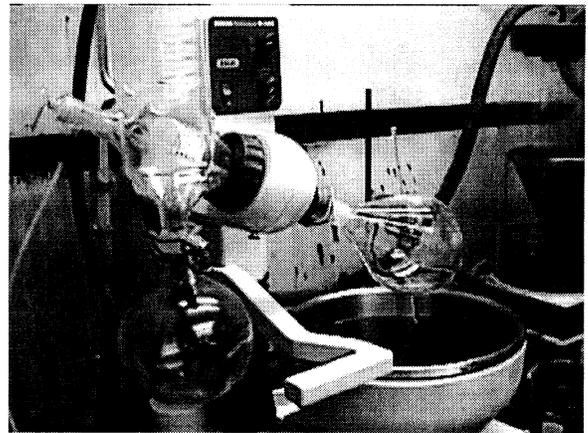
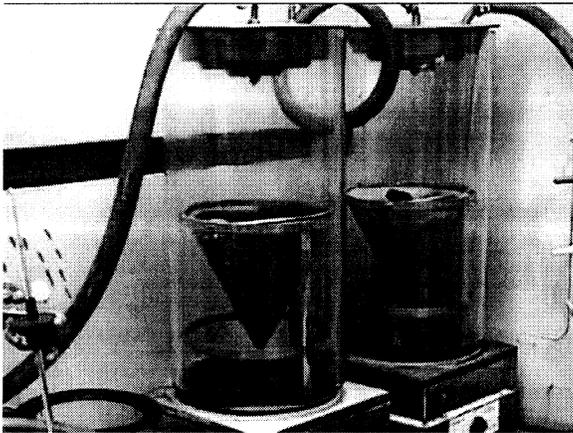

FINAL REPORT

U.F. Project No:49104504658-12
Contract No:BB881

EVALUATION OF AN ALTERNATIVE
SOLVENT FOR EXTRACTION OF ASPHALT TO
REDUCE HEALTH HAZARDS

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December 2000



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DISCLAIMER

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Prepared in cooperation with the State of Florida Department of Transportation.”

SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol	When You Know	Multiply By	To Find	Symbol
LENGTH								
in	inches	25.4	millimeters	mm	mm		inches	in
ft	feet	0.305	meters	m	m		feet	ft
yd	yards	0.914	meters	m	m		yards	yd
mi	miles	1.61	kilometers	km	km		miles	mi
AREA								
in ²	square inches	645.2	square millimeters	mm ²	square millimeters	0.0016	square inches	in ²
ft ²	square feet	0.093	square meters	m ²	square meters	10.764	square feet	ft ²
yd ²	square yards	0.836	square meters	m ²	square meters	1.195	square yards	ac
ac	acres	0.405	hectares	ha	hectares	2.47	acres	mi ²
mi ²	square miles	2.59	square kilometers	km ²	square kilometers	0.386	square miles	
VOLUME								
fl oz	fluid ounces	29.57	milliliters	ml	milliliters	0.034	fluid ounces	fl oz
gal	gallons	3.785	liters	l	liters	0.264	gallons	gal
ft ³	cubic feet	0.028	cubic meters	m ³	cubic meters	35.71	cubic feet	ft ³
yd ³	cubic yards	0.765	cubic meters	m ³	cubic meters	1.307	cubic yards	yd ³
NOTE: Volumes greater than 1000 l shall be shown in m ³ .								
MASS								
oz	ounces	28.35	grams	g	grams	0.035	ounces	oz
lb	pounds	0.454	kilograms	kg	kilograms	2.202	pounds	lb
T	short tons (2000 lb)	0.907	megagrams	Mg	megagrams	1.103	short tons (2000 lb)	T
TEMPERATURE (exact)								
°F	Fahrenheit temperature	5(F-32)/9 or (F-32)/1.8	Celsius temperature	°C	Celsius temperature	1.8C + 32	Fahrenheit temperature	°F
ILLUMINATION								
fc	foot-candles	10.76	lux	lx	lux	0.0929	foot-candles	fc
fl	foot-Lamberts	3.426	candela/m ²	cd/m ²	candela/m ²	0.2919	foot-Lamberts	fl
FORCE and PRESSURE or STRESS								
lbf	poundforce	4.45	newtons	N	newtons	0.225	poundforce	lbf
psi	poundforce per square inch	6.89	kilopascals	kPa	kilopascals	0.145	poundforce per square inch	psi

(Revised August 1992)

* SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.

ACKNOWLEDGMENTS

The Federal Highway Administration (FHWA) and the Florida Department of Transportation (FDOT) are gratefully acknowledged for providing the financial support for this study. The Materials Office of FDOT provided the additional testing equipment, materials and personnel needed for this investigation. Sincere thanks go to the project managers, Mr. Gale C. Page and Dr. Bouzid Choubane for providing the technical coordination and advice throughout the project. Sincere gratitudes are extended to the FDOT Materials Office personnel, particularly to, James Musselman, Patrick Upshaw, David Webb, Aaron Turner, and Greg Sholar. The technical inputs from Dr. Byron E. Ruth of the Civil and Coastal Engineering Department, as well as Dr. Hua Chee Ooi and Mr. Stephen Audetat of the Department of Chemistry at the University of Florida are duly acknowledged.

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TECHNICAL SUMMARY

The asphalt extraction and recovery procedure is a vital part of the quality control and assurance of asphalt pavement recycling projects in Florida. Unfortunately, the solvent trichloroethylene (TCE), which is used in the extraction and recovery procedure, has been identified as a carcinogen. TCE is also hazardous to the environment and contributes to the depletion of the earth's ozone layer. Because of the dangers of TCE, it will most likely be banned in the near future under the U.S. Clean Air Act. In order to maintain the present testing methods, it is necessary to find a less hazardous solvent that would be suitable to replace TCE.

This study investigated the suitability of using EnSolv, a n-Propyl Bromide based solvent produced by EnviroTech International, as a replacement for TCE in the asphalt solubility, extraction and recovery tests. The reclaimed EnSolv obtained from the recovery process was also evaluated for its possible re-use in the extraction and recovery procedure.

The standard asphalt solubility test (ASTM Test Method D2042) was conducted on eight different asphalt binders using EnSolv and TCE. The results indicated that there was no practical difference between the two solvents. The maximum difference in results from the two solvents was 0.11%. In addition, this test method does not need any modification when using EnSolv as the solvent.

Asphalt extraction and recovery tests were performed on three different asphalt mixtures using TCE, EnSolv, and reclaimed EnSolv. The mixtures used for the study included Marshall, Superpave and crumb rubber modified asphalt mixtures. The Marshall and Superpave mixtures both contained some RAP (Reclaimed Asphalt Pavement). The Reflux extraction procedure (ASTM standards D2172 - Method B) and the Rotary Evaporator recovery procedure (ASTM D 5404) were used to extract and recover the asphalts, and another procedure suggested by the FDOT was also investigated. The FDOT suggested change was in the recovery procedure. The difference between the two recovery procedures is that the FDOT procedure uses a higher rotating speed and vacuum for easier and quicker operation.

The results from the asphalt extraction tests indicate that, from the standpoint of asphalt content determination and extraction time, EnSolv and reclaimed EnSolv would be a suitable replacement for TCE for ASTM D 2172 Method B extraction procedure. The testing methods are applicable for the use of EnSolv as well as reclaimed EnSolv. The use of the EnSolv and reclaimed EnSolv actually reduced the time required to complete the extraction test.

The results of the recovery tests indicated that binders could be recovered faster from EnSolv and reclaimed EnSolv than from TCE. The FDOT proposed recovery method was found to take less time and to be much easier to perform.

The binders recovered from the mixtures were tested and analyzed to see if there were any differences due to the use of different solvents. The binder tests that were performed on the recovered binders included (1) penetration at 25 °C, (2) Brookfield viscosity test at 60 °C, (3) dynamic shear rheometer test at 25 and 64 °C, (4) bending

beam rheometer at $-18\text{ }^{\circ}\text{C}$, and (5) FTIR spectral analysis. The results from the tests on the recovered binders indicated that, for the most part, EnSolv and reclaimed EnSolv were not significantly different from TCE. The results also indicated that the binders recovered by the FDOT proposed recovery procedure were not significantly different from those by the standard ASTM recovery method.

An evaluation of the effects of TCE, EnSolv and reclaimed EnSolv on the physical properties of asphalt binders was also performed. A virgin asphalt binder was dissolved in each of the three solvents and recovered in accordance with ASTM D 5404 recovery procedure. The physical properties of the recovered binders were measured and compared with the properties of the virgin binder. The binder tests on the recovered binders included (1) penetration at $25\text{ }^{\circ}\text{C}$, (2) Brookfield viscosity at $60\text{ }^{\circ}\text{C}$, (3) dynamic shear rheometer at $25\text{ }^{\circ}\text{C}$ and $64\text{ }^{\circ}\text{C}$, (4) bending beam rheometer at $-18\text{ }^{\circ}\text{C}$ and (5) FTIR spectral analysis. The results of these tests indicated that, for the most part, the binders recovered from TCE and reclaimed EnSolv were similar to the virgin binder. However, significant hardening of the binders was noted for the binders recovered from the fresh EnSolv, as seen from the results of the penetration, Brookfield viscosity and dynamic shear rheometer tests. The observed hardening effect of the fresh EnSolv appeared to apply only to unaged virgin binders, but not to binders in asphalt mixtures which had already undergone some aging.

A sample of EnSolv and a sample of reclaimed EnSolv were analyzed at the Department of Chemistry of the University of Florida to determine their compositions. Results of GC-MS Analysis (Gas Chromatography – Mass Spectrometry) and ^1H nmr (nuclear magnetic resonance) spectroscopy on EnSolv indicated its composition to be

reasonably consistent with that as reported in the MSDS prepared by Enviro-Tech International Inc.

The ^1H nmr spectrum analysis on an EnSolv sample confirmed the presence of the following compounds:

(1)	1-bromopropane	88 wt%
(2)	1,3-dioxolane	5 wt%
(3)	nitromethane	<1 wt%
(4)	1,2-epoxybutane	<1 wt%
(5)	Unidentified compound(s)	6 wt%

Similar analyses on the reclaimed EnSolv indicated that it was not significantly different from the fresh EnSolv. The ^1H nmr spectrum analysis on a sample of reclaimed EnSolv confirmed the presence of the following compounds:

(1)	1-bromopropane	89 wt%
(2)	1,3-dioxolane	4 wt%
(3)	nitromethane	<1 wt%
(4)	1,2-epoxybutane	<1 wt%
(5)	Unidentified compound(s)	6 wt%

From the health and safety information available, EnSolv appears to be a viable alternative to TCE. The material should however still be considered hazardous and appropriate precautions should be exercised during its storage, transportation, handling and use. Inhalation, ingestion and contact with the skin of EnSolv should be avoided.

CHAPTER 1 INTRODUCTION

1.1 Background

The asphalt extraction and recovery procedure is a vital part of the quality control and assurance of asphalt pavement recycling projects in Florida. Unfortunately one of the main components of this process, the solvent Trichloroethylene (TCE), has been identified as a carcinogen. This poses a high health risk for the people working with the solvent. TCE is also hazardous to the environment and contributes to the depletion of the earth's ozone layer. Because of the dangers of TCE, it will most probably be banned in the future under the U.S. Clean Air Act. This means that in order to maintain the present testing methods, it is necessary to find a less hazardous alternative solvent which would be suitable to replace TCE.

There is a new solvent on the market with the trade name EnSolv that is a product of EnviroTech International (ETI). EnSolv is a solvent whose primary component is n-Propyl Bromide. This is a new solvent, but initial findings show that it is less hazardous than TCE. There is a possibility that EnSolv may be used for extraction and recovery of asphalt binder from asphalt mixtures. In addition, it is possible that the EnSolv remaining after the recovery may be recycled. This solvent may be a suitable replacement for TCE, but it is necessary to evaluate the use of this solvent for extraction and recovery procedures to see if EnSolv and reclaimed EnSolv can produce the same results when compared with TCE.

1.2 Objectives of the Study

The main objectives of this study are as follows:

1. To compare the solubility of asphalt binders in EnSolv with that in TCE.
2. To compare the procedure and results of extraction of asphalt binders from mixtures using EnSolv with those using TCE.
3. To compare the procedure and results of extraction of asphalt binders from mixtures using reclaimed EnSolv with those using TCE.
4. To compare the recovery method and the properties of recovered asphalt binders from EnSolv with those using TCE.
5. To compare the recovery method and the properties of recovered asphalt binders from reclaimed EnSolv with those using TCE.
6. To compare the properties of asphalt binders dissolved and recovered from EnSolv, reclaimed EnSolv and TCE with the properties of the virgin binders.
7. To make recommendations for modification of the asphalt extraction and recovery procedures to be used by the Florida Department of Transportation (FDOT) if EnSolv is to be used.
8. To determine the chemical composition of EnSolv and reclaimed EnSolv.

1.3 Scope of the Study

This study is mainly a laboratory investigation to evaluate the effectiveness of EnSolv and its suitability for the extraction and recovery procedures. The study investigate the use of TCE and EnSolv for the asphalt extraction and recovery procedures, the determination of binder content and the recovered binder properties will

then be evaluated for any differences. The EnSolv obtained from the recovery process will also be evaluated for its possible re-use in the extraction and recovery procedure. The purpose of this is to investigate the possibility of recycling EnSolv for purposes other than laboratory clean up.

Three plant mixtures were obtained and used in the investigation of extraction and recovery procedures. These mixtures came from existing projects, which were chosen and supplied by FDOT. The mixtures used for the study included Marshall, Superpave and crumb rubber modified asphalt mixtures. The Marshall and Superpave mixtures both contained Reclaimed Asphalt Pavement (RAP). The solvents tested included TCE, EnSolv, and reclaimed EnSolv. The extraction and recovery procedure was performed in accordance to ASTM standards D 2172 (Method B) and D 5404, but another procedure suggested by the FDOT was also investigated. The FDOT suggested change was in the recovery procedure. The difference between the two recovery procedures is that the FDOT procedure uses a higher rotating speed and vacuum for easier and quicker operation.

The recovered binders were tested and analyzed to see if there were any differences due to the use of different solvents. The binder tests that were performed included:

1. Penetration at 25° C.
2. Brookfield viscosity test at 60° C.
3. Dynamic Shear Rheometer test at 25 and 64° C.
4. Bending Beam Rheometer at -18° C.
5. FTIR Spectral Analysis.

The results of these tests were then analyzed to see if EnSolv would be a suitable replacement for TCE.

An evaluation of the effects of TCE, EnSolv and reclaimed EnSolv on the physical properties of asphalt binders was also performed. In order to provide reference samples for this evaluation, a virgin asphalt binder was dissolved in each of the three solvents and recovered in accordance with ASTM D 5404. The physical properties of the recovered binders were measured and compared with the properties of the virgin binder. The binder tests on the recovered binders included penetration at 25° C, Brookfield Viscosity at 60° C, Dynamic Shear Rheometer at 25° C and 64° C, Bending Beam Rheometer at -18° C and FTIR Spectral Analysis.

A sample of EnSolv and a sample of reclaimed EnSolv were analyzed by means of GC-MS (gas chromatography – mass spectrometry) and NMR (Nuclear Magnetic Resonance) spectroscopy at the Department of Chemistry of the University of Florida to determine their compositions.

CHAPTER 2 LITERATURE REVIEW

2.1 Background Information on TCE

When performing the asphalt extraction and recovery procedures, the main solvent presently used is TCE. Dow Chemical Corporation in Midland, MI and PPG Industries Inc. in Pittsburgh, PA developed TCE. The National Safety Council (1997) designates this solvent as a liquid that is colorless at room temperature and has a strong, sweet, unpleasant odor. Some other names for TCE include ethylene trichloride, triclene and ethylene trichloride. TCE has been primarily used as a solvent for greases, oils, fats and tars. It is also used to make other chemicals. TCE can even be found in household products such as rug cleaners, paint removers, adhesives, and typewriter correction fluid.

It is very important when working with TCE to have proper ventilation and take safety precautions such as gloves and eye protection, because this substance is highly toxic. The National Institute for Occupational Safety and Health (NIOSH) classifies TCE as a carcinogen. There are data that show that high concentrations of TCE have caused death and massive liver damage in humans. The Agency for Substances and Disease Registry (1993) states that other effects from exposure to lower concentrations of TCE include dizziness, headaches, visual disturbances, tremors, and vertigo. Even skin contact can cause burning and rashes and breathing in high levels of TCE can cause

damage to some facial nerves. Table 2.1 shows some of the problems that can occur from different exposure levels.

In order to protect people in the workplace from the hazards of TCE exposure, the Occupational Safety and Health Administration (OSHA) have established a Permissible Exposure Limit in the workplace air to 100 ppm averaged over 8 hours a day in a 40-hour work week. The U.S Environmental Protection Agency (1985) set a 15-minute exposure limit of 300 ppm. This limit was set to avoid central nervous system damage due to overexposure to TCE.

Although the effects listed are related to people who are working with TCE, the general public should also be concerned with the continued use of this substance. Exposure to TCE occurs in a variety of ways. As long as companies continue to use it, exposure can occur in something as common as the drinking water. Water contamination usually occurs when there is seepage of toxins into the groundwater at waste disposal sites. Other ways TCE has been detected is in ambient air levels at less than 1 part per billion. This is a very small amount, but for a hazardous substance, no exposure would be preferred.

The more that TCE is used, the more exposure occurs. All the used solvent is released into the environment through air, water, and land. Since the extraction process uses solvent, the toxins are being disposed of into the environment. Under the Community Right to Know Act, all of these toxic releases over one pound must be reported to the national Toxic Release Inventory (TRI), where the data is compiled and released to the public. This information explains how toxic substances have been disposed of in previous years. For example, U.S. Department of Health and Human

Table 2.1: Health Effects from Exposure to TCE

Low Exposure	Dizziness
	Headaches
Moderate Exposure	Headaches
	Vertigo
	Tremors
	Visual Disturbance
	Dizziness
High Exposure	Dizziness
	Sleepiness
	Unconsciousness
Direct Inhalation of Large Amounts	Damage to Facial Nerves
	Damage to Liver
	Damage to Organs
	Death
Chronic Effects of Occupational Exposure	Anorexia
	Nausea
	Vomiting
	Intolerance of Fatty Foods

Services (1993) ranked TCE 15th out of 336 chemicals released into the air and 20th in the chemicals released into air, water, and land.

As mentioned, there are many safety risks involved with the use of TCE. In addition to the health hazards, there are also environmental hazards. As more research is being performed in the area of ozone depletion, it has been found that chlorinated solvents are contributing to the damage. As of today, the Environmental Protection Agency (EPA) has already begun to ban some of these solvents. One of these was trichloroethane, which is a solvent used for similar purposes as TCE. In some states, such as Virginia, trichloroethane was used in the determination of asphalt content. A sample of asphalt would be put into trichloroethane, which would separate the bituminous binders from the aggregate (Prowell, 1997). Since TCE also has similar adverse effects on the environment, some project that it may be banned next.

If TCE were banned before a suitable solvent is found, the Florida highway construction industry would be severely impacted from quality control to the design of new and recycled mixes. This substance is imperative for recycling projects, and is necessary to check new mixes. In addition, this solvent is also used for many cleaning purposes.

2.2 Background on the Alternative Solvent EnSolv

Since there are a number of chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) based chemical solvents being phased out under the terms of the US Clean Air Act and the Montreal Protocols, EnviroTech International Inc. (ETI) has developed a replacement solvent (Clark, 1998). This replacement has the trade name of EnSolv and it is made primarily of n-Propyl Bromide, also called 1-Bromopropane. The

chemical formula for n-Propyl Bromide, also known as nPB, is $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (Shubkin, 1997). Table 2.2 shows a comparison of some of the properties of TCE and EnSolv. According to Larry Clark (1998), CEO of EnviroTech International, EnSolv is a Non-CFC/HCFC, nonflammable replacement for solvents like TCE. By the Department of Transportation standards, it is a non-flammable liquid and it exhibits flammability limits, which are similar to chlorinated solvents such as TCE (Shubkin, 1997). EnSolv will burn if it is in a concentration of 4.6-8.5% by volume in air (EnviroTech International, 1998), while TCE will burn at 8.0-9.2%.

In addition to the similar properties, ETI claims that this substance has reduced health and environmental hazards. It has been proven that EnSolv contains no chlorinated solvents and at this time it has not been designated a carcinogen. Unlike TCE, EnSolv has not been known to cause death or respiratory failure. It has however been found to cause irritation to the lungs, which is increased if there is a preexisting lung condition. There has also been some reported problems of skin and eye irritation. If EnSolv is used in poorly ventilated areas, it can cause headaches, dizziness, and nausea. Overall, EnSolv is considered a moderate health hazard (EnviroTech International, 1997). Since this solvent seems to be a safer alternative to TCE, the basis of this study was to find out if its effectiveness was equal.

2.3 Government Approval of EnSolv

Since there is very little information available regarding this new solvent EnSolv, consumers of the product are somewhat limited to the information given by ETI.

Table 2.2: Comparison of EnSolv and TCE

Solvent	Trichloroethylene	EnSolv
Specific Gravity (25° C)	1.465	1.332
Boiling Point	86.7° C / 188° F	69° C / 156° F
Evaporation Rate (n-Butyl acetate =1)	3.0	4.5
Flash Point	None	None
Atmospheric Lifetime	6-8 Days	6-10 Days

During the study, ETI claimed that n-Propyl Bromide was expected to be included in the EPA's Significant New Alternative Policy (SNAP) Program. This expectation was published and handed out with the consumer information packets on EnSolv (Clark, 1997). Some other information was also published in these documents which stated the exposure limit of EnSolv was 200 ppm. However, according to an article in Tecsource Magazine (1998) the EPA disagreed with the exposure limit and states it to be 100 ppm. Now EnSolv's latest information packets include a study performed by EnviroMedical Laboratories Inc. (1997) that states that there was no significant toxicity indicated in the concentrations from 100-400 ppm. Since there have been existing discrepancies, the EPA is expected to perform a study for SNAP before accepting any data provided by ETI.

