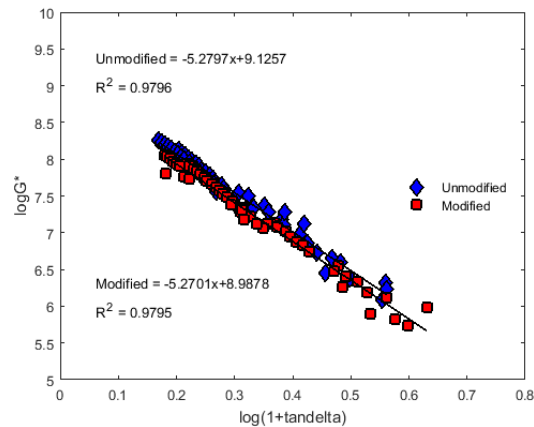**Figure 16.** *Black diagram for binders: a) Unmodified; b) Modified.*

Figure 17. *Complex shear modulus (logG*) versus log(1+tandelta) for modified and CO_2-modified binders showing limiting bitumen stiffness.*

4.8 Effect of pressure on CO_2 diffusion in bitumen

As previously noted, the amount of CO_2 gas that can be absorbed by bitumen depends on bitumen type and as well as the length of conditioning time. Previous studies suggest elevated pressure is another factor that may have significant effect on CO_2 uptake by bitumen and by extension rheology of CO_2-modified bitumen. Data presented in this paper so far have all been obtained using CO_2 at an injection pressure of 40 psi. In order to evaluate the effect of elevated pressure on bitumen rheology, additional experiments that replicated those described for CO_2 pressure of 40 psi were conducted. Basically, thin films (approximately 5 mm) of bitumen were exposed to CO_2 in a pressure vessel maintained at 300 psi. The samples were weighed periodically using a sensitive balance to develop the kinetics of CO_2 uptake and the rheology of the modified bitumen determined using a DSR to determine complex shear modulus. Figure 18 shows a comparison of CO_2 uptake at a pressure of 300 psi compared with that at 40 psi for the 50 Pen bitumen. The effect of pressure is clearly seen. The amounts of CO_2 absorbed by the binders at 300 psi were almost 10 times as large as that obtained for bitumen conditioned at 40 psi. The results suggest that pressure has a significant effect on the amount of CO_2 that could be absorbed by bitumen.
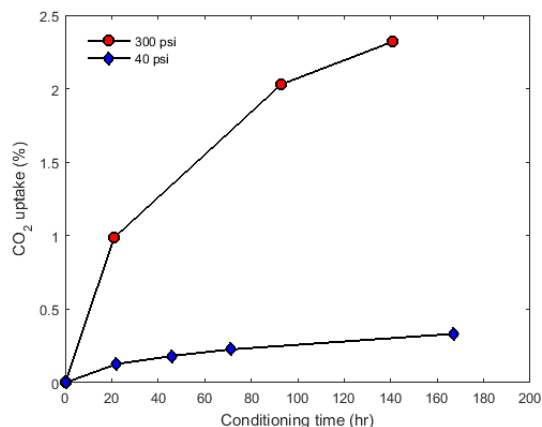

Figure 18. *Effect of conditioning pressure on CO_2 uptake for 50 Pen bitumen.*

Effect of CO_2 conditioning pressure and CO_2 uptake on bitumen rheology was also investigated using the DSR. As previously discussed, at 40 psi, the amount of CO_2 absorbed was only a fraction of the absorption at 300 psi. Therefore, it was decided that a limited study focused on CO_2 uptake at an elevated pressure of 300 psi be conducted. Measurements were undertake at two conditioning levels, 20 hours and 140 hours in order to study the effect of long-term CO_2 conditioning. Sample results are shown in Figures

19 and 20. In Figure 19, softening indices are plotted as a function of loading frequency and testing temperature for samples conditioned for 20 hours. The results showing decreasing SI with decreasing testing temperature are in good agreement with the results obtained for bitumen conditioned in 40 psi CO_2 where similar levels of viscosity reduction were observed. However, it is important to note that the amount of CO_2 absorbed at 300 psi after 20 hours was almost ten times more than that obtained at 40 psi. This suggests in addition to CO_2 uptake, the length of conditioning time might be an important factor in the softening ability of CO_2 in bitumen.