Snap proposes restrictions or prohibitions on substitutes for Ozone Depleting Substances (ODS). SNAP helps to enforce section 612 of the amended Clean Air Act of 1990, which requires the EPA to evaluate substances for the ODS's in order to reduce overall risk to human health and environment (U.S. Environmental Protection Agency, 1999). From the evaluations that have been performed, SNAP composes a list of alternatives and states whether they are acceptable or not. The goal of SNAP is to eliminate the use of ozone depleting substances and to protect the environment from any problems that may be caused by the new alternatives.

The SNAP approval of n-Propyl Bromide for solvent use has been applied for and the EPA, under specific conditions, will probably approve it (Protonique, 1998). Although this approval may be possible, as of February 1998, n-Propyl Bromide was disapproved for aerosol, coatings, and adhesive applications. At this time, there is still no

word of solvent applications for n-Propyl Bromide. The delay is most probably due to further research of the solvent. According to Chemtronics (1998), the EPA is awaiting the results of the Ozone Depletion Potential (ODP) study and examining the new toxicity data. The approval of EnSolv has been delayed several times but EnSolv will most probably be approved for exposure limits of less than 50 ppm.

Even with all the controversy surrounding the use of n-Propyl Bromide based solvents, the Federal Highway Administration (FHWA) recently adopted EnSolv as a replacement for TCE and trichloroethane in asphalt testing (FHWA, 1998). The FHWA lab in Denver recommends EnSolv as a replacement for chlorinated solvents that are still used in other laboratories performing similar asphalt testing.

2.4 Preliminary Health and Safety Studies of EnSolv

Since the investigation of n-Propyl Bromide is relatively new, there are very few observations regarding its safety for use. So far ETI claims side effects such as eye and skin irritation as well as headaches, dizziness, nausea and vomiting (EnviroTech International, 1997). Other research shows the possibility that n-Propyl Bromide is a carcinogen and may cause adverse effects on reproduction. One manufacturer in France, Elf Atochem, has actually stopped selling n-Propyl Bromide because of their concerns over health and safety of the product (Protonique, 1998). At this time, one of the most conclusive studies on n-Propyl Bromide was performed on a single rodent strain in Japan. The reported effects were loss of grip strength in both sets of limbs, decrease in motor nerve conduction velocity in the tail and decreased sperm counts (Protonique, 1998).

Although these effects can not be related directly to humans, it caused enough concern for continued research.

2.5 Disadvantages of EnSolv

Although preliminary information shows several benefits to using EnSolv as a replacement for TCE, there are a few disadvantages. EnSolv does have a strong sweet odor that tends to saturate the air much faster than TCE. It is possible that this may be attributed to the faster evaporation rate (as seen in Table 2.2). The current vent hood systems that are used for TCE may need to be modified if EnSolv is used. When speaking to employees that have tried working around EnSolv for short periods of time, some complained of the odor and mild headaches. This problem might be avoided with improved ventilation.

Another disadvantage of EnSolv is the cost. The FDOT Materials office in Gainesville, Florida presently uses about 12.5 gallons of TCE per week. This amounts to about 2.5 barrels per week. A barrel of TCE cost the FDOT about \$123. A barrel of EnSolv costs \$266.75 (EnviroTech International, 1998). One possible solution to reduce the cost would be to recycle the spent EnSolv.

Finally, one problem that plagues all solvent users is the disposal. The stringent guidelines for disposal create complications and additional expense for all users. One thing ETI has made available to aid in the disposal of EnSolv was the creation of a waste disposal program. In this program, the user of the solvent pays a fee of about \$100 to have ETI analyze the waste and determine the proper disposal method. Once the fee is

paid, the user is only required to pay a \$30 handling fee and the cost of shipping the spent EnSolv for disposal.

2.6 Asphalt Extraction and Recovery Procedures

There are five different methods of extraction in ASTM D 2172 which include Centrifuge (Method A), Reflux (Method B, C and D), and Vacuum (Method E) extraction. The most popular methods are the Centrifuge Method A and the Reflux Method B. The asphalt extraction method used by the Florida Department of Transportation (FDOT) is ASTM D 2172, Method B. It has been shown that Method B causes an aging effect on the asphalt binder (Cipione, 1991). This is most probably attributed to the high temperatures and long term exposure to the solvent. Another problem with this method is that it tends to leave some of the asphalt remaining on the aggregate, which may not give accurate results when the properties of the binders were analyzed. It has actually been suggested that this method should not be used when the asphalt properties are going to be determined and should be used for the determination of asphalt content and aggregate gradation only.

In the past, several solvents have been used for the extraction procedure. Benzene was on the first solvents to be used. Later, in the 1950s and 1960s, new solvents were used because of the toxicity of benzene. These solvents included a group of chlorinated solvents, which consisted of TCE, 1,1,1-trichloroethane, and methylene chloride (Burr, 1990). With the recent banning of 1,1,1-trichloroethane, TCE had become the most popular and effective of these solvents. Currently, this is the solvent used for the extraction procedure at the FDOT.

There are two main methods that have been used in the past for the recovery of asphalt. These methods include the Abson Recovery method, which was introduced in 1933 and the more recent Rotary Evaporation (also called Roto-vap) which has been used since the 1970s. The ASTM Standards for these methods are ASTM D 1856, Recovery of Asphalt from Solution by Abson Method, and ASTM D 5404, Recovery of Asphalt Using the Rotavapor Apparatus. Several studies have been performed to evaluate both methods for their effectiveness in the complete removal of the solvent from recovered binder (Burr, 1990). In 1983, the Pacific Coast Users Group tested the Abson and Roto-vap methods along with two other methods and found that there was no method that outperformed the rest. The Abson method had low repeatability and failed to remove all the solvent in some cases while the others caused excessive hardening. When the problem was studied closer using TCE as the solvent, there were several things noted about each method. The Abson method tended to leave significant amounts of solvent in the recovered binder (Burr, 1990). The Roto-vap method was found to be less consistent and less reproducible than the Abson method, but could be used to recover larger sample sizes (1990). Presently, the Roto-vap method is popular, because it is simple and less labor intensive than the Abson method.

Something important that has been noted in the recent years about the extraction and recovery tests is the high variability in the viscosity of the recovered binders. The results from American Association of State Highway and Transportation Officials (AASHTO) laboratory proficiency tests show that the standard deviation of the viscosities of the recovered binders have ranged from 25 to 42 percent during the years of

1986 to 1991 (Burr, 1993). Some reasons for the large variation in results are the following:

1. The asphalt is not completely extracted from the aggregate.
2. Solvent remains in the asphalt after recovery.
3. The reaction of asphalt while in solvent may alter the properties during extraction and recovery.

In an attempt to reduce these variations, several studies have been performed to find a method or combination of methods that would provide better repeatability and less variation in the properties of the recovered binders. These methods include extraction performed in a cylinder rock polishing type apparatus and low temperature and high vacuum recoveries in the roto-vap apparatus (Peterson, 1999). Presently, none of these new methods have been adopted by the FDOT.

CHAPTER 3 RESEARCH PROGRAM AND INSTRUMENTATION

3.1 Introduction

The main objective of this study was to evaluate the suitability of using EnSolv as a replacement for TCE in the extraction and recovery of asphalts. The testing program included the following:

1. Evaluation of solubility of asphalt binders in EnSolv
2. Evaluation of asphalt extraction and recovery using EnSolv
3. Evaluation of asphalt binders recovered from mixtures using EnSolv
4. Evaluation of effects of solvents on virgin binders

This chapter describes the detailed research program and instrumentation.

3.2 Testing Program to Evaluate Solubility of Asphalt Binders in EnSolv

The solubility test is aimed at determining the bitumen content and non-bitumen matter in a given sample of asphaltic material. In this test, the insoluble material is collected on a filter and measured. The test may be applied to asphalt cements, or the asphalt cement remaining in cutbacks after distilling the diluents or in emulsions after evaporating the water.

The solubility of asphalt binders in EnSolv was evaluated by performing the standard asphalt solubility test as specified in ASTM D 2042 Standard Test Method

(1995) using both TCE and EnSolv. Typical asphalt cements used in Florida were provided for testing by the FDOT. These included five AC-30 binders and one AC-20 as well as two rejuvenating asphalts. Initially, testing on each asphalt was performed with 3 replicates, then the replicates for testing were raised to 5 for greater assurance of the results. Possible differences in the behavior of EnSolv compared to TCE were studied with respect to the following aspects:

1. The time required for dissolving the asphalt in the solvent
2. The effects of testing temperature on solubility
3. The percent solubility of the asphalt

3.3 Evaluation of Extraction and Recovery of Asphalts Using EnSolv

To evaluate the effectiveness of EnSolv in the extraction and recovery procedures, FDOT personnel collected three asphalt mixtures were collected from three asphalt plants. These mixtures included a Marshall, Superpave and a crumb rubber modified mixture.

The reflux extraction in accordance with ASTM D 2172 Method B was used to extract the binder from each of the mixtures. For this method, two different extraction set-ups were available: a small (1000-gram) unit and a large (2000-gram) unit. The difference in the set-ups is the size of the sample baskets, burners and glass jar. Figure 3.1 shows both extraction units to provide a visual comparison of size. Both extraction set-ups were used and the ease of operation was evaluated. For simplicity, all extractions were performed using only one basket in the glass jar as suggested by the FDOT. In

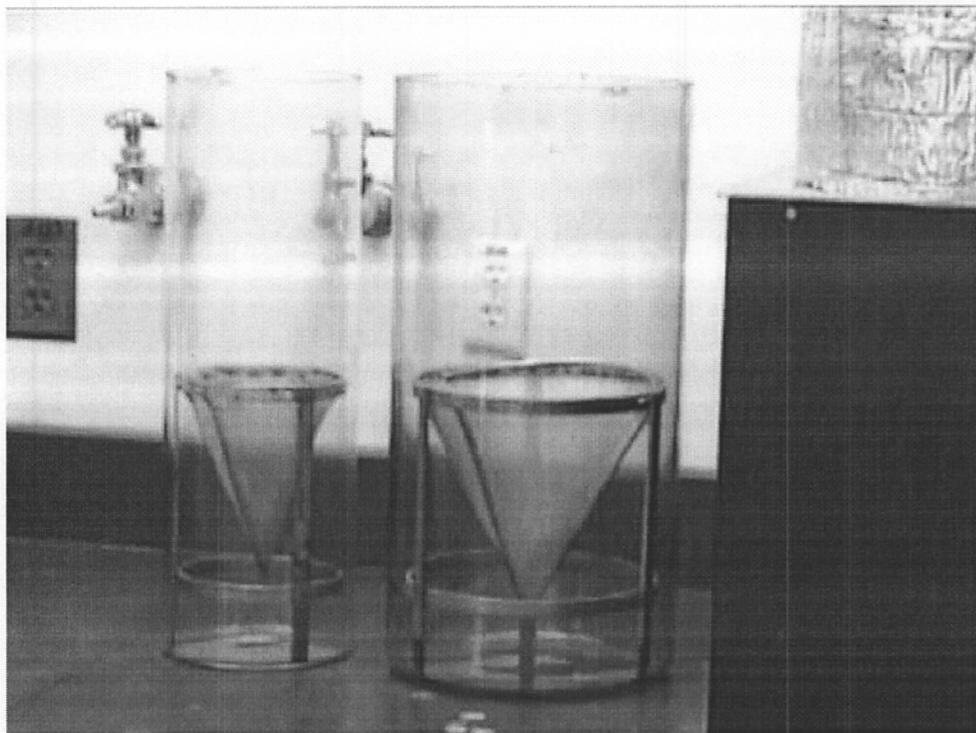


Figure 3.1: Two Sizes of Extraction Set-Ups

addition, for the large extraction set-up 800 ml of solvent was used and for the small set-up 400 ml of solvent was used. The moisture content calculations in ASTM D 2172 were not performed in this study since it was not necessary for comparison.

All extracted solutions were placed in weighed 8-oz. polyethylene centrifuge bottles. They were then placed into a large floor standing swinging centrifuge and centrifuged at force of at least 770 times gravity for 30 minutes to remove the fine particles that passed through the filter during extraction. Using the rotating radius of 19.7 cm and a rotating speed of 1876 rpm, the relative centrifugal force (RCF) can be calculated to be 775 g (gravity) based on the following equation:

$$\text{Acceleration} = \omega^2 r$$

$$\text{Acceleration} = \left(2\pi(1876) \frac{1}{60\text{sec}} \right)^2 (0.197\text{m}) = 7603 \frac{\text{m}}{\text{s}^2}$$

$$\text{RCF} = \frac{\text{Acceleration}}{g} = \frac{7603 \frac{\text{m}}{\text{s}^2}}{9.81 \frac{\text{m}}{\text{s}^2}} = 775$$

Once the centrifuge process was complete, the asphalt solution was poured from the bottles and the remaining material was dried and weighed to be included in the calculations for asphalt content. The aggregate remaining from the extraction was dried in an oven at 110° C and weighed. The procedure for drying the aggregates began with heating them in an oven until a constant mass was obtained, and followed by cooling them in a desiccator for three hours before weighing. The purpose of this procedure was to be sure that the aggregate did not contain any excess moisture when weighing.

For the recovery of the asphalt from the solution, the rotavapor apparatus was used in accordance with ASTM D 5404. Figure 3.2 shows the Buchi rotavapor apparatus

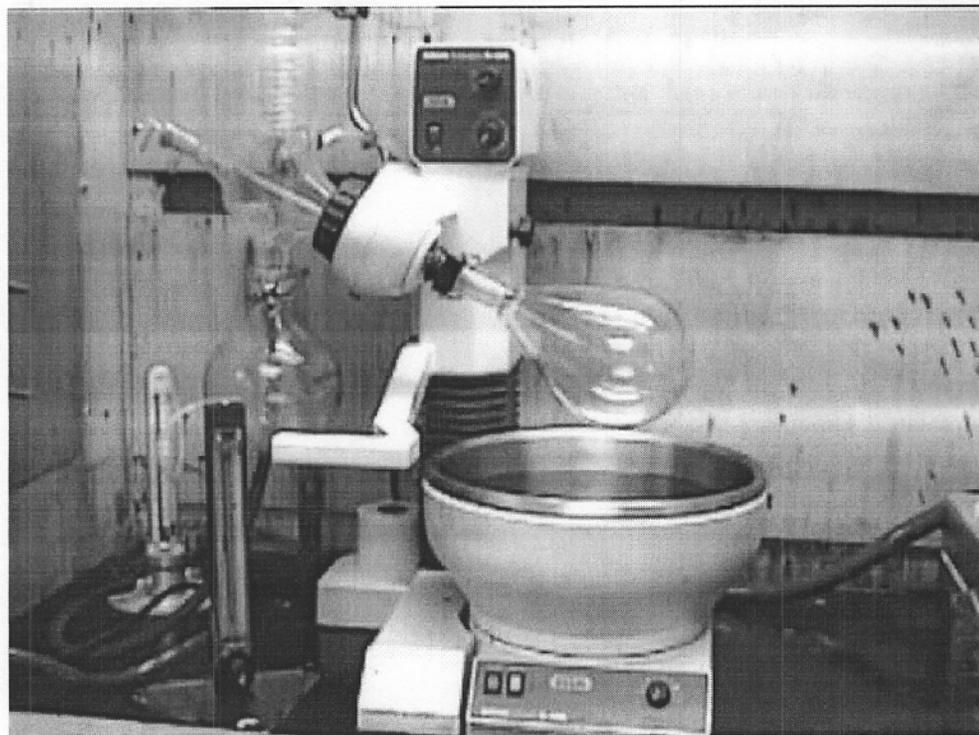


Figure 3.2: Rotavapor Apparatus Used for Testing

used for testing. A modified rotavapor recovery method used by the FDOT was also used. In this method the vacuum was set at 25 in of Hg, the initial flask rotation is 60 rpm and the final rotating speed is 80 rpm. This method was used to recover asphalt binders from mixtures using EnSolv and TCE, and the results were compared to those obtained using the ASTM standard method.

For each of the testing conditions, three replicates were performed. The differences in the behavior of TCE, EnSolv and reclaimed EnSolv in the extraction and recovery processes were evaluated with respect to:

1. Asphalt content obtained in the extraction test.
2. The amount of time required performing each operation.
3. Ease of operation.

3.4 Evaluation of Recovered Binders from the Mixtures

The recovered binders obtained were characterized to determine if there were any differences in the effects of TCE, EnSolv and reclaimed EnSolv on the recovered binders. The following tests were run on the recovered binders:

1. Penetration at 25° C. (ASTM D5)
2. Brookfield viscosity test at 60° C.
3. Dynamic shear rheometer test at 25 and 64° C.
4. Bending beam rheometer test at -18° C.
5. FTIR Spectral Analysis

Three replicate samples were tested and any difference between the effects of the solvents and recovery methods were evaluated by means of Student's t-tests.

3.4.1 Brookfield Viscosity Test

The Brookfield Thermosel apparatus, model HB DV-3, was used to measure the apparent viscosity of asphalt at 60° C. Figure 3.3 shows the set-up used for testing.

The viscosity determinations were made according to ASTM D 4402 (1995) which is also under the SHRP designation of B-007 (1993). This method measures the apparent viscosity, which is the ratio of shear stress to shear rate.

The Brookfield Rheometer is a rotational viscometer that measures the torque required to rotate a spindle at a constant speed while immersed in an asphalt sample at a constant temperature. The torque required to rotate the spindle immersed in the asphalt binder and the angular velocity are both used to determine the shear stress and shear rate. All the tests were performed at nine rotational speeds (shear rates). Once the data points were collected, a power law model was used to analyze the data and the viscosity at a shear rate equal to 1 1/sec was selected to be the viscosity result.

The HBDV-3 model (shown in Figure 3.3) used for testing was connected to a personal computer data acquisition system. Computer software developed by Brookfield Engineering Laboratories was used to read, store, and analyze the data. This software contained the power law model, which was used to calculate the viscosity.



Figure 3.3: Brookfield Viscosity Testing Equipment

3.4.2 Dynamic Shear Rheometer Test

The dynamic shear rheometer was used to determine the rheological properties of the binder in terms of G^* (complex shear modulus or stiffness) and δ (phase angle). This testing is normally performed at two temperatures and the results are used to characterize binder behaviors at both high and intermediate pavement temperatures to control rutting and fatigue cracking of the pavement respectively. The values of G^* and δ provide an indication of the visco-elastic behavior of the asphalt at different temperatures. The Bohlin Instruments DSR II, shown in Figure 3.4, was used for this study. The procedure for testing was in accordance with SHRP B-003 (1993). The set-up for DSR testing included placing a small asphalt sample between two circular plates. One of these plates is fixed and one oscillates back and forth. The test can be run by applying either a constant stress or constant strain. Constant stress means that the spindle (attached to one of the plates) is rotated through a distance until a fixed stress is achieved. Constant strain means that the spindle is always rotated through the same fixed distance. Either way, the oscillating plate is rotated and the resulting stress or strain is recorded. For this study the constant strain method of testing was performed at three temperatures which were 25, and 60° C. These testing temperatures were chosen to represent standard testing temperatures typical for Florida for Performance Graded (PG) asphalt specifications and a standard testing temperature for AC-graded asphalt binders.



Figure 3.4: Bohlin Instruments DSR II

3.4.3 Bending Beam Rheometer Test

The BBR was used as part of the evaluation to determine the rheological properties of the recovered binder samples in terms of flexural creep stiffness (S) and the rate at which the creep stiffness changes with loading time (m-value). This test is a low-temperature stiffness test, which is normally performed at 10° C above the lowest expected service pavement temperature.

The BBR tests were performed in accordance with AASHTO TP1-98 at a temperature of -18° C. The set-up for the BBR testing includes the construction of a beam of asphalt with a length of 127±0.5 mm, a width of 12.7±0.05 mm, and a thickness of 6.35±0.05 mm. The beam is placed in a controlled temperature fluid bath and loaded with a constant load (980±50mN) for 240 seconds. The test load and the midpoint deflection of the beam are monitored over time using a computerized data acquisition system. The maximum bending stress at the midpoint of the beam is calculated from the beam dimensions, the span length, and the load applied to the beam for loading times of 8, 15, 30, 60, 120, and 240 seconds. The maximum bending strain in the beam is calculated for the same loading times from the dimensions of the beam and its deflections. The stiffness is calculated by dividing the maximum stress by the maximum strain. The equipment used to perform this test was a Cannon Instruments TE-BBR, as shown in Figure 3.5.

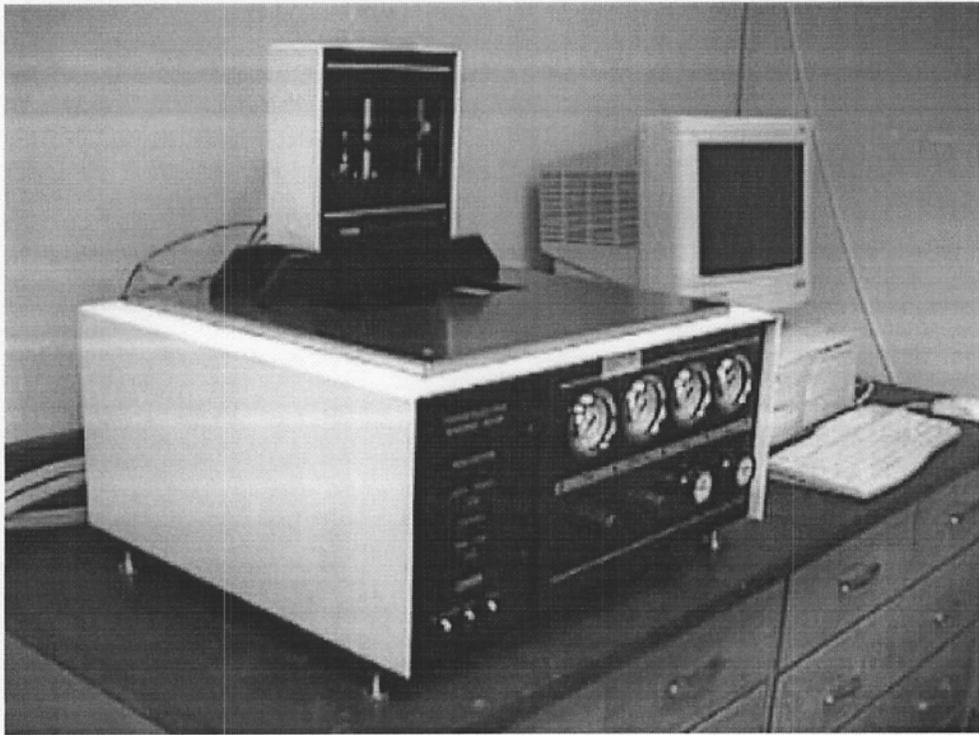


Figure 3.5: Bending Beam Rheometer Testing Apparatus

3.4.4 Fourier Transform Infrared Spectral Analysis

The infrared spectral analysis was performed on all recovered binders using the Fourier Transform Infrared (FTIR) spectrometer. The FTIR analysis provides an infrared (IR) absorption spectrum of the tested material, which can serve as a “fingerprint” of the chemical characteristics (functional groups) of the tested material. Materials that have dissimilar chemical compositions will show dissimilar IR absorption spectra. The IR absorption spectrum between wavenumbers 1500 cm^{-1} and 2000 cm^{-1} is of particular interest (and will be focused on) since it contains the absorption bands for the functional groups of carboxylic acids, ketones, and anhydrides, which are usually formed upon age-hardening of asphalts [Tia, 1994].

The recovered binders that were tested were all dissolved in an HPLC-grade tetrahydrofuran (THF) at a 5% (by weight) concentration. The solution containing the THF and the asphalt was then injected into a de-mountable cell and scanned in the FTIR spectrometer. Each sample was scanned four times and the spectrums were averaged to get more reliable readings. To remove the absorption spectrums due to the THF, the cell and the environment, a background scan was done on the cell containing only the pure THF. This background scan was then subtracted from the total IR absorption spectrum (by means of the software SPECTRUM used to operate the equipment) to obtain the absorption spectrum of the recovered asphalt sample.

The IR absorption spectra of the EnSolv and reclaimed EnSolv recovered asphalt binders were compared with those of the TCE recovered asphalt binders using the COMPARE function provided in the software program SPECTRUM. The compare function calculates the correlation coefficient between the two spectra being compared.

A perfect match between the two spectra will have a correlation coefficient of 1.00, while a correlation coefficient of zero means that the two spectra are completely dissimilar. These correlation coefficients were then used to compare the variability between replicates with the variability between solvents and recovery procedures. These comparisons were done through observations of the correlation coefficients since no statistical models would be appropriate. The apparatus and materials required for this test included the use of a 1600 series Fourier Transform Infrared spectrometer, HPLC-grade THF, a syringe, and a de-mountable cell with NaCl salt windows and a 1-mm teflon spacer. The apparatus required to perform the FTIR spectral analysis is presented in Figure 3.6.

3.5 Evaluation of the Effects of Solvents on Virgin Binders

To evaluate the effects (if any) solvents have on asphalt binders, a procedure was developed to dissolve various binders in each of the three solvents and then to recover the binders back from the solvents. After taking into consideration the amount of asphalt required for the binder evaluation, 60 grams of asphalt was poured directly into the recovery flasks and dissolved in 400 ml of solvent. When the binder was completely dissolved, the flask was attached to the rotavapor recovery apparatus and the binder was recovered. For this evaluation, typical asphalt cements used in Florida were used for the testing. These included AC-30 and AC-20 grades of asphalt. Each of the asphalt binders were dissolved in each of the three solvents used in the first phase of the study (TCE, EnSolv and reclaimed EnSolv) and three replicates were completed for each combination of binder and solvent.

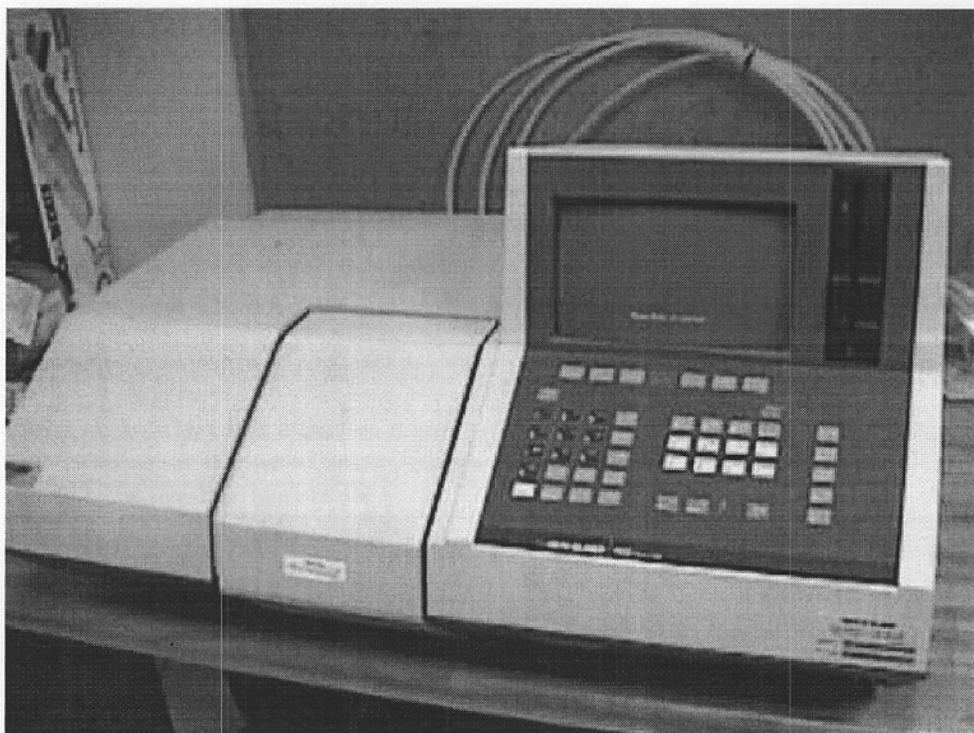


Figure 3.6: Fourier Transform Infrared Spectrometer

The rotavapor apparatus was used in accordance with ASTM D 5404 for the recovery of the asphalt from the solution. The recovered binders were characterized to see if the solvents had any effect on the asphalt binders during the dissolving and recovery procedure. The following tests were performed on the recovered binders:

1. Penetration Test at 25 °C (ASTM D 5)
2. Brookfield Viscosity Test at 60 °C (ASTM D 4402)
3. Dynamic Shear Rheometer at 64 and 25 °C (AASHTO TP5-98)
4. Bending Beam Rheometer at -18 °C (AASHTO TP1-98)
5. FTIR Spectral Analysis

Three replicate samples were tested and any differences between the effects of the recovered samples, along with the virgin material were evaluated by means of the Student's t-test. All tests were performed as described in the previous sections.

3.6 Statistical Analysis

The Student's t-test is a comparison model that tests the hypothesis that two means from different populations are equal. The means of the two groups were evaluated to see if there were any significant differences between the two solvents. To perform this type of analysis, it was necessary to calculate the test statistic "t". The following equation (McCuen, 1985) was used to determine the value of t.

$$t = \frac{X_1 - X_2}{S(1/n_1 + 1/n_2)^{0.5}}$$

Where X_1 and X_2 are the population means for groups 1 and 2 and n_1 and n_2 are the corresponding sample sizes for groups 1 and 2 respectively. S is the weighted standard deviation of the data and is calculated from the following formula.

$$S^2 = \frac{(n_1-1)s_1^2 + (n_2-1)s_2^2}{n_1 + n_2 - 2}$$

In the equation, s_1^2 and s_2^2 are the variances from each of the populations (McCuen, 1985). The degree of freedom used was (n_1+n_2-2) . A confidence interval of 95% was used to test if the difference was significant. All calculated t-values were compared to the critical t-value (for a 95% confidence) to determine if there were any significant differences between the population means. If the $t_{\text{calculated}}$ were less than the t_{critical} , there would be no significant difference between the populations analyzed.

CHAPTER 4
EVALUATION OF SOLUBILITY OF ASPHALT BINDERS IN ENSOLV

4.1 Results of the Solubility of Asphalt Binders in EnSolv and TCE

The testing program for the evaluation of solubility of asphalt binders in EnSolv is described in Section 3.2. Initially, the solubility test was performed on five different asphalt cements with three replicates per asphalt. The asphalt tested included two AC-30s, one AC-20, one RA-1225 (Recycling Agent – 1225) and one RA-700. The test method was performed in accordance with ASTM D 2042 for both solvents. This method was followed to see if EnSolv could be used in place of TCE without making any changes to the current specifications for testing. The results from the first five solubility test sets are shown in Table 4.1. The mean and the standard deviation of the test results were computed for each combination of solvent and asphalt tested. It can be seen that the difference between the mean solubility in TCE and that in EnSolv varies from 0.01% (for Asphalt #1) to 0.07% (for Asphalt #5). The standard deviation of the solubility in TCE varies from 0.0058% (for Asphalt #3 and 5) to 0.0404% (for Asphalt #1). The standard deviation of the solubility in EnSolv varies from 0.0153% (for Asphalt #3) to 0.0321% (for Asphalt #5).

Table 4.1: Results from the First Set of the Solubility Tests

Asphalt Type	Solvent	Replicate			Mean	Standard Deviation
		1	2	3		
(1) AC-30	TCE	99.97%	99.90%	99.97%	99.947%	0.0404%
	EnSolv	99.93%	99.97%	99.97%	99.957%	0.0231%
(2) AC-20	TCE	99.96%	99.96%	99.93%	99.950%	0.0173%
	EnSolv	99.98%	99.92%	99.96%	99.953%	0.0306%
(3) RA-1225	TCE	99.98%	99.97%	99.97%	99.973%	0.0058%
	EnSolv	99.95%	99.98%	99.97%	99.967%	0.0153%
(4) RA-700	TCE	99.98%	99.95%	100.00%	99.977%	0.0252%
	EnSolv	99.96%	99.99%	100.00%	99.983%	0.0208%
(5) AC-30	TCE	99.98%	99.99%	99.99%	99.987%	0.0058%
	EnSolv	99.96%	99.90%	99.91%	99.923%	0.0321%

A Student's t-test was run on the data for each type of asphalt to determine if the solubility in EnSolv was significantly different from that in TCE. A confidence level of 95% was used. The results from the statistical analysis are shown in Table 4.2. The results from the Student's t-test indicate that the difference in solubility in the two solvents is statistically insignificant for 4 out of the 5 asphalts tested.

At this point it was decided to run more solubility tests for improved reliability. There were now five replicates for each combination of asphalt and solvent. The data from the initial solubility tests was included as part of the data for this analysis. Samples that included previous data were analyzed to be sure that there were no outliers, which would act as confounding variables in the statistical analysis. An outlier for this analysis was defined as any point that was more than two standard deviations away from the mean. After analysis it was determined that there were no outliers and all the previous data were included.

The results from all the solubility tests are displayed in Table 4.3. The mean and standard deviation of the results were calculated and are also displayed in Table 4.3, which shows that the difference between the mean solubility in TCE and that in EnSolv varies from 0.098 % (for Asphalt #7) to 0.000% (for Asphalt #1). The standard deviation of the solubility in TCE varies from 0.0084% (for Asphalt #3) to 0.0303% (for Asphalt #1). The standard deviation of the solubility in EnSolv varies from 0.0090% (for Asphalt #8) to 0.1077% (for Asphalt #2).

Table 4.2: Results of the Student's t-Tests on the First Set of Solubility Tests

Asphalt Type	Solvent	Sample Size	Mean	$t_{\text{Calculated}}$	$t_{\text{Critical for 95\% Confidence}}$	Significantly Different
(1) AC-30	TCE	3	99.947%	0.372	2.775	NO
	EnSolv	3	99.957%			
(2) AC-20	TCE	3	99.950%	0.164	2.775	NO
	EnSolv	3	99.953%			
(3) RA-1225	TCE	3	99.973%	0.707	2.775	NO
	EnSolv	3	99.967%			
(4) RA-700	TCE	3	99.977%	0.354	2.775	NO
	EnSolv	3	99.983%			
(5) AC-30	TCE	3	99.987%	3.588	2.775	YES
	EnSolv	3	99.923%			

Table 4.3: Results of All the Solubility Tests

Asphalt Type	Solvent	Replicate					Mean	Standard Deviation (%)
		1	2	3	4	5		
(1) AC-30	TCE	99.97%	99.90%	99.97%	99.97%	99.95%	99.952%	0.0303
	EnSolv	99.93%	99.97%	99.97%	99.96%	99.93%	99.952%	0.0205
(2) AC-20	TCE	99.96%	99.96%	99.93%	99.94%	99.93%	99.944%	0.0152
	EnSolv	99.98%	99.92%	99.96%	99.88%	99.71%	99.890%	0.1077
(3) RA-1225	TCE	99.98%	99.97%	99.97%	99.99%	99.98%	99.978%	0.0084
	EnSolv	99.95%	99.98%	99.97%	99.96%	99.82%	99.936%	0.0658
(4) RA-700	TCE	99.98%	99.95%	100.00%	99.98%	99.99%	99.980%	0.0182
	EnSolv	99.96%	99.99%	100.00%	99.99%	99.97%	99.982%	0.0164
(5) AC-30	TCE	99.98%	99.99%	99.99%	99.98%	99.96%	99.980%	0.0123
	EnSolv	99.96%	99.90%	99.91%	99.83%	99.99%	99.918%	0.0614
(6) AC-30	TCE	99.98%	99.97%	99.96%	99.96%	99.96%	99.966%	0.0089
	EnSolv	99.96%	99.95%	99.94%	99.94%	99.96%	99.950%	0.0100
(6) AC-30 (Repeat)	TCE	99.97%	99.95%	99.98%	99.96%	99.98%	99.968%	0.0105
	EnSolv	99.96%	99.93%	99.96%	99.97%	99.97%	99.958%	0.0166
(7) AC-30	TCE	99.95%	99.96%	99.98%	99.99%	99.99%	99.974%	0.0182
	EnSolv	99.86%	99.78%	99.87%	99.94%	99.93%	99.876%	0.0643
(7) AC-30 (Repeat)	TCE	99.99%	99.97%	99.99%	99.95%	99.97%	99.974%	0.0148
	EnSolv	99.98%	99.82%	99.80%	99.85%	99.86%	99.862%	0.0698
(8) AC-30	TCE	99.99%	99.97%	100.00%	99.99%	99.99%	99.988%	0.0110
	EnSolv	99.99%	99.98%	99.98%	100.00%	99.98%	99.986%	0.0089

Once again, the Student's t-test was run on the data for each of the asphalt cements to determine if the solubility in EnSolv is significantly different from that of TCE at a confidence level of 95%. The results from this analysis are displayed in Table 4.4, which indicates that with the exception of Asphalts #6 and #7, the difference in solubility in the two solvents is statistically insignificant.

In order to verify the results of the tests on Asphalts #6 and #7, solubility tests were repeated on these two asphalts with 5 replicates per asphalt. The results of the repeated tests are also displayed in Table 4.3. The same statistical analysis was performed on the data and the analysis results are also displayed in Table 4.4. The results of the analysis on the two new sets of data indicate that the difference in solubility is not significant for Asphalt #6, but was still significant for Asphalt #7. In addition to analyzing each sample set separately, all the replicates for Asphalt #6 were grouped together so that each set had a total of ten replicates. The same was done for Asphalt #7. The Student's t-test was performed on the data comparing the solvents and the results showed that in both asphalt samples there was a significant statistical difference. Since the difference of the means for Asphalt #6 was only 0.013% and 0.105% for Asphalt #7, the small values indicate that for all practical purposes, there was really very little difference between the solvents.

Table 4.4: Results of the Student's t-Test for the Results from All Solubility Tests

Asphalt Type	Solvent	Sample Size	Mean (%)	$t_{\text{Calculated}}$	$t_{\text{Critical for 95\% Confidence}}$	Significantly Different
(1) AC-30	TCE	5	99.952	0.000	2.306	NO
	EnSolv	5	99.952			
(2) AC-20	TCE	5	99.944	1.110	2.306	NO
	EnSolv	5	99.890			
(3) RA-1225	TCE	5	99.975	1.416	2.306	NO
	EnSolv	5	99.936			
(4) RA-700	TCE	5	99.980	0.180	2.306	NO
	EnSolv	5	99.982			
(5) AC-30	TCE	5	99.980	2.214	2.306	NO
	EnSolv	5	99.918			
(6) AC-30	TCE	5	99.966	2.667	2.306	YES
	EnSolv	5	99.950			
(6) AC-30 (Repeat)	TCE	5	99.968	1.925	2.306	NO
	EnSolv	5	99.958			
(7) AC-30	TCE	5	99.974	3.281	2.306	YES
	EnSolv	5	99.876			
(7) AC-30 (Repeat)	TCE	5	99.974	5.053	2.306	YES
	EnSolv	5	99.862			
(8) AC-30	TCE	5	99.988	0.316	2.306	NO
	EnSolv	5	99.986			

One final analysis was performed on the solubility data to see how the results conformed to the precision statement of ASTM D 2042. In order to perform this analysis the standard deviation value from both within laboratory variability and between laboratory variability was taken from the standard and this value was used to calculate the maximum allowable difference between the means of the data. The formula used for the allowable difference is as follows:

$$\text{AllowableDifference} = \frac{\sigma * 2\sqrt{2}}{\sqrt{N}}$$

Where σ is the standard deviation obtained from the precision statement and N is the sample size (number of replicates in this case). The results from this analysis are displayed in Table 4.5. The results conformed to the within laboratory precision statement in 6 out of 10 cases, while the results for between laboratory results conformed for all 10 cases.

Since there is no specified temperature for running this test, all tests were initially run at ambient temperature. Five samples from each solvent type were chosen and the time it took to dissolve each sample was observed. The way the times were observed was by turning the flask sideways to see if the sample was still remaining on the bottom. Once the sample was completely dissolved, the time was recorded.

Table 4.5: Results of the ASTM Allowable Difference Results from All Solubility Tests

Asphalt Type	Solvent	Sample Size	Mean (%)	Difference in the Means (%)	Allowable Difference Within the Laboratory	ASTM Standard Met	Allowable Difference Between Laboratories	ASTM Standard Met
(1) AC-30	TCE	5	99.952	0.000	0.044	YES	0.116	YES
	EnSolv	5	99.952					
(2) AC-20	TCE	5	99.944	0.054	0.044	NO	0.116	YES
	EnSolv	5	99.890					
(3) RA-1225	TCE	5	99.975	0.039	0.044	YES	0.116	YES
	EnSolv	5	99.936					
(4) RA-700	TCE	5	99.980	0.002	0.044	YES	0.116	YES
	EnSolv	5	99.982					
(5) AC-30	TCE	5	99.980	0.062	0.044	NO	0.116	YES
	EnSolv	5	99.918					
(6) AC-30	TCE	5	99.966	0.016	0.044	YES	0.116	YES
	EnSolv	5	99.950					
(6) AC-30 (Repeat)	TCE	5	99.968	0.010	0.044	YES	0.116	YES
	EnSolv	5	99.958					
(7) AC-30	TCE	5	99.974	0.098	0.044	NO	0.116	YES
	EnSolv	5	99.876					
(7) AC-30 (Repeat)	TCE	5	99.974	0.112	0.044	NO	0.116	YES
	EnSolv	5	99.862					
(8) AC-30	TCE	5	99.988	0.002	0.044	YES	0.116	YES
	EnSolv	5	99.986					

The amount of time required to dissolve the asphalt samples was noted to be very close to one another. The average time for TCE was 5.94 minutes while the average time for EnSolv was 6.57 minutes. These times would be considered about the same for practical purposes since the amount of time required to dissolve the sample would be dependent on the variable surface area of the asphalt sample exposed to the solvent.

Since there was no problem with the required time to dissolve the asphalt samples, and the test method was easy to perform with EnSolv, it was decided that there was no need to investigate the effects of temperature on asphalt solubility in EnSolv. The solubility test using EnSolv can be run at ambient temperature in the laboratory.

4.2 Conclusions

The results of the solubility tests indicate that the EnSolv is not statistically different from TCE in 7 out of a total of 10 sets of tests. In the sets of tests that were statistically different, the maximum difference between the means was 0.114%. This difference is so small that it really has no practical significance in this test. From the data, it seems that EnSolv is a suitable replacement for TCE in the ASTM test method, D 2042. In addition, this test method does not need any modifications when using EnSolv as the solvent.