Figure 20 shows SI data obtained for 50 Pen bitumen conditioned in CO_2 at 300 psi and 140 hours. Similar to data depicted in Figure 19, a trend of increasing softening power of CO_2 with decreasing testing temperature is observed. More importantly, the level of softening, as indicated by SI, is significantly lower after 140 hours of conditioning compared to 20 hours of conditioning and or 40 psi of injection pressure. A clear trend of increasing SI with loading frequency can be seen in Figure 20, especially at the lower temperatures. This trend, even though common in most modified bitumens, was not observed in the case of bitumen conditioned at 40 psi. The later observation suggests CO_2 might be more miscible and therefore might have more solvent properties at higher pressures than at lower pressures. The results support the assertion that CO_2 might be useful for reducing bitumen viscosity under certain conditions.
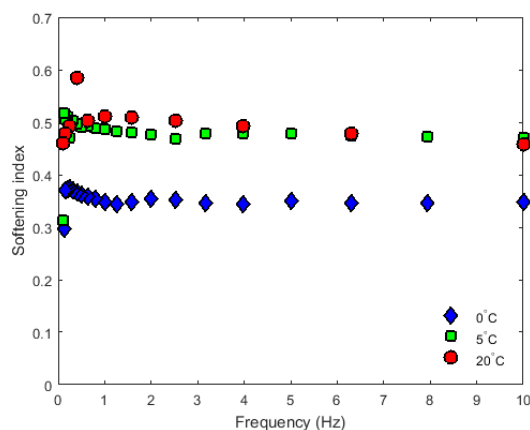

Figure 19. *Softening index as a function of pressure and conditioning time for 50 pen bitumen conditioned in CO_2 at 300 psi for 20 hours.*
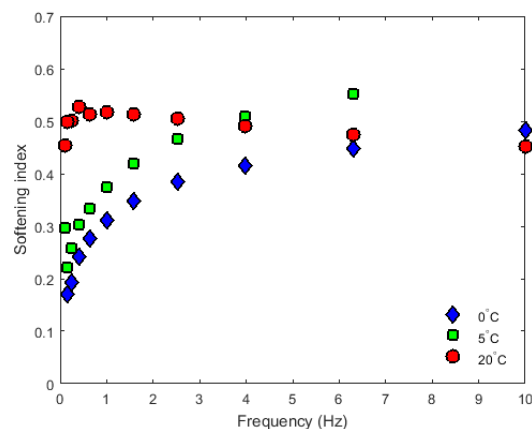
Figure 20. *Softening index as a function of pressure and conditioning time for 50 pen bitumen conditioned in CO_2 at 300 psi for 140 hours.*

5. Conclusions

The physico-chemical and rheological properties of paving grade bitumen were characterized as a function of CO_2 uptake in order to establish baseline data that could be exploited for low-emission, low-energy asphalt production. The following conclusions were reached based on the data presented in the paper:

- The kinetics of CO_2 diffusion in bitumen is influenced by both bitumen type and CO_2 pressure. The rate of CO_2 diffusion and the equilibrium CO_2 uptake were relatively higher in softer binder compared with stiffer binders. For the two binders considered, diffusion coefficients were of the same order of magnitude (190 Pen, 40.2E-12 m2/s and 50 Pen, 36.3E-12 m2/s) at 40 psi CO_2 pressure. Rate of CO_2 desorption (at ambient conditions) was also found to be of the same order of magnitude for both binders.

- Carbon dioxide uptake was found to be highly dependent on conditioning pressure. A 10 fold increase in equilibrium CO_2 uptake was observed when binders were conditioned in CO_2 at 300 psi versus at 40 psi.

- Substantial reduction in bitumen stiffness (viscosity) was observed with increasing CO_2 uptake, conditioning time and conditioning pressure. The level of reduction was also found to be dependent on testing temperature and loading frequency. The largest decrease in stiffness due to CO_2 absorption was found at the lowest testing temperatures.

- Analysis of the complex modulus master curves, constructed using time-temperature superposition principles, showed that temperature-dependent shift-factors for the CO_2-modified bitumen were similar to the base bitumen. In addition, the results showed that concentration-dependent scaling (shift) factors could be used to reduce the master curves of the modified bitumen into a single master curve with respect to the base bitumen.

- The results suggest the viscosity-lowering effect of CO_2 on bitumen stiffness is analogues to the well-known trend of increasing temperature with decreasing bitumen viscosity or the viscosity-lowering ability of conventional solvents. Therefore, the study concludes that CO_2 modification of bitumen for paving application appears promising.

7.0 References

Apeagyei, A.K., Grenfell, J.R.A. and Airey, G.D. "Evaluation of Moisture Sorption and Diffusion Characteristics of Asphalt Mastics Using Manual and Automated Gravimetric Sorption Techniques." *Journal of Materials in Civil Engineering*, 2013, 10.1061/(ASCE)MT.1943-5533.0000929.

Civan, F., Rasmussen, M.L. (2006). "Determination of gas-diffusion and interface-mass-transfer coefficients for quiescent reservoir liquids." SPE Journal, 11 (1), pp. 71-79.

Collop, A.C., Choi, Y.K., Airey, G.D. and Elliott, R.C. "Development of the saturation ageing tensile stiffness (SATS) test." *Proceedings of the Institution of Civil Engineers, Transport*, 2004, 157(3): 163-171.