CHAPTER 5
EVALUATION OF EXTRACTION AND RECOVERY OF ASPHALTS USING
ENSOLV

5.1 Testing Program

In the investigation of the extraction of asphalt binders from mixtures, a total of 4 mixtures were used. Of the 4 mixtures, one was a laboratory produced Marshall mixture and the three remaining were plant mixtures. The plant mixtures included Marshall and Superpave mixtures containing some RAP and a crumb rubber modified mixture. All the mixtures were provided by the FDOT and were representative of current projects in the state of Florida. Observations of the extraction test included time for extraction, asphalt content and ease of the method. The statistical model used to evaluate the results was the Student's t-test, which was explained in Section 3.6.

The recovery procedure was performed only on the plant mixtures. Two recovery methods were investigated in this study; they are the standard ASTM Method D 5404, and the method proposed by the FDOT which increases the vacuum and rotating speed of the rotavapor apparatus as explained in Section 3.3. Observations of each recovery method included length of time for recovery and ease of method. All testing was investigated to see if EnSolv would be a suitable solvent for the existing methods before making any variations in the existing test methods.

5.2 Results from the Extraction Procedure

5.2.1 Results from the Smaller Extraction Unit

The Reflux Extraction test was performed using two different types of equipment set-ups, a small unit (1000-gram) and a large unit (2000-gram). Although two different types of units were used, all testing was performed in accordance with ASTM D 2172 Method B with only one basket used in the extraction glass jar. The testing on laboratory and crumb rubber modified mixture was performed in the smaller unit with a sample size of 500 grams. Five replicates were performed for each test. The lengths of time that were required for performing the Reflux Extraction using TCE and EnSolv, as well as the means and standard deviations for these two mixtures are shown in Tables 5.1 and 5.2. . A graphical representation of the average extraction time required for the testing is shown in Figure 5.1. The results for the asphalt contents of these mixtures are shown in Tables 5.3 and 5.4.

5.2.2 Results from the Larger Extraction Unit

The larger extraction unit was used for the extraction of the Marshall, Superpave and crumb rubber modified mixtures. For this unit, 1500-gram samples were used to make sure that there would be a sufficient amount of asphalt binder after recovery for further testing. The solvents used for testing included TCE, EnSolv and reclaimed EnSolv.

The reason for testing the crumb rubber modified mixture again in the larger set-up was to enable that the entire extraction and recovery procedure to be completed in 8 hours. From the results shown in Table 5.2, it is seen that the extraction time using TCE

Table 5.1: Extraction Times for the Laboratory Mixture (500 Gram Sample)
(Hours:Minutes)

Trial	Trichloroethylene	EnSolv
1	6:07	2:43
2	4:36	3:51
3	5:17	2:23
4	5:43	2:57
5	5:34	3:33
Mean	5:27	3:05
Standard Deviation	0:34	0:36

Table 5.2: Extraction Times for the Crumb Rubber Modified Mixture (500 Gram Sample)
(Hours:Minutes)

Trial	Trichloroethylene	EnSolv
1	5:33	3:05
2	6:33	3:39
3	6:35	3:37
4	8:02	4:50
5	8:39	4:05
Mean	7:04	3:51
Standard Deviation	1:19	0:39

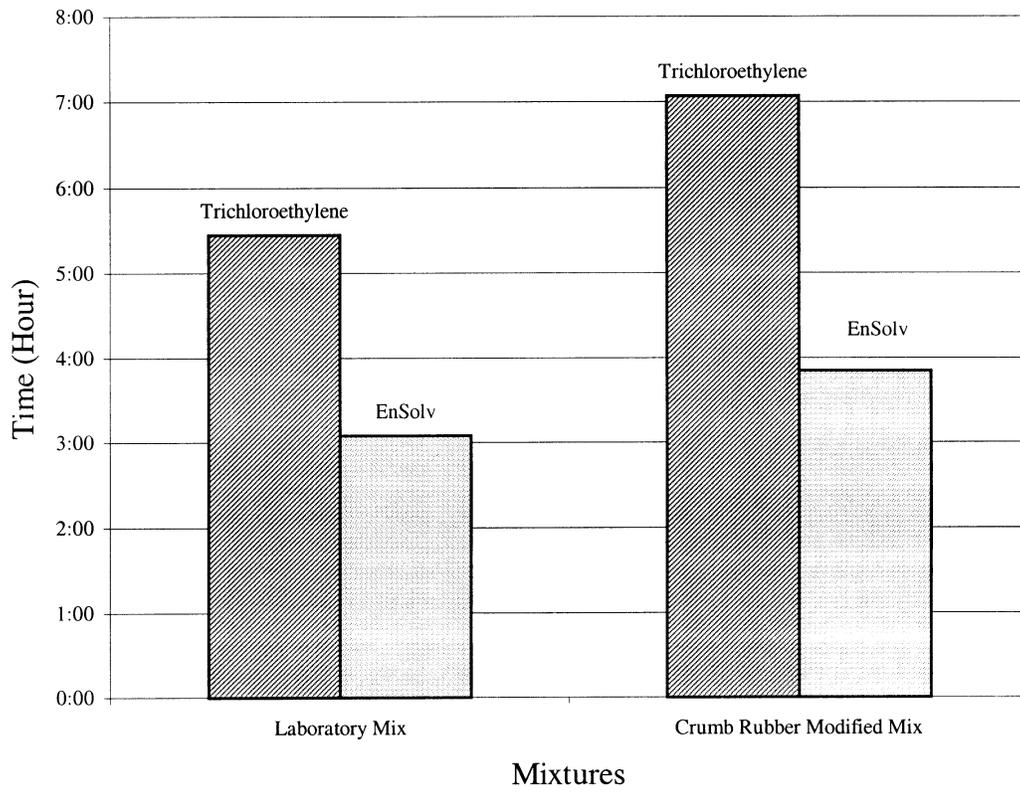


Figure 5.1: Comparison of the Average Extraction Times Required (500 gram sample)

Table 5.3: Asphalt Content for the Laboratory Mixture
(500-Gram Sample)

Trial	Trichloroethylene	EnSolv
1	4.97%	5.16%
2	4.96%	4.75%
3	5.04%	4.78%
4	5.04%	4.92%
5	4.72%	5.29%
Mean	4.95%	4.98%
Standard Deviation	0.132%	0.237%

Table 5.4: Asphalt Content for the Crumb Rubber Modified
Mixture (500-Gram Sample)

Trial	Trichloroethylene	EnSolv
1	4.76%	4.77%
2	4.93%	4.93%
3	4.85%	5.20%
4	4.60%	5.18%
5	4.84%	4.97%
Mean	4.80%	5.01%
Standard Deviation	0.125%	0.181%

was from 6 to 8 hours which would not allow the recovery to be completed within the time limit.

In order to meet the 8-hour time limit for the complete extraction and recovery process in the smaller unit, the time of extraction was limited to 4 hours regardless of whether or not all the asphalt was completely extracted. The properties of the recovered binders from this extraction procedure were then compared with those from the extraction procedure performed in the larger unit.

The initial tests using the larger Reflux Extraction apparatus were still taking too long and the rubber in the mixture was also causing clogging problems in the filter paper. It was not only difficult to complete the test in the time allotted, but too much solvent was accumulating in the cone. There were two problems with the excess solvent in the cone. The first one was that there was not enough solvent remaining on the bottom of the jar. The second problem was that any rubber that was floating on the top of the solvent in the cone splashed out when the solvent dripped down from the condenser. This caused an addition of rubber into the solvent solution.

The first problem could be solved by the addition of more solvent at the beginning of the test. The second, however, was slightly more difficult to resolve. In an attempt to speed up the flow of the filter in the extraction unit, a new filter paper was used for the procedure. This filter paper, which is used regularly by the FDOT, consists of a three-layer system of towel like paper with thread woven through it. This paper is called Teri and it is a 4 ply reinforced paper wipe. This modification enabled the process to be completed in the time allowed with fewer complications.

The results for the time required to perform the Reflux Extraction test, as well as the mean and standard deviation of the data for the Marshall, Superpave and crumb rubber modified mixtures are displayed in Tables 5.5, 5.6 and 5.7. A graphical representation of the average extraction times required for testing is shown in Figure 5.2. The results for the asphalt content of the mixtures are displayed in Tables 5.8, 5.9 and 5.10.

5.2.3 Statistical Analysis of Extraction Data

A statistical analysis was performed on all the data using the Student's t-test for paired data. The first part of the analysis was performed on the length of time required for extraction of the mixtures to see if there was a statistical difference between TCE, EnSolv and reclaimed EnSolv. The results from the analysis are displayed in Table 5.11. The Student's t-test revealed that at a 95% confidence level, there was a significant statistical difference between TCE and EnSolv for all mixtures tested. The results from testing showed that EnSolv worked faster than TCE for the reflux Extraction procedure. The range of the means of extraction time for TCE for all mixtures was from 2 hours 20 minutes to 8 hours 39 minutes. The range of the means of extraction time for EnSolv for all mixtures was from 1 hour 20 minutes to 4 hours 50 minutes. In addition, it was also noticed that the reclaimed EnSolv also worked faster than the TCE and when comparing the means. The reclaimed EnSolv was just as effective as the new EnSolv for the Reflux Extraction procedure.

Table 5.5: Extraction Times for the Marshall Mixture
(1500 Gram Sample) (Hours:Minutes)

Trial	Trichloroethylene	EnSolv	Reclaimed EnSolv
1	3:08	1:53	2:23
2	3:33	1:54	1:53
3	3:08	2:12	1:43
4	3:19	1:50	2:07
5	3:54	2:05	2:20
6	3:38	2:09	1:57
Mean	3:27	2:00	2:04
Standard Deviation	0:18	0:09	0:16

Table 5.6: Extraction Times for the Superpave Mixture
(1500 Gram Sample) (Hours:Minutes)

Trial	Trichloroethylene	EnSolv	Reclaimed EnSolv
1	2:20	1:30	1:55
2	2:24	1:32	1:40
3	2:49	1:43	1:43
4	2:23	1:20	-
5	2:45	1:38	-
6	2:32	1:44	-
Mean	2:32	1:35	1:46
Standard Deviation	0:12	0:09	0:08

Table 5.7: Extraction Times for the Crumb Rubber Modified Mixture (1500 Gram Sample) (Hours:Minutes)

Trial	Trichloroethylene	EnSolv	Reclaimed EnSolv
1	3:32	1:56	2:07
2	4:04	2:13	2:17
3	3:49	2:17	2:30
4	3:21	2:23	-
5	3:47	2:46	-
6	3:28	2:14	-
Mean	3:40	2:18	2:18
Standard Deviation	0:16	0:16	0:12

Table 5.8: Asphalt Content for the Marshall Mixture (1500 Gram Sample)

Trial	Trichloroethylene	EnSolv	Reclaimed EnSolv
1	6.60%	6.44%	6.72%
2	6.62%	6.75%	6.59%
3	6.41%	6.72%	6.57%
4	6.68%	6.69%	6.42%
5	6.67%	6.42%	6.78%
6	6.69%	6.78%	6.66%
Mean	6.61%	6.63%	6.62%
Standard Deviation	0.105%	0.161%	0.127%

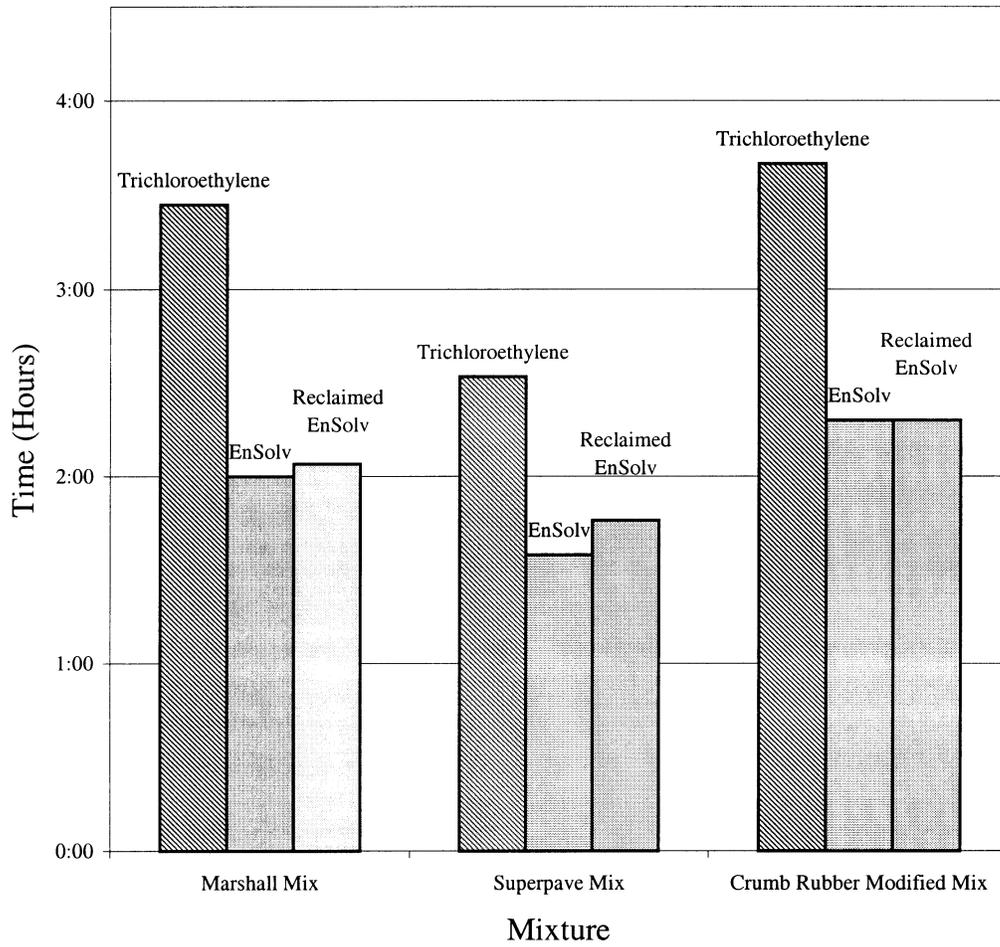


Figure 5.2: Comparison of Average Extraction Times
(1500 gram sample)

Table 5.9: Asphalt Content for the Superpave Mixture
(1500-Gram Sample)

Trial	Trichloroethylene	EnSolv	Reclaimed EnSolv
1	4.71%	4.50%	4.45%
2	4.64%	4.68%	4.63%
3	4.36%	4.42%	4.63%
4	4.07%	4.54%	-
5	4.28%	4.57%	-
6	4.01%	4.56%	-
Mean	4.35%	4.55%	4.57%
Standard Deviation	0.287%	0.086%	0.104%

Table 5.10: Asphalt Content for the Crumb Rubber Modified
Mixture (1500-Gram Sample)

Trial	Trichloroethylene	EnSolv	Reclaimed EnSolv
1	5.13%	5.24%	5.02%
2	4.88%	5.47%	4.71%
3	4.72%	5.00%	5.43%
4	5.32%	5.01%	-
5	5.02%	5.35%	-
6	5.17%	5.25%	-
Mean	5.04%	5.22%	5.05%
Standard Deviation	0.215%	0.186%	0.361%

Table 5.11: Results from the Student's t-Test Performed on
Time Required for Extraction Data

Mixture Type	Solvent	Mean (Minutes)	Sample Size	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
Laboratory (500g)	TCE	327	5	6.409	2.306	YES
	EnSolv	185	5			
Crumb Rubber Modified (500g)	TCE	424	5	5.004	2.306	YES
	EnSolv	231	5			
Marshall	TCE	207	6	10.287	2.228	YES
	EnSolv	120	6			
	TCE	207	6	8.413	2.228	YES
	RE*	124	6			
Superpave	TCE	152	6	9.278	2.228	YES
	EnSolv	95	6			
	TCE	152	6	5.846	2.365	YES
	RE*	106	3			
Crumb Rubber Modified	TCE	220	6	8.792	2.228	YES
	EnSolv	138	6			
	TCE	220	6	7.832	2.365	YES
	RE*	138	3			

Note: RE* denotes the use of reclaimed EnSolv

Table 5.12: Results from the Student's t-Test Performed on Asphalt Content Data

Mixture Type	Solvent	Sample Size	Mean (%)	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
Laboratory (500g)	TCE	5	4.95	0.280	2.306	NO
	EnSolv	5	4.98			
Crumb Rubber Modified (500g)	TCE	5	4.80	2.178	2.306	NO
	EnSolv	5	5.01			
Marshall	TCE	6	6.61	0.277	2.228	NO
	EnSolv	6	6.63			
	TCE	6	6.61	0.174	2.228	NO
	RE*	6	6.62			
Superpave	TCE	6	4.35	1.634	2.228	NO
	EnSolv	6	4.55			
	TCE	6	4.35	1.278	2.365	NO
	RE*	3	4.57			
Crumb Rubber Modified	TCE	6	5.04	1.549	2.228	NO
	EnSolv	6	5.22			
	TCE	6	5.04	0.071	2.365	NO
	RE*	3	5.05			

Note: RE* denotes the use of reclaimed EnSolv

The Student's t-test was also performed on the asphalt content data. The results of the Student's t-test, which are displayed in Table 5.12, indicate that at a confidence level of 95%, the asphalt content as determined by using EnSolv, is statistically not different from that determined by using TCE. Also, the asphalt content that was determined by using the reclaimed EnSolv is statistically no different from the asphalt content determined by using TCE.

5.3 Results from the Recovery Procedure

The recovery procedure was only performed on the three plant mixtures. For each of the mixtures, three replicate tests were performed for each of the following combinations of solvent and recovery methods.

1. TCE and the ASTM Recovery Method
2. EnSolv and the ASTM Recovery Method
3. Reclaimed EnSolv and the ASTM Recovery Method
4. TCE and the FDOT Proposed Recovery Method
5. EnSolv and the FDOT Proposed Recovery Method

For all these five combinations, the extraction process was performed using the larger extraction set-up and a sample size of 1500 grams. In addition to these recovery tests, the recovery procedure was also performed on the crumb rubber mixture samples that had been extracted for only four hours in the smaller extraction unit using TCE.

The times for the recovery process for the Marshall mixture following the ASTM and FDOT procedures are displayed in Tables 5.13 and 5.14 respectively. The corresponding times for the recovery process for the Superpave mixture are displayed in Tables 5.15 and 5.16, while those for the crumb rubber modified mix are shown in Tables 5.17 and 5.18. The recovery times from the crumb rubber modified mixture with the 4-hour extraction are shown in Tables 5.19 and 5.20. The means and standard deviation for the data are also displayed on each of these tables. Graphical representations for the average recovery times for the different solvents for each of the mixes are displayed in Figures 5.3.

A Student's t-test was performed on the time necessary to completely recover the binder. The purpose of this analysis was to see if there were any significant differences in the time data obtained with the various combinations of solvents and recovery methods as compared with those using TCE and the ASTM recovery method. The results from the analysis are shown in Tables 5.21-24. The results for the Superpave mixture indicate a significant difference between recovery times for the solvents in all cases except when comparing EnSolv with TCE when using the ASTM procedure on the Marshall mixture. In all other mixtures, there was a significant statistical difference in the recovery time data when different solvents or extraction procedures were used.

The difference noted by the Student's t-test could be easily explained by examining the means of the recovery time data. For the most part, the binders in TCE take longer to recover when using the ASTM recovery than do the binders in EnSolv or

Table 5.13: Recovery Times for the Marshall Mixture Following ASTM Procedure (Hours:Minutes)

Trial	Trichloroethylene	EnSolv	Reclaimed EnSolv
1	1:49	1:35	1:28
2	1:43	1:25	1:22
3	1:38	1:29	1:25
Mean	1:43	1:29	1:25
Standard Deviation	0:06	0:05	0:03

Table 5.14: Recovery Times for the Marshall Mixture Following FDOT Proposed Procedure (Hours:Minutes)

Trial	Trichloroethylene	EnSolv
1	0:44	1:04
2	0:54	0:58
3	1:10	1:03
Mean	0:56	1:02
Standard Deviation	0:13	0:03

Table 5.15: Recovery Times for the Superpave Mixture Following ASTM Procedure (Hours:Minutes)

Trial	Trichloroethylene	EnSolv	Reclaimed EnSolv
1	1:27	1:17	1:27
2	1:28	1:11	1:28
3	1:40	1:39	1:23
Mean	1:32	1:23	1:26
Standard Deviation	0:07	0:06	0:03

Table 5.16: Recovery Times for the Superpave Mixture Following FDOT Proposed Procedure (Hours:Minutes)

Trial	Trichloroethylene	EnSolv
1	0:58	0:45
2	0:59	0:42
3	0:59	0:58
Mean	0:59	0:48
Standard Deviation	0:01	0:09

Table 5.17: Recovery Times for the Crumb Rubber Modified Mixture
Following ASTM Procedure (Hours:Minutes)

Trial	Trichloroethylene	EnSolv	Recovered EnSolv
1	2:00	1:34	1:47
2	1:51	1:29	1:39
3	1:55	1:30	1:38
Mean	1:55	1:31	1:41
Standard Deviation	0:05	0:03	0:05

Table 5.18: Recovery Times for the Crumb Rubber
Modified Mixture Following FDOT
Proposed Procedure (Hours:Minutes)

Trial	Trichloroethylene	EnSolv
1	0:54	0:49
2	1:01	0:45
3	0:57	0:56
Mean	0:57	0:50
Standard Deviation	0:04	0:06

Table 5.19: Recovery Times for the Crumb Rubber Modified Mixture
Following ASTM Procedure for the 4 Hour Extraction
(Hours:Minutes)

Trial	Trichloroethylene
1	1:44
2	1:34
3	1:21
4	1:30
5	1:38
Mean	1:33
Standard Deviation	0:09

Table 5.20: Recovery Times for the Crumb Rubber
Modified Mixture Following FDOT
Proposed Procedure for the 4 Hour
Extraction (Hours:Minutes)

Trial	Trichloroethylene
1	0:43
2	1:05
3	1:16
4	0:45
5	0:56
Mean	0:57
Standard Deviation	0:14

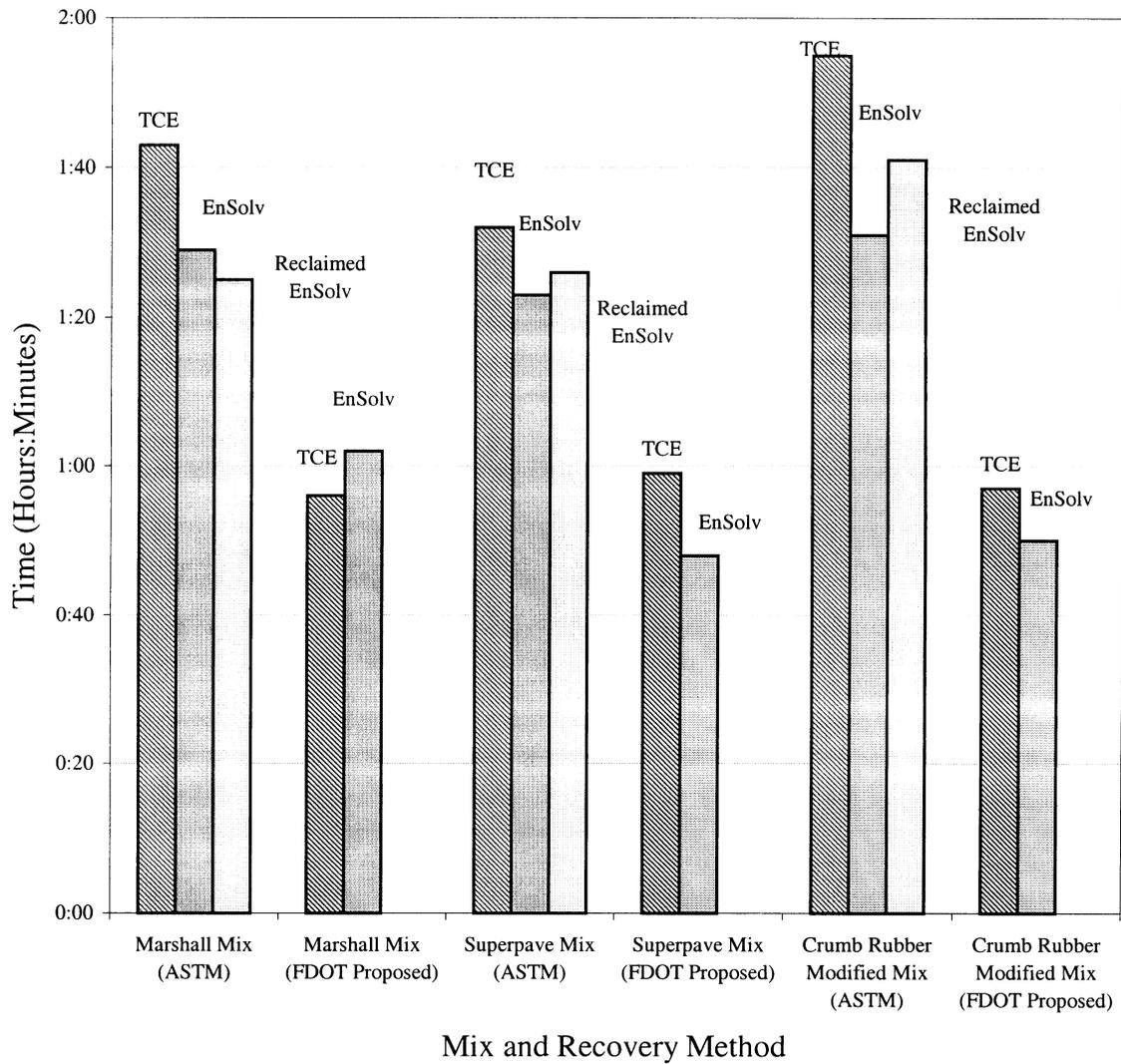


Figure 5.3: Average Time Required for the Recovery Procedure for Different Solvents

Table 5.21: Results of the Student's t-Tests on Recovery Time for
the Marshall Mixture

Solvent	Recovery Method	Sample Size	Mean (Minutes)	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
TCE	ASTM	3	103	3.128	2.776	YES
EnSolv	ASTM	3	89			
TCE	ASTM	3	103	4.976	2.776	YES
RE*	ASTM	3	85			
TCE	ASTM	3	103	5.739	2.776	YES
TCE	FDOT	3	56			
TCE	ASTM	3	103	11.150	2.776	YES
EnSolv	FDOT	3	62			

Note: RE* denotes the use of reclaimed EnSolv

Table 5.22: Results of the Student's t-Tests on Recovery Time for the Superpave Mixture

Solvent	Recovery Method	Sample Size	Mean (Minutes)	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
TCE	ASTM	3	92	1.715	2.776	NO
EnSolv	ASTM	3	83			
TCE	ASTM	3	92	1.274	2.776	NO
RE*	ASTM	3	86			
TCE	ASTM	3	92	7.876	2.776	YES
TCE	FDOT	3	59			
TCE	ASTM	3	92	6.721	2.776	YES
EnSolv	FDOT	3	48			

Note: RE* denotes the use of reclaimed EnSolv

Table 5.23: Results of the Student's t-Tests on Recovery Time for
the Crumb Rubber Modified Mixture

Solvent	Recovery Method	Sample Size	Mean (Minutes)	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
TCE	ASTM	3	115	8.060	2.776	YES
EnSolv	ASTM	3	91			
TCE	ASTM	3	115	3.629	2.776	YES
RE*	ASTM	3	101			
TCE	ASTM	3	115	17.576	2.776	YES
TCE	FDOT	3	57			
TCE	ASTM	3	115	15.796	2.776	YES
EnSolv	FDOT	3	50			

Note: RE* denotes the use of reclaimed EnSolv

Table 5.24: Results of the Student's t-Tests on Recovery Time for the Crumb Rubber Modified Mixture Using 4-Hour Extraction Procedure

Solvent	Recovery Method	Sample Size	Mean (Minutes)	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
TCE	ASTM	5	93	4.988	2.306	YES
TCE	FDOT	5	57			

reclaimed EnSolv. The mean times to recover a binder from TCE using the ASTM method range from 1 hour 33 minutes to 1 hour 56 minutes. The mean times to recover a binder from EnSolv using the ASTM method range from 1 hour 23 minutes to 1 hour 31 minutes and means from reclaimed EnSolv range from 1 hour 25 minutes to 1 hour 41 minutes. When changing the method to the FDOT proposed method, the recovery times were reduced for all solvents tested.

5.4 Conclusions

The results from the asphalt extraction tests indicate that from the standpoint of asphalt content determination and extraction time, EnSolv and reclaimed EnSolv would be a suitable replacement for TCE for ASTM D 2172 Method B. The testing methods are applicable for the use of EnSolv as well as reclaimed EnSolv. The use of the EnSolv and reclaimed EnSolv actually reduced the time required to complete the test.

When evaluating the ease of the Reflux extraction procedure, several conclusions can be made. First is that the method is not specific and leaves the investigator making several decisions. For the purpose of repeatability of the extraction test between laboratories, it would be better if the method would give specifications on the amount of solvent needed, sample size and temperature for the hot plate. It was also discovered that the larger unit provides a faster and less complicated extraction. It allows for more mixture to be extracted at one time. In addition, the use of the three-layer filter paper as recommended by the FDOT reduced the extraction time needed when recovering mixtures that contain ground tire rubber. This filter may also enable a more accurate asphalt content result. For example, the mean of the asphalt content for a crumb rubber

modified asphalt mixture obtained when using the ASTM standard filter paper was 4.80% for TCE and 5.01% for EnSolv. The mean asphalt content obtained when using the three layer filtering system is 5.04% for TCE and 5.22% for EnSolv. The actual asphalt content for this mixture, according to the mix specifications, is 5.27% (as shown in Appendix A, Table A-3).

The results of the recovery method indicated that binders recovered from EnSolv and reclaimed EnSolv were recovered faster than those recovered from TCE. Also, the FDOT proposed recovery method reduced the time needed for the recovery procedure and was much easier to perform.

CHAPTER 6 EVALUATION OF RECOVERED BINDERS

6.1 Testing Program on Recovered Binders

In the investigation of the effects of EnSolv on the recovered binders, three mixtures were used. These three included the same Marshall, Superpave and crumb rubber modified mixtures that were described in Section 5.1. There were three replicates for each combination of solvent and recovery method. The main purpose for testing the recovered binders was to determine if each combination of solvent and recovery method would yield the same results as TCE using the ASTM Standard Method. The tests performed on these binders included Penetration, Brookfield Viscosity, Dynamic Shear Rheometer tests, Bending Beam Rheometer tests, and FTIR Spectral Analysis. The results from these tests were analyzed using the Student's t-test described in Section 3.6.

6.2 Results from the Penetration Test

The Penetration test was performed in accordance with ASTM D 5 at a temperature of 25° C. The results of the penetration of the recovered binder from the Marshall mixture are displayed in Table 6.1. The means of the penetration data for all solvents and recovery methods range from 34.7 to 39.3.

Table 6.1: Penetration of the Recovered Binder from the Marshall Mixture

Trial	Solvent	Recovery Method	Penetration (Pen)	Mean	Standard Deviation
1	Trichloroethylene	ASTM	41	39.3	2.89
2			36		
3			41		
1	EnSolv	ASTM	37	36.7	0.58
2			37		
3			36		
1	Reclaimed EnSolv	ASTM	34	35.0	1.73
2			37		
3			34		
1	Trichloroethylene	FDOT	42	37.7	5.13
2			39		
3			32		
1	EnSolv	FDOT	33	34.7	1.53
2			36		
3			35		

The highest mean penetration value came from the binder recovered from ASTM recovery method using TCE, while the lowest mean value resulted from FDOT proposed recovery using EnSolv.

The results from the recovered binder from the Superpave mixture are displayed in Table 6.2. The means of the penetration data range from 33.7 to 37.0. Once again the highest mean penetration value came from the binder recovered from TCE with the ASTM recovery, while the lowest mean value resulted from the FDOT proposed recovery using EnSolv.

The results of the penetration tests on the recovered binder from the crumb rubber modified mixture are displayed in two tables. Table 6.3 shows the penetration values for the binder recovered from the full extraction procedure. Table 6.4 shows the penetration values for the 4-hour extraction procedure. For the penetration data for the full extraction the means range from 46.3 to 48.3. The means of the penetration data for the 4-hour extraction range from 45.2 to 45.4.

The Student's t-test was performed on the penetration data and the results for the Marshall, Superpave and crumb rubber modified (full extraction) mixtures are displayed in Tables 6.5, 6.7 and 6.9 respectively. Each solvent and recovery combination was compared with TCE using the ASTM Standard recovery method. In all cases but one, there was no significant difference in the penetration using EnSolv, reclaimed EnSolv or the FDOT proposed method. The one result that did have a significant difference was when EnSolv was used for extraction with the FDOT proposed recovery method on the Superpave Mixture.

Table 6.2: Penetration of the Recovered Binder from the Superpave Mixture

Trial	Solvent	Recovery Method	Penetration (Pen)	Mean	Standard Deviation
1	Trichloroethylene	ASTM	36	37.0	1.00
2			38		
3			37		
1	EnSolv	ASTM	33	34.3	2.31
2			37		
3			33		
1	Reclaimed EnSolv	ASTM	34	34.3	1.53
2			33		
3			36		
1	Trichloroethylene	FDOT	36	34.7	1.53
2			33		
3			35		
1	EnSolv	FDOT	34	33.7	1.53
2			35		
3			32		

Table 6.3: Penetration of the Recovered Binder from the Crumb Rubber Modified Mixture

Trial	Solvent	Recovery Method	Penetration (Pen)	Mean	Standard Deviation
1	Trichloroethylene	ASTM	50	46.3	3.21
2			44		
3			45		
1	EnSolv	ASTM	47	47.3	1.53
2			46		
3			49		
1	Reclaimed EnSolv	ASTM	46	46.7	1.15
2			48		
3			46		
1	Trichloroethylene	FDOT	48	46.7	1.15
2			46		
3			46		
1	EnSolv	FDOT	49	48.3	1.15
2			49		
3			47		

Table 6.4: Penetration of the Recovered Binder from the Crumb Rubber Modified Mixture Using the 4-Hour Extraction Procedure

Trial	Solvent	Recovery Method	Penetration (Pen)	Mean	Standard Deviation
1	Trichloroethylene	ASTM	46	45.4	1.52
2			45		
3			43		
4			47		
5			46		
1	Trichloroethylene	FDOT	46	45.2	2.39
2			44		
3			44		
4			43		
5			49		

Table 6.5: Results from the Student's t-Test on Penetration of the Recovered Binder from the Marshall Mixture

Solvent	Recovery Method	Sample Size	Mean	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
TCE	ASTM	3	39.33	1.569	2.776	NO
EnSolv	ASTM	3	36.67			
TCE	ASTM	3	39.33	2.229	2.776	NO
RE*	ASTM	3	35.00			
TCE	ASTM	3	39.33	0.490	2.776	NO
TCE	FDOT	3	37.67			
TCE	ASTM	3	39.33	2.475	2.776	NO
EnSolv	FDOT	3	34.67			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.6: Results from the Student's t-Test on Penetration of the Recovered Binder from the Superpave Mixture

Solvent	Recovery Method	Sample Size	Mean	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
TCE	ASTM	3	37.00	1.835	2.776	NO
EnSolv	ASTM	3	34.33			
TCE	ASTM	3	37.00	2.530	2.776	NO
RE*	ASTM	3	34.33			
TCE	ASTM	3	37.00	2.214	2.776	NO
TCE	FDOT	3	34.67			
TCE	ASTM	3	37.00	3.162	2.776	YES
EnSolv	FDOT	3	33.67			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.7: Results from the Student's t-Test on Penetration of the Recovered Binder from the Crumb Rubber Modified Mixture

Solvent	Recovery Method	Sample Size	Mean	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
TCE	ASTM	3	46.33	0.487	2.776	NO
EnSolv	ASTM	3	47.33			
TCE	ASTM	3	46.33	0.169	2.776	NO
RE*	ASTM	3	46.67			
TCE	ASTM	3	46.33	0.169	2.776	NO
TCE	FDOT	3	46.67			
TCE	ASTM	3	46.33	1.014	2.776	NO
EnSolv	FDOT	3	48.33			

Note: RE* denotes the use of reclaimed EnSolv

Another Student's t-test was performed on the data from the 4-hour extraction performed on the crumb rubber modified mixture. The results are displayed in Table 6.8. The analysis showed that there was no statistical difference in penetration between the ASTM and FDOT recovery methods when the 4-hour extraction was performed. The analysis was also used to compare the penetration from the 4-hour extraction with the penetration from the full extraction. In this analysis, the Student's t-test revealed that there was no significant difference in the penetration results for the two extraction methods. This shows that there was no significant difference even though some asphalt remained on the aggregate in the 4-hour test.

In addition to the Student's t-test, another analysis was performed on the penetration data to see if the difference in penetration from the different solvents was within that allowed in the precision statement for penetration of recovered binders in ASTM D5404. In this analysis the value for the acceptable range between two results (recorded as a percent of the mean) within the laboratory was obtained from the precision statement, and was then compared to the range of the means for the data. For example, in the penetration test the acceptable range for two results was 27.2% of the mean, so the mean of the two sample means was obtained and multiplied by 27.2%. This value gave the acceptable range between the two means, which was compared with the actual range to see if the data fall within the ASTM standard allowable amount. The results of this analysis for all the mixtures studied are shown in Tables 6.9-6.12. In all tests, the results fall within the allowable range as set in the ASTM standard. This means that the difference in penetration due to the use of different solvents was set within the allowable variation between replicate samples when the same solvent was used.

Table 6.8: Results from the Student's t-Test on Penetration of the Recovered Binder from the Crumb Rubber Modified Mixture

Solvent	Extraction	Recovery Method	Sample Size	Mean	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
TCE	4-Hour	ASTM	5	45.40	0.158	2.306	NO
TCE	4-Hour	FDOT	5	45.20			
TCE	4-Hour	ASTM	5	45.40	0.573	2.365	NO
TCE	Full	ASTM	3	46.33			
TCE	4-Hour	FDOT	5	45.20	0.975	2.365	NO
TCE	Full	FDOT	3	46.67			

Table 6.9: ASTM Acceptable Range Results from Penetration of the Recovered Binder from the Marshall Mixture

Solvent	Recovery Method	Sample Size	Mean	Range of the Means	ASTM Acceptable Range Between Two Results 27.2% (Percent of Mean)	Requirement Met
TCE	ASTM	3	39.33	2.66	10.34	YES
EnSolv	ASTM	3	36.67			
TCE	ASTM	3	39.33	4.33	10.11	YES
RE*	ASTM	3	35.00			
TCE	ASTM	3	39.33	1.66	10.47	YES
TCE	FDOT	3	37.67			
TCE	ASTM	3	39.33	4.66	10.06	YES
EnSolv	FDOT	3	34.67			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.10: ASTM Acceptable Range Results from Penetration of the Recovered Binder from the Superpave Mixture

Solvent	Recovery Method	Sample Size	Mean	Range of the Means	ASTM Acceptable Range Between Two Results 27.2% (Percent of Mean)	Requirement Met
TCE	ASTM	3	37.00	2.67	9.70	YES
EnSolv	ASTM	3	34.33			
TCE	ASTM	3	37.00	2.67	9.70	YES
RE*	ASTM	3	34.33			
TCE	ASTM	3	37.00	2.33	9.75	YES
TCE	FDOT	3	34.67			
TCE	ASTM	3	37.00	3.33	9.61	YES
EnSolv	FDOT	3	33.67			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.11: ASTM Acceptable Range Results from Penetration of the Binder from the Crumb Rubber Modified Mixture

Solvent	Recovery Method	Sample Size	Mean	Range of the Means	ASTM Acceptable Range Between Two Results 27.2% (Percent of Mean)	Requirement Met
TCE	ASTM	3	46.33	1.00	12.74	YES
EnSolv	ASTM	3	47.33			
TCE	ASTM	3	46.33	0.34	12.65	YES
RE*	ASTM	3	46.67			
TCE	ASTM	3	46.33	0.34	12.65	YES
TCE	FDOT	3	46.67			
TCE	ASTM	3	46.33	2.00	12.87	YES
EnSolv	FDOT	3	48.33			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.12: ASTM Acceptable Range Results from Penetration of the Recovered Binder from the Crumb Rubber Modified Mix

Solvent	Extraction	Recovery Method	Sample Size	Mean	Range of the Means	ASTM Acceptable Range Between Two Results 27.2% (Percent of Mean)	Requirement Met
TCE	4-Hour	ASTM	5	45.40	0.20	12.32	YES
TCE	4-Hour	FDOT	5	45.20			
TCE	4-Hour	ASTM	5	45.40	0.93	12.48	YES
TCE	Full	ASTM	3	46.33			
TCE	4-Hour	FDOT	5	45.20	1.47	12.49	YES
TCE	Full	FDOT	3	46.67			

6.3 Results from Brookfield Viscosity Test

The Brookfield viscosity test was performed at 60°C on all recovered binders. The results from the recovered binders from the Marshall mixture are displayed in Table 6.13. The means of the viscosity data for all solvents and recovery methods range from 12,002 to 13,734 poises. The lowest mean viscosity value came from the binder recovered from TCE using the ASTM recovery method, while the highest mean resulted from the FDOT proposed recovery method using EnSolv. These results were consistent with the penetration data.

The viscosity results from the recovered binders from the Superpave mixture are displayed in Table 6.14. The means of the viscosity data range from 13,060 to 14,177 poises. Once again the lowest mean viscosity value came from the binder recovered from TCE using the ASTM recovery method, but this time the highest mean resulted from the ASTM recovery using EnSolv. This was not consistent with the penetration data.

The results of the viscosity test on the recovered binder from the crumb rubber modified mixture are displayed in Tables 6.15 and 6.16. Table 6.15 shows the viscosity values for the binder recovered from the full extraction procedure. Table 6.16 shows the viscosity values for the 4-hour extraction procedure. For the viscosity data for the full extraction, the means range from 7,933 to 9,376 poises. The means of the viscosity data for the limited extraction range from 9,093 to 10,343 poises. It is apparent that the full extraction procedure yields lower viscosity values.