Crank, J. "The Mathematics of Diffusion." 2nd ed.; Oxford University Press: New York, 1975, pp. 414.

Gerhardt, L.J., Manke, C.W., and Gulari, E. Rheology of polydimethylsiloxane swollen with supercritical carbon dioxide. J*ournal of Polymer Science Part B: Polymer Physics*, 35(3), 1997: 523–534.

Jacobs, M. "Carbon dioxide pressure-temperature phase diagram." http://en.wikipedia.org/wiki/Supercritical_carbon_dioxide#mediaviewer/File:Carbon_dioxide_pressure-temperature_phase_diagram.svg. Accessed July 10, 2014.

Jones, D., Tsai, B. W., and Signore, J. Warm-mix asphalt study: Laboratory test results for AkzoNobel Rediset WMX, 2010. Richmond, California: University of California Pavement Research Center (UCPRC).

Koenders, B. G., Stoker, D. A., Bowen, C., de Groot, P., Larsen, O., Hardy, D., and Wilms, K. P. "Innovative process in asphalt production and application to obtain lower operating temperatures." P*roceedings of the 2nd Eurasphalt & Eurobitume Congress*, 2000, Barcelona, Spain.

Kvasnak, A., Taylor, A., Signore, J., & Bukhari, S. (2010). Evaluation of gencor green machine ultrafoam GX (NCAT Report 10-03). Auburn, AL: National Center for Asphalt Technology.

Mehrotra, A.K. and Svrcek, W.Y. Properties of Cold Lake bitumen saturated with pure gases and mixtures. *Can. J. Chem. Eng.,* 1988, 66(8): 656-665.

Meehl et al. (2007) Global Climate Projections. Contribution of Working Group I to the 4th Assessment Report of the IPCC, Cambridge.

Peleg, M. "An Empirical Model for the Description of Moisture Sorption Curves." *Journal of Food Science*, 1988, 53(4): 1216-1219.

Prowell, B. D. and Hurley, G. C. "Warm-mix asphalt: Best practices." Publication of National Asphalt Pavement Association, *Quality Improvement Series 125*, 2007. Lanham, MD.

Tutuncu, M. A., and T. P. Labuza. 1996. "Effect of geometry on the effective moisture transfer diffusion coefficient." *Journal of Food Engineering*, 1996, 30(3-4): 433-447.

Ratnakar, R. R., & Dindoruk, B. (2015). Measurement of gas diffusivity in heavy oils and bitumens by use of pressure-decay test and establishment of minimum time criteria for experiments. SPE Journal, 20(5), 1167-1180

Romier, A., Audeon, M., David, J., Martineau, Y., and Olard, F. "Low-Energy Asphalt with Performance of Hot-Mix Asphalt." Transportation Research Record: Journal of the Transportation Research Board 2006, 1962: 101-112.

Saboorian-Jooybari, H., Dejam, M. and Chen, Z. (2014). Equilibrium or Nonequilibrium Models: a Critical Issue in Determination of Gas Diffusivity in Oil, Paper SPE 170030, 2014 SPE Heavy Oil Conference, Calgary, Alberta, Canada,

Saboorian-Jooybari, H., Dejam, M. and Chen, Z. (2015). "Half-century of Heavy Oil Polymer Flooding from Laboratory Core Floods to Pilot Tests and Field Applications," Paper SPE 174402, 2015 SPE Canada Heavy Oil Technical Conference, Calgary, Alberta, Canada.

Saboorian-Jooybari, H., Dejam, M. and Chen, Z. (2016), "Heavy Oil polymer Flooding from Laboratory Core Floods to Pilot tests and Field Applications: Half-century Studies." Journal of Petroleum Science and Engineering, 142: 85-100.

Seright, R.S. (2017) How Much Polymer Should Be Injected During a Polymer Flood? Review of Previous and Current Practices, IOR 2017-19th European Symposium on Improved Oil Recovery, Stavanger, Norway, 24 - 27.

Seright, R.S. (2017). "How Much Polymer Should Be Injected During a Polymer Flood?" Paper SPE 179543, SPE Improved Oil Recovery Conference, Tulsa, Oklahoma, USA.

Sheikha H., Pooladi-Darvish M., and, and Mehrotra A.K. (2005). "Development of Graphical Methods for Estimating the Diffusivity Coefficient of Gases in Bitumen from Pressure-Decay Data." *Energy & Fuels*, 2005, 19(5), 2041-2049.

Tharanivasan A.K, Yang C., and Gu Y. "Measurements of Molecular Diffusion Coefficients of Carbon Dioxide, Methane, and Propane in Heavy Oil under Reservoir Conditions." *Energy & Fuels,* 2006 20(6): 2509-2517.