Table 6.13: Viscosity of the Recovered Binder from the Marshall Mixture

Trial	Solvent	Recovery Method	Viscosity (Poises)	Mean	Standard Deviation
1	Trichloroethylene	ASTM	11112	12002	791.5
2			12267		
3			12627		
1	EnSolv	ASTM	12054	12262	417.8
2			12743		
3			11989		
1	Reclaimed EnSolv	ASTM	14346	13376	2004.5
2			11071		
3			14711		
1	Trichloroethylene	FDOT	10247	12342	3227.4
2			10721		
3			16059		
1	EnSolv	FDOT	14906	13734	1396.4
2			12189		
3			14107		

Table 6.14: Viscosity of the Recovered Binder from the Superpave Mixture

Trial	Solvent	Recovery Method	Viscosity (Poises)	Mean	Standard Deviation
1	Trichloroethylene	ASTM	13494	13060	423.9
2			12647		
3			13040		
1	EnSolv	ASTM	15096	14177	1923.8
2			11966		
3			15469		
1	Reclaimed EnSolv	ASTM	13657	13198	403.4
2			12901		
3			13035		
1	Trichloroethylene	FDOT	13763	14146	753.4
2			15014		
3			13661		
1	EnSolv	FDOT	13248	13916	1414.4
2			12960		
3			15541		

Table 6.15: Viscosity of the Recovered Binder from the Crumb Rubber Modified Mixture Using a Full Extraction Procedure

Trial	Solvent	Recovery Method	Viscosity (Poises)	Mean	Standard Deviation
1	Trichloroethylene	ASTM	8471	9015	484.2
2			9398		
3			9177		
1	EnSolv	ASTM	8828	8913	78.9
2			8984		
3			8927		
1	Reclaimed EnSolv	ASTM	9171	9376	1512.0
2			7977		
3			10980		
1	Trichloroethylene	FDOT	6598	8224	1417.0
2			8882		
3			9193		
1	EnSolv	FDOT	7398	7933	717.0
2			7654		
3			8748		

Table 6.16: Viscosity of the Recovered Binder from the Crumb Rubber Modified Mixture Using a 4-Hour Extraction Procedure

Trial	Solvent	Recovery Method	Viscosity (Poises)	Mean	Standard Deviation
1	Trichloroethylene	ASTM	11660	10343	1350.7
2			9130		
3			10522		
4			8783		
5			11618		
1	Trichloroethylene	ASTM	7994	9093	1564.6
2			9846		
3			10560		
4			10150		
5			6914		

The Student's t-test was performed on the viscosity data. The analysis results for the Marshall, Superpave and crumb rubber modified (full extraction) mixtures are displayed in Tables 6.17, 6.18 and 6.19 respectively. Each solvent and recovery combination was compared with TCE using the ASTM Standard recovery method. In all cases there was no significant difference in the viscosity of the recovered binder due to the use of EnSolv, reclaimed EnSolv or the FDOT proposed recovery method.

Another Student's t-test was performed on the data from the 4-hour extraction performed on the crumb rubber modified mixture. The results are displayed in Table 6.20. The analysis results showed that there was no statistical difference in terms of viscosity of the recovered binder between the ASTM and FDOT recovery methods when the 4-hour extraction was performed. The analysis was also used to compare the viscosity of the binder from the 4-hour extraction with those from the full extraction. In this analysis, the Student's t-test revealed that there was no significant difference in the viscosity results for the two extraction methods.

Although there were no statistical differences, the fact that the viscosity was lower in the three-layer filter caused an investigation to see if the lower viscosity was related to the change in filter papers. To do so, a 4500-gram conventional laboratory mixture was made and separated into 1000-gram samples. Two of these samples were placed into the large extraction baskets with the standard ASTM filter paper while the two remaining were placed into baskets with the FDOT three-layer filter. The ASTM Reflux extraction procedure was performed as described in Section 3.3. For this mixture, the extraction times were within 10 minutes of each other regardless of filter paper used.

Table 6.17: Results of the Student's t-Test on Viscosity of the Recovered Binder
From the Marshall Mixture

Solvent	Recovery Method	Sample Size	Mean	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
TCE	ASTM	3	12002	0.503	2.776	NO
EnSolv	ASTM	3	12262			
TCE	ASTM	3	12002	1.104	2.776	NO
RE*	ASTM	3	13376			
TCE	ASTM	3	12002	0.177	2.776	NO
TCE	FDOT	3	12342			
TCE	ASTM	3	12002	1.869	2.776	NO
EnSolv	FDOT	3	13734			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.18: Results of the Student's t-Test on Viscosity of the Recovered Binder
From the Superpave Mixture

Solvent	Recovery Method	Sample Size	Mean	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
TCE	ASTM	3	13060	0.982	2.776	NO
EnSolv	ASTM	3	14177			
TCE	ASTM	3	13060	0.407	2.776	NO
RE*	ASTM	3	13198			
TCE	ASTM	3	13060	2.175	2.776	NO
TCE	FDOT	3	14146			
TCE	ASTM	3	13060	1.004	2.776	NO
EnSolv	FDOT	3	13916			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.19: Results of the Student's t-Test on Viscosity of the Recovered Binder
From the Crumb Rubber Modified Mixture

Solvent	Recovery Method	Sample Size	Mean	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
TCE	ASTM	3	9015	0.361	2.776	NO
EnSolv	ASTM	3	8913			
TCE	ASTM	3	9015	0.393	2.776	NO
RE*	ASTM	3	9376			
TCE	ASTM	3	9015	0.915	2.776	NO
TCE	FDOT	3	8224			
TCE	ASTM	3	9015	2.166	2.776	NO
EnSolv	FDOT	3	7933			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.20: Results of the Student's t-Test on Viscosity of the Recovered Binder
From the Crumb Rubber Modified Mixture Using the 4-Hour Extraction

Solvent	Extraction	Recovery Method	Sample Size	Mean	t _{Calculated}	t _{Critical} for 95% Confidence	Significantly Different
TCE	4-Hour	ASTM	5	10343	1.352	2.306	NO
TCE	4-Hour	FDOT	5	9093			
TCE	4-Hour	ASTM	5	10343	1.597	2.365	NO
TCE	Full	ASTM	3	9015			
TCE	4-Hour	FDOT	5	9093	0.784	2.365	NO
TCE	Full	FDOT	3	8224			

The data showed that the mean penetration for the mix using the ASTM filter paper was 47 while that using the three layer filter was 50. In addition, the mean viscosity obtained from the three layer system was 7707 poises which was lower than 9613 poises which was obtained from the ASTM filter paper.

A Student's t-test was performed on the viscosity data. The t calculated was 3.76 and the critical t for a 95% confidence level with 2 degrees of freedom was 4.303. The Student's t-test results showed no significant difference in the viscosity obtained from the filter paper used in the ASTM method and the FDOT three-layer filter.

Something else unrelated to the viscosity was noted when heating the binder for all the viscosity tests. The binder that was recovered from the EnSolv and the reclaimed EnSolv had a slight odor that resembled the solvent. This was an indication that there was most likely some residual solvent remaining in the binder from the recovery procedure. Studies that have been performed on binders recovered from TCE have shown that this occurrence is not uncommon (Burr, 1990).

Similar to the penetration test data, another analysis was performed on the viscosity data to see if the difference in viscosity from the use of different solvents fall within the allowable amount as specified in the precision statement for viscosity of recovered binders in ASTM D5404. For the viscosity test the acceptable range for two results was 23.8% of the mean, so the mean of the two sample means was obtained and multiplied by 23.8%. This value gave the acceptable range between the two means, which was compared with the actual range to see if the data fall within the allowable amount in the ASTM standard. The results of this analysis for all the mixtures studied are shown in Tables 6.21-6.24. In all tests, the results indicate that the difference in

Table 6.21: ASTM Allowable Difference Results from Viscosity of the Recovered Binder from the Marshall Mix

Solvent	Recovery Method	Sample Size	Mean	Range of the Means	ASTM Acceptable Range Between Two Results 23.8% (Percent of Mean)	Requirement Met
TCE	ASTM	3	12002	260	2887	YES
EnSolv	ASTM	3	12262			
TCE	ASTM	3	12002	1374	3020	YES
RE*	ASTM	3	13376			
TCE	ASTM	3	12002	340	2897	YES
TCE	FDOT	3	12342			
TCE	ASTM	3	12002	1732	3063	YES
EnSolv	FDOT	3	13734			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.22: ASTM Allowable Difference Results from Viscosity of the Recovered Binder from the Superpave Mix

Solvent	Recovery Method	Sample Size	Mean	Range of the Means	ASTM Acceptable Range Between Two Results 23.8% (Percent of Mean)	Requirement Met
TCE	ASTM	3	13060	1117	3241	YES
EnSolv	ASTM	3	14177			
TCE	ASTM	3	13060	138	3125	YES
RE*	ASTM	3	13198			
TCE	ASTM	3	13060	1086	3238	YES
TCE	FDOT	3	14146			
TCE	ASTM	3	13060	856	3210	YES
EnSolv	FDOT	3	13916			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.23: ASTM Allowable Difference Results from Viscosity of the Recovered Binder from the Crumb Rubber Modified Mix

Solvent	Recovery Method	Sample Size	Mean	Range of the Means	ASTM Acceptable Range Between Two Results 23.8% (Percent of Mean)	Requirement Met
TCE	ASTM	3	9015	102	2133	YES
EnSolv	ASTM	3	8913			
TCE	ASTM	3	9015	361	2189	YES
RE*	ASTM	3	9376			
TCE	ASTM	3	9015	791	2051	YES
TCE	FDOT	3	8224			
TCE	ASTM	3	9015	1082	2017	YES
EnSolv	FDOT	3	7933			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.24: ASTM Allowable Difference Results from Viscosity of the Recovered Binder from the Crumb Rubber Modified Mix Using the 4-Hour Extraction

Solvent	Extraction	Recovery Method	Sample Size	Mean	Range of the Means	ASTM Acceptable Range Between Two Results 23.8% (Percent of Mean)	Requirement Met
TCE	4-Hour	ASTM	5	10343	1250	2313	YES
TCE	4-Hour	FDOT	5	9093			
TCE	4-Hour	ASTM	5	10343	1328	2304	YES
TCE	Full	ASTM	3	9015			
TCE	4-Hour	FDOT	5	9093	869	2061	YES
TCE	Full	FDOT	3	8224			

viscosity due to the use of different solvents was within the allowable variation between replicates when the same solvent was used.

6.4 Results from Dynamic Shear Rheometer Testing

The DSR testing was performed at two different testing temperatures, which included 64 and 25° C. The results of the DSR tests performed at both temperatures on the recovered binders from the Marshall mix are shown in Tables 6.25 and 6.26. Similarly for the Superpave mix and the crumb rubber modified mixture, test results for both temperatures are provided in Tables 6.27 through 6.30.

The Student's t-test was performed on the $G^*/\sin(\delta)$ for the tests performed at 64° C for all mixtures. For the tests performed at 25° C the Student's t-test was performed on the $G^*\sin(\delta)$ values. The results of the statistical analysis are displayed in Tables 6.31, 6.32 and 6.33. For the Marshall mixture, a significant difference was seen between the ASTM standard recovery method using reclaimed EnSolv as the solvent and the ASTM standard method using TCE as the solvent at 64° C. At 25° C, for the same mixture, a significant difference was also determined to exist between the FDOT proposed recovery method with EnSolv as the solvent and the ASTM standard recovery method using TCE.

The results of the Student's t-test for the Superpave mixture also showed two comparisons with a significant difference. At 64° C, a difference was determined between the FDOT proposed method using TCE and the ASTM standard recovery

Table 6.25: Results of the DSR Test Performed at 64 °C on the Binder Recovered from the Marshall Mixture

Trial	Solvent	Recovery Method	G* (Pa)	δ (°)	G*/Sin δ (Pa)
1	TCE	ASTM	5.85E+03	77.1	6.00E+03
2			5.98E+03	76.8	6.15E+03
3			7.08E+03	75.6	7.31E+03
1	EnSolv	ASTM	5.41E+03	77.8	5.53E+03
2			5.50E+03	77.4	5.64E+03
3			4.44E+03	78.0	4.54E+03
1	RE*	ASTM	5.28E+03	77.4	5.41E+03
2			4.03E+03	79.0	4.11E+03
3			4.99E+03	77.5	5.11E+03
1	TCE	FDOT	5.34E+03	77.6	5.47E+03
2			5.15E+03	78.0	5.27E+03
3			7.41E+03	75.9	7.64E+03
1	EnSolv	FDOT	6.13E+03	77.4	6.28E+03
2			5.28E+03	78.4	5.39E+03
3			6.05E+03	77.8	6.19E+03

Note: RE* denotes the use of reclaimed EnSolv

Table 6.26: Results of the DSR Test Performed at 25 °C on the Binder Recovered from the Marshall Mixture

Trial	Solvent	Recovery Method	G* (Pa)	δ (°)	G*(Sin δ) (Pa)
1	TCE	ASTM	1.33E+06	54.1	1.07E+06
2			1.62E+06	53.1	1.30E+06
3			1.69E+06	52.4	1.34E+06
1	EnSolv	ASTM	1.43E+06	54.3	1.16E+06
2			1.60E+06	53.8	1.29E+06
3			1.45E+06	53.7	1.17E+06
1	RE*	ASTM	1.91E+06	53.2	1.53E+06
2			1.51E+06	54.6	1.23E+06
3			1.79E+06	53.2	1.43E+06
1	TCE	FDOT	1.45E+06	53.9	1.17E+06
2			1.58E+06	54.6	1.28E+06
3			2.03E+06	51.8	1.60E+06
1	EnSolv	FDOT	1.97E+06	52.5	1.56E+06
2			1.80E+06	52.1	1.42E+06
3			2.06E+06	53.2	1.65E+06

Note: RE* denotes the use of reclaimed EnSolv

Table 6.27: Results of the DSR Test Performed at 64 °C on the Binder Recovered from the Superpave Mixture

Trial	Solvent	Recovery Method	G* (Pa)	δ (°)	G*/Sin δ (Pa)
1	TCE	ASTM	6.00E+03	77.2	6.15E+03
2			6.61E+03	77.3	6.77E+03
3			6.18E+03	77.1	6.34E+03
1	EnSolv	ASTM	6.56E+03	77.3	6.73E+03
2			4.93E+03	78.5	5.04E+03
3			6.45E+03	77.2	6.61E+03
1	RE*	ASTM	6.41E+03	77.3	6.57E+03
2			5.23E+03	76.6	5.38E+03
3			5.20E+03	77.6	5.32E+03
1	TCE	FDOT	5.60E+03	77.6	5.74E+03
2			4.96E+03	78.1	5.07E+03
3			5.46E+03	77.4	5.59E+03
1	EnSolv	FDOT	5.06E+03	78.7	5.16E+03
2			5.20E+03	78.3	5.31E+03
3			6.41E+03	77.0	6.58E+03

Note: RE* denotes the use of reclaimed EnSolv

Table 6.28: Results of the DSR Test Performed at 25 °C on the Binder Recovered from the Superpave Mixture

Trial	Solvent	Recovery Method	G* (Pa)	δ (°)	G*(Sin δ) (Pa)
1	TCE	ASTM	2.03E+06	52.6	1.61E+06
2			1.89E+06	52.6	1.50E+06
3			1.72E+06	53.0	1.37E+06
1	EnSolv	ASTM	1.75E+06	52.7	1.39E+06
2			1.43E+06	54.3	1.16E+06
3			1.88E+06	52.0	1.48E+06
1	RE*	ASTM	2.08E+06	52.2	1.65E+06
2			1.74E+06	53.4	1.39E+06
3			1.49E+06	53.9	1.20E+06
1	TCE	FDOT	1.53E+06	53.6	1.23E+06
2			1.52E+06	53.9	1.23E+06
3			1.52E+06	53.1	1.22E+06
1	EnSolv	FDOT	1.74E+06	53.6	1.40E+06
2			1.65E+06	53.9	1.33E+06
3			1.98E+06	51.8	1.55E+06

Note: RE* denotes the use of reclaimed EnSolv

Table 6.29: Results of the DSR Test Performed at 64 °C on the Binder Recovered from the Crumb Rubber Modified Mixture

Trial	Solvent	Recovery Method	G* (Pa)	δ (°)	G*/Sin δ (Pa)
1	TCE	ASTM	3.78E+03	76.9	3.88E+03
2			4.03E+03	76.5	4.14E+03
3			3.93E+03	76.1	4.05E+03
1	EnSolv	ASTM	3.74E+03	77.8	3.83E+03
2			4.22E+03	77.0	4.34E+03
3			4.07E+03	76.9	4.18E+03
1	RE*	ASTM	4.39E+03	76.8	4.50E+03
2			3.80E+03	76.6	3.70E+03
3			4.79E+03	76.1	4.94E+03
1	TCE	FDOT	3.90E+03	77.6	3.99E+03
2			3.26E+03	78.7	3.32E+03
3			3.87E+03	77.1	3.97E+03
1	EnSolv	FDOT	3.06E+03	79.1	3.11E+03
2			3.36E+03	77.9	3.44E+03
3			3.98E+03	77.9	4.07E+03

Note: RE* denotes the use of reclaimed EnSolv

Table 6.30: Results of the DSR Test Performed at 25 °C on the Binder Recovered from the Crumb Rubber Modified Mixture

Trial	Solvent	Recovery Method	G* (Pa)	δ (°)	G*(Sin δ) (Pa)
1	TCE	ASTM	9.75E+05	56.5	8.13E+05
2			1.23E+06	55.3	1.01E+06
3			9.11E+05	56.0	7.55E+05
1	EnSolv	ASTM	9.17E+05	56.8	7.67E+05
2			9.91E+05	55.8	8.20E+05
3			9.75E+05	55.7	8.06E+05
1	RE*	ASTM	1.10E+06	55.8	9.08E+05
2			9.67E+05	55.6	7.98E+05
3			1.11E+06	54.8	9.05E+05
1	TCE	FDOT	1.15E+06	55.6	9.51E+05
2			9.47E+05	56.7	7.92E+05
3			1.05E+06	55.3	8.62E+05
1	EnSolv	FDOT	8.91E+05	56.8	7.46E+05
2			7.92E+05	56.9	6.63E+05
3			1.19E+06	55.5	9.80E+05

Note: RE* denotes the use of reclaimed EnSolv

Table 6.31: Results from the Student's t-Test Performed on the Results from the DSR Tests on the Recovered Binder from the Marshall Mixture

Test Temp	Solvent	Recovery Method	Mean (Pascals)	Standard Deviation	t _{Calc}	t _{Critical for 95% Confidence}	Significantly Different
64°C (G*/Sin δ)	TCE	ASTM	6483	717	2.298	2.776	NO
	EnSolv	ASTM	5236	608			
	TCE	ASTM	6483	717	2.819	2.776	YES
	RE*	ASTM	4875	680			
	TCE	ASTM	6483	717	0.417	2.776	NO
	TCE	FDOT	6123	1315			
	TCE	ASTM	6483	717	1.054	2.776	NO
EnSolv	FDOT	5955	490				
25°C (G*(Sin δ))	TCE	ASTM	1.24E+06	1.41E+05	0.306	2.776	NO
	EnSolv	ASTM	1.21E+06	7.39E+04			
	TCE	ASTM	1.24E+06	1.41E+05	1.368	2.776	NO
	RE*	ASTM	1.40E+06	1.51E+05			
	TCE	ASTM	1.24E+06	1.41E+05	0.764	2.776	NO
	TCE	FDOT	1.35E+06	2.19E+05			
	TCE	ASTM	1.24E+06	1.41E+05	2.902	2.776	YES
EnSolv	FDOT	1.54E+06	1.16E+05				

Note: RE* denotes the use of reclaimed EnSolv

Table 6.32: Results from the Student's t-Test Performed on the Results from the DSR Tests on the Recovered Binder from the Superpave Mixture

Test Temp	Solvent	Recovery Method	Mean (Pascals)	Standard Deviation	t _{Calc}	t _{Critical for 95% Confidence}	Significantly Different
64°C (G*/Sin δ)	TCE	ASTM	6421	320	0.514	2.776	NO
	EnSolv	ASTM	6125	946			
	TCE	ASTM	6421	320	1.485	2.776	NO
	RE*	ASTM	5757	706			
	TCE	ASTM	6421	320	3.498	2.776	YES
	TCE	FDOT	5466	349			
	TCE	ASTM	6421	320	1.516	2.776	NO
EnSolv	FDOT	5682	782				
25°C (G*(Sin δ))	TCE	ASTM	1.49E+06	1.21E+05	1.277	2.776	NO
	EnSolv	ASTM	1.34E+06	1.65E+05			
	TCE	ASTM	1.49E+06	1.21E+05	0.558	2.776	NO
	RE*	ASTM	1.41E+06	2.23E+05			
	TCE	ASTM	1.49E+06	1.21E+05	3.812	2.776	YES
	TCE	FDOT	1.23E+06	9.65E+03			
	TCE	ASTM	1.49E+06	1.21E+05	0.700	2.776	NO
EnSolv	FDOT	1.43E+06	1.14E+05				

Note: RE* denotes the use of reclaimed EnSolv

Table 6.33: Results from the Student's t-Test Performed on the Results from the DSR Tests on the Recovered Binder from the Crumb Rubber Modified Mixture

Test Temp	Solvent	Recovery Method	Mean (Pascals)	Standard Deviation	t_{Calc}	$t_{Critical}$ for 95% Confidence	Significantly Different
64°C (G*/Sin δ)	TCE	ASTM	4025	131	0.529	2.776	NO
	EnSolv	ASTM	4115	265			
	TCE	ASTM	4025	131	0.961	2.776	NO
	RE*	ASTM	4381	629			
	TCE	ASTM	4025	131	1.148	2.776	NO
	TCE	FDOT	3759	378			
	TCE	ASTM	4025	131	1.681	2.776	NO
EnSolv	FDOT	3538	484				
25°C (G*(Sin δ))	TCE	ASTM	8.60E+05	1.35E+05	0.789	2.776	NO
	EnSolv	ASTM	7.97E+05	2.72E+04			
	TCE	ASTM	8.60E+05	1.35E+05	0.118	2.776	NO
	RE*	ASTM	8.71E+05	6.28E+04			
	TCE	ASTM	8.60E+05	1.35E+05	0.087	2.776	NO
	TCE	FDOT	8.68E+05	7.96E+04			
	TCE	ASTM	8.60E+05	1.35E+05	0.521	2.776	NO
EnSolv	FDOT	7.96E+05	1.64E+05				

Note: RE* denotes the use of reclaimed EnSolv

method using TCE as the solvent. The other comparison found to be significantly different was at 25° C, where the difference was found between the FDOT proposed recovery method using TCE and the ASTM standard recovery method using TCE as the solvent. As for the crumb rubber modified mixture, no significant statistical difference was found when comparing each combination of solvent and recovery method to the ASTM recovery method with TCE as the solvent.

6.5 Results from Bending Beam Rheometer Testing

The BBR is used to measure the stiffness of asphalt binders at very low temperatures. The temperatures selected for this study was -18° C. This test measures the stiffness of an asphalt beam under a constant load. Two parameters are determined from the BBR test. Creep stiffness (S) is a measure of how the asphalt resists constant loading and the m-value is a measure of how fast the asphalt stiffness changes as loads are applied. The results for the BBR tests performed on all three mixtures are presented in Tables 6.34 through 6.36.

The Student's t-test was performed on both tested parameters (S and the m-value) for all mixtures. The results of the statistical analysis are presented in Table 6.37, 6.38 and 6.39. The results for the Marshall and crumb rubber modified mixtures showed no significant difference when comparing each combination of solvents and recovery method to the ASTM standard recovery method using TCE as the solvent. For the Superpave mixture, however, a significant difference was found in both parameters between the FDOT proposed recovery method using TCE and the ASTM standard recovery method with TCE as the solvent.

Table 6.34: Results of the BBR Test Performed at $-18\text{ }^{\circ}\text{C}$ on the Binder Recovered from the Marshall Mixture

Trial	Solvent	Recovery Method	Test Results		Stiffness		m-value	
			Stiffness (MPa)	m-value	Average	Standard Deviation	Average	Standard Deviation
1	TCE	ASTM	166	0.340	167	16	0.335	0.007
2			184	0.327				
3			152	0.338				
1	EnSolv	ASTM	172	0.338	168	7	0.332	0.010
2			160	0.320				
3			171	0.337				
1	RE*	ASTM	175	0.324	183	9	0.324	0.003
2			181	0.327				
3			193	0.322				
1	TCE	FDOT	153	0.342	165	19	0.337	0.011
2			155	0.345				
3			186	0.325				
1	EnSolv	FDOT	197	0.321	184	13	0.327	0.006
2			172	0.333				
3			182	0.326				

Note: RE* denotes the use of reclaimed EnSolv

Table 6.35: Results of the BBR Test Performed at $-18\text{ }^{\circ}\text{C}$ on the Binder Recovered from the Superpave Mixture

Trial	Solvent	Recovery Method	Test Results		Stiffness		m-value	
			Stiffness (MPa)	m-value	Average	Standard Deviation	Average	Standard Deviation
1	TCE	ASTM	172	0.325	181	9	0.325	0.002
2			190	0.323				
3			182	0.326				
1	EnSolv	ASTM	192	0.316	178	22	0.326	0.015
2			152	0.344				
3			189	0.319				
1	RE*	ASTM	187	0.322	166	22	0.332	0.010
2			143	0.342				
3			168	0.332				
1	TCE	FDOT	159	0.331	159	2	0.330	0.001
2			157	0.331				
3			160	0.329				
1	EnSolv	FDOT	183	0.324	179	3	0.324	0.006
2			177	0.330				
3			178	0.318				

Note: RE* denotes the use of reclaimed EnSolv

Table 6.36: Results of the BBR Test Performed at $-18\text{ }^{\circ}\text{C}$ on the Binder Recovered from the Crumb Rubber Modified Mixture

Trial	Solvent	Recovery Method	Test Results		Stiffness		m-value	
			Stiffness (MPa)	m-value	Average	Standard Deviation	Average	Standard Deviation
1	TCE	ASTM	131	0.349	129	6	0.352	0.008
2			134	0.346				
3			123	0.361				
1	EnSolv	ASTM	129	0.357	127	2	0.356	0.001
2			128	0.355				
3			125	0.355				
1	RE*	ASTM	131	0.352	127	9	0.348	0.004
2			116	0.345				
3			133	0.347				
1	TCE	FDOT	131	0.353	128	6	0.355	0.012
2			121	0.368				
3			132	0.345				
1	EnSolv	FDOT	121	0.358	123	3	0.361	0.008
2			121	0.370				
3			126	0.356				

Note: RE* denotes the use of reclaimed EnSolv

Table 6.37: Results from the Student's t-Test Performed on the Results from the BBR Tests on the Recovered Binder from the Marshall Mixture

Testing Parameters	Solvent	Recovery Method	Mean	Standard Deviation	t_{Calc}	$t_{Critical}$ for 95% Confidence	Significantly Different
Stiffness (MPa)	TCE	ASTM	167	16	0.099	2.776	NO
	EnSolv	ASTM	168	7			
	TCE	ASTM	167	16	1.510	2.776	NO
	RE*	ASTM	183	9			
	TCE	ASTM	167	16	0.139	2.776	NO
	TCE	FDOT	165	19			
	TCE	ASTM	167	16	1.428	2.776	NO
	EnSolv	FDOT	184	13			
m-value	TCE	ASTM	0.335	0.007	0.426	2.776	NO
	EnSolv	ASTM	0.332	0.010			
	TCE	ASTM	0.335	0.007	2.502	2.776	NO
	RE*	ASTM	0.324	0.003			
	TCE	ASTM	0.335	0.007	0.266	2.776	NO
	TCE	FDOT	0.337	0.011			
	TCE	ASTM	0.335	0.007	1.503	2.776	NO
	EnSolv	FDOT	0.327	0.006			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.38: Results from the Student's t-Test Performed on the Results from the BBR Tests on the Recovered Binder from the Superpave Mixture

Testing Parameters	Solvent	Recovery Method	Mean	Standard Deviation	t _{Calc}	t _{Critical for 95% Confidence}	Significantly Different
Stiffness (MPa)	TCE	ASTM	181	9	0.219	2.776	NO
	EnSolv	ASTM	178	22			
	TCE	ASTM	181	9	1.093	2.776	NO
	RE*	ASTM	166	22			
	TCE	ASTM	181	9	4.133	2.776	YES
	TCE	FDOT	159	2			
	TCE	ASTM	181	9	0.365	2.776	NO
	EnSolv	FDOT	179	3			
m-value	TCE	ASTM	0.325	0.002	0.114	2.776	NO
	EnSolv	ASTM	0.326	0.015			
	TCE	ASTM	0.325	0.002	1.189	2.776	NO
	RE*	ASTM	0.332	0.010			
	TCE	ASTM	0.325	0.002	3.873	2.776	YES
	TCE	FDOT	0.330	0.001			
	TCE	ASTM	0.325	0.002	0.274	2.776	NO
	EnSolv	FDOT	0.324	0.006			

Note: RE* denotes the use of reclaimed EnSolv

Table 6.39: Results from the Student's t-Test Performed on the Results from the BBR Tests on the Recovered Binder from the Crumb Rubber Modified Mixture

Testing Parameters	Solvent	Recovery Method	Mean	Standard Deviation	t _{Calc}	t _{Critical for 95% Confidence}	Significantly Different
Stiffness (MPa)	TCE	ASTM	129	6	0.548	2.776	NO
	EnSolv	ASTM	127	2			
	TCE	ASTM	129	6	0.320	2.776	NO
	RE*	ASTM	127	9			
	TCE	ASTM	129	6	0.204	2.776	NO
	TCE	FDOT	128	6			
	TCE	ASTM	129	6	1.549	2.776	NO
	EnSolv	FDOT	123	3			
m-value	TCE	ASTM	0.352	0.008	0.859	2.776	NO
	EnSolv	ASTM	0.356	0.001			
	TCE	ASTM	0.352	0.008	0.775	2.776	NO
	RE*	ASTM	0.348	0.004			
	TCE	ASTM	0.352	0.008	0.360	2.776	NO
	TCE	FDOT	0.355	0.012			
	TCE	ASTM	0.352	0.008	1.378	2.776	NO
	EnSolv	FDOT	0.361	0.008			

Note: RE* denotes the use of reclaimed EnSolv

6.6 Results from FTIR Spectral Analysis

The FTIR spectral analysis provides an infrared (IR) absorption spectrum of the tested material. These spectrums can serve as “fingerprints” to determine the chemical characteristics (functional groups) of the tested material. Samples with similar chemical characteristics will produce similar IR absorption spectra, while different functional groups will show different spectra. All samples were scanned for the IR absorption spectrum between wavenumbers of 1500 cm^{-1} and 2000 cm^{-1} , since this region contains the absorption bands for many functional groups formed upon age-hardening of asphalt binders.

The samples were scanned and analyzed using the software program SPECTRUM developed by Perkin-Elmer. For the analysis of the spectra, SPECTRUM allows the user to compare multiple IR absorption spectra with each other and outputs a correlation coefficient (between 0.00 and 1.00) to indicate how comparable the spectra are. Tables 6.40 through 6.45 display the correlation coefficients between the IR spectra of all sample replicates, as well as the coefficients between each EnSolv and reclaimed EnSolv recovered sample replicates to the replicates of the TCE recovered asphalt binders.

It can be observed, with the exception of the correlations between TCE (ASTM) and EnSolv (FDOT) replicates which are substantially lower, that the ranges of the correlation coefficients for the comparison between the replicates within the same solvent overlap with those for the comparison between different solvents. The variation of the FTIR spectra for the same solvent is as large as those between different solvents. Thus, it cannot be concluded that the different solvents provide substantially different effects.

Table 6.40: Correlation of FTIR Spectra for Binders Recovered from the Marshall Mixture by Means of the ASTM Asphalt Recovery Procedure

	Comparisons	Correlation
Correlations Between TCE Replicates	1-2	0.9300
	1-3	0.9785
	2-3	0.9138
Correlations Between EnSolv Replicates	1-2	0.7669
	1-3	0.9570
	2-3	0.7284
Correlations Between Reclaimed EnSolv Replicates	1-2	0.9462
	1-3	0.9456
	2-3	0.9253
Correlations Between TCE and EnSolv Replicates	TCE1 - EnSolv1	0.9221
	TCE1 - EnSolv2	0.8910
	TCE1 - EnSolv3	0.8833
	TCE2 - EnSolv1	0.8964
	TCE2 - EnSolv2	0.8631
	TCE2 - EnSolv3	0.8836
	TCE3 - EnSolv1	0.9320
	TCE3 - EnSolv2	0.8480
	TCE3 - EnSolv3	0.9065
Correlations Between TCE and Reclaimed EnSolv Replicates	TCE1 - RE*1	0.9272
	TCE1 - RE*2	0.9413
	TCE1 - RE*3	0.9456
	TCE2 - RE*1	0.8979
	TCE2 - RE*2	0.8937
	TCE2 - RE*3	0.8941
	TCE3 - RE*1	0.9314
	TCE3 - RE*2	0.9470
	TCE3 - RE*3	0.9613

Note: RE* denotes the use of reclaimed EnSolv

Table 6.41: Correlation of FTIR Spectra for Binders Recovered from the Marshall Mixture by Means of the ASTM and the FDOT Proposed Asphalt Recovery Procedure

	Comparisons	Correlation
Correlations Between TCE (ASTM) Replicates	1-2	0.9300
	1-3	0.9785
	2-3	0.9138
Correlations Between TCE (FDOT) Replicates	1-2	0.8266
	1-3	0.9081
	2-3	0.8936
Correlations Between EnSolv (FDOT) Replicates	1-2	0.9013
	1-3	0.8338
	2-3	0.8326
Correlations Between TCE (ASTM) and TCE (FDOT) Replicates	TCE(ASTM)1 - TCE(FDOT)1	0.9110
	TCE(ASTM)1 - TCE(FDOT)2	0.9260
	TCE(ASTM)1 - TCE(FDOT)3	0.9139
	TCE(ASTM)2 - TCE(FDOT)1	0.8646
	TCE(ASTM)2 - TCE(FDOT)2	0.8620
	TCE(ASTM)2 - TCE(FDOT)3	0.8314
	TCE(ASTM)3 - TCE(FDOT)1	0.8860
	TCE(ASTM)3 - TCE(FDOT)2	0.9288
	TCE(ASTM)3 - TCE(FDOT)3	0.9005
Correlations Between TCE (ASTM) and EnSolv (FDOT) Replicates	TCE(ASTM)1 - EnSolv(FDOT)1	0.7463
	TCE(ASTM)1 - EnSolv(FDOT)2	0.7103
	TCE(ASTM)1 - EnSolv(FDOT)3	0.6280
	TCE(ASTM)2 - EnSolv(FDOT)1	0.7499
	TCE(ASTM)2 - EnSolv(FDOT)2	0.6721
	TCE(ASTM)2 - EnSolv(FDOT)3	0.5949
	TCE(ASTM)3 - EnSolv(FDOT)1	0.7513
	TCE(ASTM)3 - EnSolv(FDOT)2	0.7300
	TCE(ASTM)3 - EnSolv(FDOT)3	0.6817

Table 6.42: Correlation of FTIR Spectra for Binders Recovered from the Superpave Mixture by Means of the ASTM Asphalt Recovery Procedure

	Comparisons	Correlation
Correlations Between TCE Replicates	1-2	0.8928
	1-3	0.9109
	2-3	0.8973
Correlations Between EnSolv Replicates	1-2	0.6992
	1-3	0.8867
	2-3	0.6319
Correlations Between Reclaimed EnSolv Replicates	1-2	0.8754
	1-3	0.8934
	2-3	0.8618
Correlations Between TCE and EnSolv Replicates	TCE1 - EnSolv1	0.9239
	TCE1 - EnSolv2	0.7684
	TCE1 - EnSolv3	0.8937
	TCE2 - EnSolv1	0.8614
	TCE2 - EnSolv2	0.7351
	TCE2 - EnSolv3	0.8219
	TCE3 - EnSolv1	0.9032
	TCE3 - EnSolv2	0.7802
	TCE3 - EnSolv3	0.8546
Correlations Between TCE and Reclaimed EnSolv Replicates	TCE1 - RE*1	0.8808
	TCE1 - RE*2	0.8978
	TCE1 - RE*3	0.8013
	TCE2 - RE*1	0.8486
	TCE2 - RE*2	0.8614
	TCE2 - RE*3	0.8058
	TCE3 - RE*1	0.9010
	TCE3 - RE*2	0.8869
	TCE3 - RE*3	0.8288

Note: RE* denotes the use of reclaimed EnSolv

Table 6.43: Correlation of FTIR Spectra for Binders Recovered from the Superpave Mixture by Means of the ASTM and the FDOT Proposed Asphalt Recovery Procedure

	Comparisons	Correlation
Correlations Between TCE (ASTM) Replicates	1-2	0.8928
	1-3	0.9109
	2-3	0.8973
Correlations Between TCE (FDOT) Replicates	1-2	0.9482
	1-3	0.9044
	2-3	0.9344
Correlations Between EnSolv (FDOT) Replicates	1-2	0.9177
	1-3	0.8994
	2-3	0.9505
Correlations Between TCE (ASTM) and TCE (FDOT) Replicates	TCE(ASTM)1 - TCE(FDOT)1	0.9029
	TCE(ASTM)1 - TCE(FDOT)2	0.9333
	TCE(ASTM)1 - TCE(FDOT)3	0.9380
	TCE(ASTM)2 - TCE(FDOT)1	0.8730
	TCE(ASTM)2 - TCE(FDOT)2	0.8961
	TCE(ASTM)2 - TCE(FDOT)3	0.8600
	TCE(ASTM)3 - TCE(FDOT)1	0.8463
	TCE(ASTM)3 - TCE(FDOT)2	0.8717
	TCE(ASTM)3 - TCE(FDOT)3	0.8491
Correlations Between TCE (ASTM) and EnSolv (FDOT) Replicates	TCE(ASTM)1 - EnSolv(FDOT)1	0.9241
	TCE(ASTM)1 - EnSolv(FDOT)2	0.9348
	TCE(ASTM)1 - EnSolv(FDOT)3	0.9313
	TCE(ASTM)2 - EnSolv(FDOT)1	0.8992
	TCE(ASTM)2 - EnSolv(FDOT)2	0.9018
	TCE(ASTM)2 - EnSolv(FDOT)3	0.8830
	TCE(ASTM)3 - EnSolv(FDOT)1	0.8705
	TCE(ASTM)3 - EnSolv(FDOT)2	0.8937
	TCE(ASTM)3 - EnSolv(FDOT)3	0.8754

Table 6.44: Correlation of FTIR Spectra for Binders Recovered from the Crumb Rubber Modified Mixture by Means of the ASTM Asphalt Recovery Procedure

	Comparisons	Correlation
Correlations Between TCE Replicates	1-2	0.7908
	1-3	0.8123
	2-3	0.7131
Correlations Between EnSolv Replicates	1-2	0.9298
	1-3	0.9073
	2-3	0.8887
Correlations Between Reclaimed EnSolv Replicates	1-2	0.7261
	1-3	0.8952
	2-3	0.8124
Correlations Between TCE and EnSolv Replicates	TCE1 - EnSolv1	0.8986
	TCE1 - EnSolv2	0.8829
	TCE1 - EnSolv3	0.8198
	TCE2 - EnSolv1	0.7803
	TCE2 - EnSolv2	0.8120
	TCE2 - EnSolv3	0.7991
	TCE3 - EnSolv1	0.9144
	TCE3 - EnSolv2	0.8866
	TCE3 - EnSolv3	0.8712
Correlations Between TCE and Reclaimed EnSolv Replicates	TCE1 - RE*1	0.7959
	TCE1 - RE*2	0.7777
	TCE1 - RE*3	0.8787
	TCE2 - RE*1	0.7250
	TCE2 - RE*2	0.6707
	TCE2 - RE*3	0.8419
	TCE3 - RE*1	0.8608
	TCE3 - RE*2	0.7974
	TCE3 - RE*3	0.8888

Note: RE* denotes the use of reclaimed EnSolv

Table 6.45: Correlation of FTIR Spectra for Binders Recovered from the Crumb Rubber Modified Mixture by Means of the ASTM and the FDOT Proposed Asphalt Recovery Procedure

	Comparisons	Correlation
Correlations Between TCE (ASTM) Replicates	1-2	0.7908
	1-3	0.8123
	2-3	0.7131
Correlations Between TCE (FDOT) Replicates	1-2	0.8932
	1-3	0.8879
	2-3	0.8934
Correlations Between EnSolv (FDOT) Replicates	1-2	0.7857
	1-3	0.8301
	2-3	0.8137
Correlations Between TCE (ASTM) and TCE (FDOT) Replicates	TCE(ASTM)1 - TCE(FDOT)1	0.8835
	TCE(ASTM)1 - TCE(FDOT)2	0.8765
	TCE(ASTM)1 - TCE(FDOT)3	0.8504
	TCE(ASTM)2 - TCE(FDOT)1	0.8003
	TCE(ASTM)2 - TCE(FDOT)2	0.7778
	TCE(ASTM)2 - TCE(FDOT)3	0.8013
	TCE(ASTM)3 - TCE(FDOT)1	0.7522
	TCE(ASTM)3 - TCE(FDOT)2	0.7978
	TCE(ASTM)3 - TCE(FDOT)3	0.8939
Correlations Between TCE (ASTM) and EnSolv (FDOT) Replicates	TCE(ASTM)1 - EnSolv(FDOT)1	0.8065
	TCE(ASTM)1 - EnSolv(FDOT)2	0.8932
	TCE(ASTM)1 - EnSolv(FDOT)3	0.7258
	TCE(ASTM)2 - EnSolv(FDOT)1	0.7979
	TCE(ASTM)2 - EnSolv(FDOT)2	0.7702
	TCE(ASTM)2 - EnSolv(FDOT)3	0.7835
	TCE(ASTM)3 - EnSolv(FDOT)1	0.7587
	TCE(ASTM)3 - EnSolv(FDOT)2	0.8902
	TCE(ASTM)3 - EnSolv(FDOT)3	0.8251

6.7 Conclusions

The results from the penetration test on the recovered binders indicate that for the most part EnSolv and reclaimed EnSolv are not significantly different from TCE. These results also show that FDOT proposed recovery procedure is not significantly different from the ASTM recovery method.

The results of the viscosity test on the recovered binder show that there are no significant differences between the EnSolv, reclaimed EnSolv and TCE. There are also no significant differences between the FDOT proposed recovery procedure and the ASTM recovery procedure.

In addition to the analysis performed on the solvent data, it was also concluded that the 4-hour extraction was not significantly different when comparing the penetration and viscosity values to those obtained from the full extraction of the crumb rubber mixture. When comparing the ASTM method to the FDOT method, it was concluded that the FDOT method would be a suitable replacement for the ASTM standard method. It was noted that the means of the viscosity of the recovered binder from the crumb rubber mixes using the full extraction with the three layer filter paper was lower than that obtained with the ASTM filter paper. To investigate the possibility that the lower viscosity could be related to the change in filter paper, a study of a laboratory mixture with no crumb rubber was performed. This study revealed that although the viscosity of the binder which was recovered from the extraction using the three layer filter was lower than that using the ASTM filter, the difference was not statistically significant. In addition, it was noted that the reduction in the time required for full extraction when the three layer filter was used in the extraction of the crumb rubber modified mix was not

observed in the laboratory conventional mix. The times required for extraction of the laboratory mix were almost the same for either filter type.