Upretit, S.R. and Mehrotra, A.K. Diffusivity of CO_2 CH_4 C_2H_6 and N_2 in Athabasca Bitumen, *Can. J. Chem. Eng.*, 2002, 80(1):116-125.Visscher, J.D., Vervaecke, F., Vanelstraete, A., Soenen, H., Tanghe, T. and Redelius, P. "Asphalt Production at Reduced Temperatures using Zeolites and the Impact on Asphalt Performance." *Road Materials and Pavement Design*, 2010, 11(1): 65-81.

Whiteoak, D. "The Shell Bitumen Handbook." Shell Bitumen UK, Surrey, 1991 p. 336.

Zelelew, H., Paugh, C., Corrigan, M., Belagutti, S., & Ramakrishnareddy, J. "Laboratory evaluation of the mechanical properties of plant-produced warm-mix asphalt mixtures." *Road Materials and Pavement Design*, 2013, 14: 49–70.

Zhang Y.P., Hyndman C.L., Maini B.B. "Measurement of gas diffusivity in heavy oils." *Journal of Petroleum Science and Engineering*, 2000, 25 (1–2):37-47.

Graphical Abstract
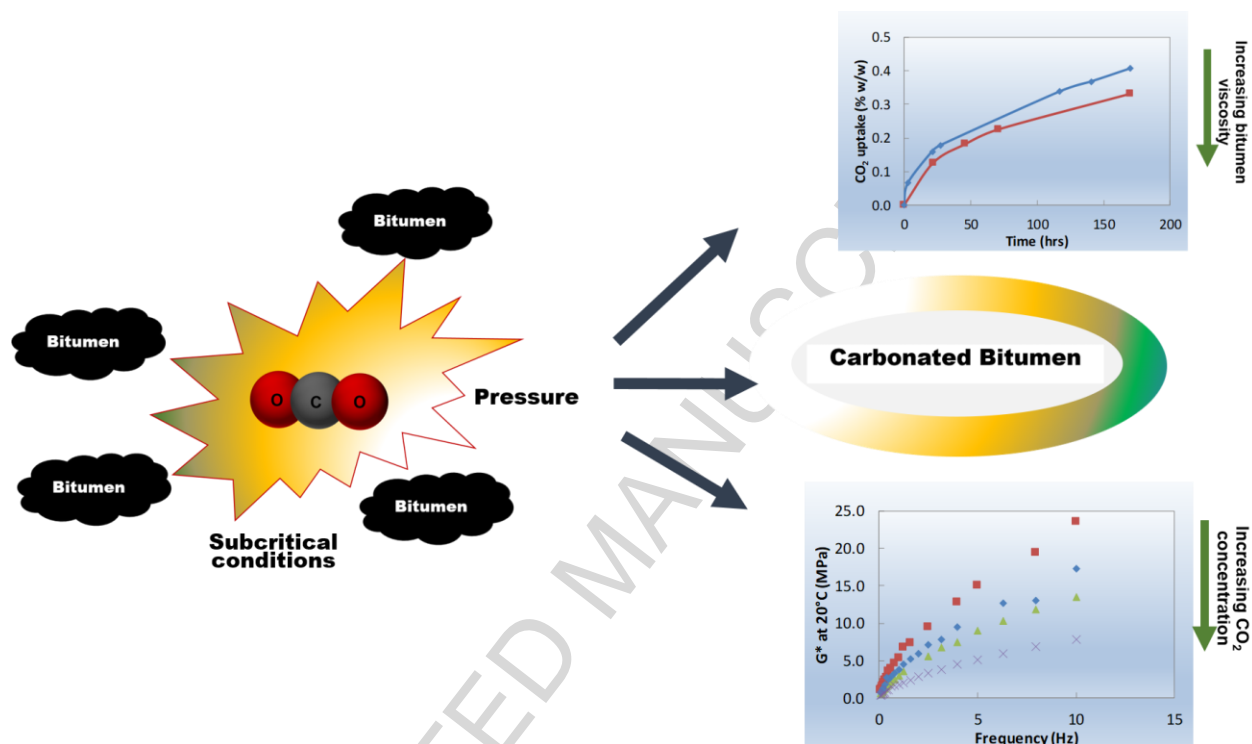
Highlights

- Under subcritical conditions (23°C and 40 psi), the equilibrium concentration of CO_2 in paving-grade bitumen ranged from 0.33 – 0.41% w/w
- CO_2-modified bitumen showed thermorheologically simple behavior when modeled using the frequency-temperature superposition principle
- Significant changes in bitumen rheology (up to three-fold decrease in viscosity) was observed with sub-critical CO_2 concentration of up to 0.40% w/w
- The carbonated bitumen was thermally stable, under ambient condition, longer than typical timeframes for producing asphalt mixtures. This finding has important implications for producing lower energy asphalt mixtures.