One thing noted in the heated binders recovered from EnSolv and reclaimed EnSolv was that there was a slight odor resembling the solvent. Although there was no significant difference in the results that indicates that this was a problem, a future study of the binders is necessary to see if there are any possible effects of any residual solvent.

Finally, the DSR data at three different temperatures were also analyzed. In all but two cases, there was no significant difference in the results from the DSR when comparing each solvent extraction and recovery method with the ASTM extraction and recovery method using TCE.

It can be concluded from the results of the binder testing that the FDOT recovery method would be a suitable replacement for the ASTM method. In addition, both EnSolv and reclaimed EnSolv could be suitable replacements for TCE for use in the Reflux extraction process.

The results from the DSR tests on the recovered binders indicate that for the most part EnSolv and reclaimed EnSolv are not significantly different from TCE. The results also show that the FDOT proposed recovery procedure is not significantly different from the ASTM recovery method.

The results of the BBR test also indicate that for the most part no significant difference was found between any of the solvent-recovery procedure combinations tested. All combinations gave similar results when compared to the ASTM standard recovery method using TCE as the solvent.

The results of the FTIR spectral analysis led to the conclusion that there was no substantial difference in the chemical characteristics of the recovered binders using EnSolv and reclaimed EnSolv as compared with the TCE samples. Similarly, the samples recovered with the FDOT proposed recovery procedure showed similar characteristics as the samples of the ASTM standard recovery method, regardless of the solvent used.

It can be concluded from the results of the binder testing that the FDOT proposed recovery method would be a suitable replacement for the ASTM method. Furthermore, conclusions can be drawn that both EnSolv and reclaimed EnSolv could be used as a suitable replacement for TCE in the Reflux extraction and Rotavapor recovery procedures.

CHAPTER 7 EVALUATION OF THE EFFECTS OF SOLVENTS ON PROPERTIES OF THE ORIGINAL BINDERS

7.1 Testing Program

The evaluation on the effects of solvents on the original asphalt binders was performed on two different AC-graded binders. These asphalt binders include an AC-30 and an AC-20. The solvents used include EnSolv, reclaimed EnSolv and TCE. This evaluation determined the effects these chemical solvents may have on asphalt binders during the extraction and recovery procedures. The original binders were first dissolved in the solvents and then recovered from them. The effects of the solvents on these recovered asphalt binders were determined by comparing their physical properties with the physical properties of the virgin material. The tests performed on all binder samples included penetration, Brookfield viscosity, Dynamic Shear Rheometer, Bending Beam Rheometer and FTIR spectral analysis. All test results, except for the FTIR analysis, were analyzed using the Student's t-test as described in section 3.6.

7.2 Results from the Recovery Procedure

Asphalt samples for this evaluation were dissolved in each of the solvents and recovered using the Rotavapor apparatus in accordance with ASTM D5404. For each combination of binder and solvent, three replicate samples of asphalt were used.

The time required for the recovery procedure was observed to see if the results would compare with the recovery times observed in the first phase of the study.

The recovery times for each of the dissolved samples are presented in Table 7.1, while the results of the Student's t-test on these times are provided in Table 7.2. The analysis of the time data indicated that there was a significant difference in the times required to recover the binders using TCE as compared with both EnSolv and reclaimed EnSolv for both binders.

The results indicated that the recovery time using EnSolv and reclaimed EnSolv were consistently faster than that using TCE, for all binders tested. These results support the conclusions made in the first part of the study, that the use of EnSolv and reclaimed EnSolv provides a significant reduction of recovery times as compared with the use of TCE.

7.3 Results from the Penetration Test

The penetration test on the recovered asphalt binders from the various solvents was performed in accordance with ASTM D 5, at a temperature of 25° C. The results of the penetration of the virgin and the recovered samples from the AC-30 binder are displayed in Table 7.3. The EnSolv appears to have caused a substantial reduction in the penetration of the binder, while the TCE and the reclaimed EnSolv appear to have caused a slight increase in penetration.

The results of the penetration data for the AC-20 binder are displayed in Table 7.4. Once again the EnSolv appears to have caused a substantial reduction in the penetration of the binder, while the TCE and the reclaimed EnSolv appear to have caused a slight increase in penetration.

Table 7.1: Recovery Times Required for Each Solvent

Tested Material	Solvent	Trial	Recovery Times (minutes)	Average (minutes)	Standard Deviation
AC-30	EnSolv	1	51	53.7	2.31
		2	55		
		3	55		
	RE*	1	55	55.0	0.00
		2	55		
		3	55		
	TCE	1	85	83.3	7.64
		2	90		
		3	75		
AC-20	EnSolv	1	50	51.0	1.73
		2	50		
		3	53		
	RE*	1	55	52.7	2.52
		2	50		
		3	53		
	TCE	1	75	78.3	10.41
		2	70		
		3	90		

Note: RE* denotes the use of reclaimed EnSolv

Table 7.2: Results of the Student's t-Test Performed on the Recovery Times for Each Solvent

Tested Material	Solvent	Mean (Minutes)	Standard Deviation	$t_{\text{Calculated}}$	t_{Critical} for 95% Confidence	Significantly Different
AC-30	TCE	83.3	7.64	6.423	2.776	YES
	EnSolv	53.7	2.31			
	TCE	83.3	7.64	6.416	2.776	YES
	RE*	55.0	0.00			
AC-20	TCE	78.3	10.41	4.481	2.776	YES
	EnSolv	51.0	1.73			
	TCE	78.3	10.41	4.140	2.776	YES
	RE*	52.7	2.52			

Note: RE* denotes the use of reclaimed EnSolv

Table 7.3: Results of the Penetration Test Performed at 25° C
on all AC-30 Binder Samples

Trial	Solvent	Penetration	Average	Standard Deviation
1	None	47.8	48.47	0.58
2		48.8		
3		48.8		
1	EnSolv	38.0	38.60	0.60
2		39.2		
3		38.5		
1	RE*	48.8	48.93	1.50
2		47.5		
3		50.5		
1	TCE	51.3	51.60	1.57
2		53.3		
3		50.2		

Note: RE* denotes the use of reclaimed EnSolv

Table 7.4: Results of the Penetration Test Performed at 25° C
on all AC-20 Binder Samples

Trial	Solvent	Penetration	Average	Standard Deviation
1	None	69.7	69.20	0.50
2		69.2		
3		68.7		
1	EnSolv	66.0	65.50	2.00
2		67.2		
3		63.3		
1	RE*	73.3	72.00	1.30
2		70.7		
3		72.0		
1	TCE	76.3	73.16	3.99
2		74.5		
3		68.7		

Note: RE* denotes the use of reclaimed EnSolv

The mean and standard deviation of the results, along with the results of the Student's t-test performed on the penetration data, are provided in Table 7.5. The results of the statistical analysis identified significant difference between the virgin binder and both EnSolv and TCE recovered binders, as well as between the TCE recovered binders and the EnSolv recovered samples, for the AC-30 asphalt binder. For the AC-20 graded asphalt, the results identified a much closer comparison with a significant difference being found in the comparison between the virgin binder and the reclaimed EnSolv.

7.4 Results from Brookfield Viscosity Test

The Brookfield viscosity test was performed at 60° C on all binder samples and the viscosity for both the AC-30 binder and the AC-20 binder are displayed in Tables 7.6 and 7.7 respectively. For both binders, the EnSolv appears to have caused a substantial hardening of the binder, while the reclaimed EnSolv and the TCE appear to have caused less effects on the binders.

The Student's t-test was performed on the means and standard deviations of the viscosity data and the results are displayed in Table 7.8. Comparisons using the statistical analysis were conducted between the recovered binders and the virgin material, as well as between the TCE recovered binders and the samples recovered using EnSolv and reclaimed EnSolv. The results of the comparison performed on the AC-30 material identified significant differences between all comparisons, with the exception of the two comparisons. These exceptions include the comparisons of the virgin material to the TCE recovered samples and the TCE-recovered samples to the recovered binders using

Table 7.5: Results of the Student's t-Test Performed on the Results of the Penetration Test on all Binder Samples

Tested Material	Solvent	Mean (0.1 mm)	Standard Deviation	$t_{\text{Calculated}}$	$t_{\text{Critical for 95\% Confidence}}$	Significantly Different
AC-30	Virgin	48.5	0.58	20.662	2.776	YES
	EnSolv	38.6	0.60			
	Virgin	48.5	0.58	0.431	2.776	NO
	RE*	48.9	1.50			
	Virgin	48.5	0.58	3.210	2.776	YES
	TCE	51.6	1.57			
	TCE	51.6	1.57	13.397	2.776	YES
	EnSolv	38.6	0.60			
	TCE	51.6	1.57	2.154	2.776	NO
	RE*	48.9	1.50			
AC-20	Virgin	69.2	0.50	3.109	2.776	YES
	EnSolv	65.5	2.00			
	Virgin	69.2	0.50	3.482	2.776	YES
	RE*	72.0	1.30			
	Virgin	69.2	0.50	1.723	2.776	NO
	TCE	73.2	3.99			
	TCE	73.2	3.99	2.988	2.776	YES
	EnSolv	65.5	2.00			
	TCE	73.2	3.99	0.495	2.776	NO
	RE*	72.0	1.30			

Note: RE* denotes the use of reclaimed EnSolv

Table 7.6: Results of the Brookfield Viscosity Test Performed at 60° C on all AC-30 Binder Samples

Trial	Solvent	Viscosity (Poises)	Mean	Standard Deviation
1	None	4683	4759	83.8
2		4849		
3		4746		
1	EnSolv	9256	8963	266.2
2		8897		
3		8736		
1	RE*	5724	5737	173.4
2		5571		
3		5917		
1	TCE	6921	5611	1155.2
2		4737		
3		5176		

Note: RE* denotes the use of reclaimed EnSolv

Table 7.7: Results of the Brookfield Viscosity Test Performed at 60° C on all AC-20 Binder Samples

Trial	Solvent	Viscosity (Poises)	Mean	Standard Deviation
1	None	2453	2442	22.3
2		2416		
3		2456		
1	EnSolv	3712	3378	302.2
2		3300		
3		3123		
1	RE*	2204	2381	155.2
2		2445		
3		2494		
1	TCE	2354	2590	288.6
2		2912		
3		2505		

Note: RE* denotes the use of reclaimed EnSolv

Table 7.8: Results of the Student's t-Test Performed on the Results of the Brookfield Viscosity Test on all Binder Samples

Tested Material	Solvent	Mean (Poises)	Standard Deviation	$t_{\text{Calculated}}$	$t_{\text{Critical for 95\% Confidence}}$	Significantly Different
AC-30	Virgin	4759	83.8	26.091	2.776	YES
	EnSolv	8963	266.2			
	Virgin	4759	83.8	8.796	2.776	YES
	RE*	5737	173.4			
	Virgin	4759	83.8	1.274	2.776	NO
	TCE	5611	1155.2			
	TCE	5611	1155.2	4.897	2.776	YES
	EnSolv	8963	266.2			
	TCE	5611	1155.2	0.187	2.776	NO
RE*	5737	173.4				
AC-20	Virgin	2442	22.3	5.350	2.776	YES
	EnSolv	3378	302.2			
	Virgin	2442	22.3	0.674	2.776	NO
	RE*	2381	155.2			
	Virgin	2442	22.3	0.886	2.776	NO
	TCE	2590	288.6			
	TCE	2590	288.6	3.266	2.776	YES
	EnSolv	3378	302.2			
	TCE	2590	288.6	1.105	2.776	NO
RE*	2381	155.2				

Note: RE* denotes the use of reclaimed EnSolv

reclaimed EnSolv. For the AC-20 binder, significant differences were identified when comparing the EnSolv recovered samples to both the virgin material and the TCE recovered binders.

7.5 Results from Dynamic Shear Rheometer Testing

Following the same procedure for the DSR as in the evaluation of the recovered binders from the mixtures, DSR tests were performed on the virgin and all recovered binders at both 64 and 25° C. The results of the DSR test performed at both testing temperatures on all AC-30 samples are presented in Tables 7.9 and 7.10, while the results for the AC-20 binder are presented in Tables 7.11 and 7.12.

The results of the Student's t-test performed on the data for both testing temperatures and both binders are presented in Table 7.13. These results indicate that there was a significant difference between the virgin binder and the samples recovered using EnSolv. This difference was consistent for both binders and at both temperatures tested. The remaining two solvents (reclaimed EnSolv and TCE) were found to provide statistically similar results when compared to the virgin binder.

7.6 Results from Bending Beam Rheometer Testing

The BBR tests were once again performed at -18° C, following the same procedure as outlined in the evaluation of recovered binders from mixtures. The tested results of the measured parameters (Stiffness and m-value) are provided in Tables 7.14 and 7.15 for both binders tested. Both of the parameters were analyzed using the Student's t-test and the results are provided in Table 7.16. For both binders tested, only

Table 7.9: Results of the DSR Test Performed at 64° C on all AC-30 Binder Samples

Trial	Solvent	G* (Pa)	δ (°)	G*/Sin δ (Pa)	Average	Standard Deviation
1	Virgin Binder	2.30E+03	84.7	2.31E+03	2329	37.1
2		2.30E+03	84.6	2.31E+03		
3		2.36E+03	84.4	2.37E+03		
1	EnSolv	3.35E+03	82.4	3.38E+03	3566	201.3
2		3.75E+03	82.1	3.78E+03		
3		3.50E+03	81.9	3.54E+03		
1	RE*	2.42E+03	83.8	2.43E+03	2432	68.1
2		2.49E+03	83.4	2.50E+03		
3		2.35E+03	83.6	2.37E+03		
1	TCE	2.44E+03	83.6	2.46E+03	2306	198.3
2		2.07E+03	84.0	2.08E+03		
3		2.36E+03	83.8	2.38E+03		

Note: RE* denotes the use of reclaimed EnSolv

Table 7.10: Results of the DSR Test Performed at 25° C on all AC-30 Binder Samples

Trial	Solvent	G* (Pa)	δ (°)	G*(Sin δ) (Pa)	Average	Standard Deviation
1	Virgin Binder	9.84E+05	62.7	8.74E+05	8.62E+05	1.70E+04
2		9.46E+05	63.0	8.43E+05		
3		9.81E+05	62.4	8.69E+05		
1	EnSolv	1.36E+06	58.6	1.16E+06	1.21E+06	1.64E+05
2		1.64E+06	57.8	1.39E+06		
3		1.26E+06	58.6	1.07E+06		
1	RE*	9.54E+05	62.1	8.43E+05	8.17E+05	3.09E+04
2		9.34E+05	62.0	8.24E+05		
3		8.83E+05	62.5	7.83E+05		
1	TCE	9.25E+05	61.2	8.10E+05	8.13E+05	4.61E+04
2		8.68E+05	62.2	7.68E+05		
3		9.81E+05	61.3	8.60E+05		

Note: RE* denotes the use of reclaimed EnSolv

Table 7.11: Results of the DSR Test Performed at 64° C on all AC-20 Binder Samples

Trial	Solvent	G* (Pa)	δ (°)	G*/Sin δ (Pa)	Average	Standard Deviation
1	Virgin Binder	1.24E+03	87.0	1.24E+03	1231	10.5
2		1.23E+03	87.2	1.23E+03		
3		1.22E+03	87.3	1.22E+03		
1	EnSolv	2.02E+03	85.9	2.02E+03	1765	224.3
2		1.61E+03	86.4	1.61E+03		
3		1.66E+03	86.0	1.66E+03		
1	RE*	1.21E+03	87.2	1.21E+03	1249	37.4
2		1.26E+03	87.1	1.26E+03		
3		1.28E+03	86.8	1.28E+03		
1	TCE	1.18E+03	87.0	1.18E+03	1335	170.3
2		1.51E+03	86.2	1.52E+03		
3		1.31E+03	86.5	1.31E+03		

Note: RE* denotes the use of reclaimed EnSolv

Table 7.12: Results of the DSR Test Performed at 25° C on all AC-20 Binder Samples

Trial	Solvent	G* (Pa)	δ (°)	G*(Sin δ) (Pa)	Average	Standard Deviation
1	Original Binder	6.34E+05	71.7	6.02E+05	5.90E+05	2.68E+04
2		5.88E+05	72.0	5.59E+05		
3		6.42E+05	71.5	6.09E+05		
1	EnSolv	1.03E+06	67.4	9.50E+05	8.34E+05	1.12E+05
2		8.83E+05	69.3	8.26E+05		
3		7.79E+05	68.6	7.25E+05		
1	RE*	6.01E+05	71.7	5.71E+05	5.92E+05	6.82E+04
2		5.67E+05	71.4	5.37E+05		
3		7.08E+05	70.9	6.69E+05		
1	TCE	5.54E+05	71.7	5.26E+05	6.14E+05	1.02E+05
2		7.74E+05	69.8	7.26E+05		
3		6.22E+05	71.0	5.88E+05		

Note: RE* denotes the use of reclaimed EnSolv

Table 7.13: Results of the Student's t-Test Performed on the Results of the DSR Test on all Binder Samples

Tested Material	Test Temp	Solvent	Mean (Pa)	Standard Deviation	t_{Calc}	$t_{Critical}$ for 95% Confidence	Significantly Different
AC-30	64° C (G*/Sin δ)	Virgin	2329	37	10.483	2.776	YES
		EnSolv	3566	201			
		Virgin	2329	37	2.304	2.776	NO
		RE*	2432	68			
		Virgin	2329	37	0.198	2.776	NO
		TCE	2306	198			
	25° C (G*Sin δ)	Virgin	8.62E+05	1.70E+04	3.652	2.776	YES
		EnSolv	1.21E+06	1.64E+05			
		Virgin	8.62E+05	1.70E+04	2.227	2.776	NO
		RE*	8.17E+05	3.09E+04			
Virgin		8.62E+05	1.70E+04	1.740	2.776	NO	
TCE		8.13E+05	4.61E+04				
AC-20	64° C (G*/Sin δ)	Virgin	1231	11	4.119	2.776	YES
		EnSolv	1765	224			
		Virgin	1231	11	0.803	2.776	NO
		RE*	1249	37			
		Virgin	1231	11	1.053	2.776	NO
		TCE	1335	170			
	25° C (G*Sin δ)	Virgin	5.90E+05	2.68E+04	3.657	2.776	YES
		EnSolv	8.34E+05	1.12E+05			
		Virgin	5.90E+05	2.68E+04	0.057	2.776	NO
		RE*	5.92E+05	6.82E+04			
Virgin		5.90E+05	2.68E+04	0.386	2.776	NO	
TCE		6.14E+05	1.02E+05				

Note: RE* denotes the use of reclaimed EnSolv

Table 7.14: Results of the BBR Test Performed at -18° C on all AC-30 Binder Samples

Trial	Solvent	Test Results		Stiffness		m-value	
		Stiffness (MPa)	m-value	Average	Standard Deviation	Average	Standard Deviation
1	Virgin Binder	185	0.357	184	1	0.359	0.004
2		184	0.357				
3		183	0.364				
1	EnSolv	192	0.352	193	11	0.346	0.006
2		205	0.341				
3		183	0.344				
1	RE*	187	0.362	173	13	0.364	0.005
2		170	0.360				
3		161	0.370				
1	TCE	178	0.352	166	14	0.361	0.009
2		151	0.370				
3		170	0.360				

Note: RE* denotes the use of reclaimed EnSolv

Table 7.15: Results of the BBR Test Performed at -18° C on all AC-20 Binder Samples

Trial	Solvent	Test Results		Stiffness		m-value	
		Stiffness (MPa)	m-value	Average	Standard Deviation	Average	Standard Deviation
1	Virgin Binder	235	0.366	251	15	0.379	0.013
2		265	0.392				
3		252	0.378				
1	EnSolv	286	0.353	260	23	0.370	0.015
2		244	0.381				
3		249	0.376				
1	RE*	223	0.396	232	13	0.391	0.010
2		227	0.398				
3		247	0.380				
1	TCE	202	0.408	227	28	0.396	0.015
2		257	0.380				
3		221	0.401				

Note: RE* denotes the use of reclaimed EnSolv

Table 7.16: Results of the Student's t-Test Performed on the Results of the BBR Test on all Binder Samples

Tested Material	Test Parameter	Solvent	Mean	Standard Deviation	t _{Calc}	t _{Critical for 95% Confidence}	Significantly Different		
AC-30	Stiffness (MPa)	Virgin	184	1	1.464	2.776	NO		
		EnSolv	193	11					
		Virgin	184	1	1.479				
		RE*	173	13					
		Virgin	184	1	2.200				
		TCE	166	14					
	m-value	Virgin	0.359	0.004	3.234	2.776	YES		
		EnSolv	0.346	0.006					
		Virgin	0.359	0.004	1.304			2.776	NO
		RE*	0.364	0.005					
Virgin		0.359	0.004	0.352					
TCE		0.361	0.009						
AC-20	Stiffness (MPa)	Virgin	251	15	0.568	2.776	NO		
		EnSolv	260	23					
		Virgin	251	15	1.658				
		RE*	232	13					
		Virgin	251	15	1.309				
		TCE	227	28					
	m-value	Virgin	0.379	0.013	0.785	2.776	NO		
		EnSolv	0.370	0.015					
		Virgin	0.379	0.013	1.267			2.776	NO
		RE*	0.391	0.010					
		Virgin	0.379	0.013	1.483				
		TCE	0.396	0.015					

Note: RE* denotes the use of reclaimed EnSolv

one comparison was determined to be statistically different from its virgin binder. The comparison of the m-value, for the AC-30 material, between the virgin binder and the EnSolv recovered samples was found to be the only comparison that was significantly differently at a 95% confidence level.

7.7 Results from FTIR Spectral Analysis

The infrared spectral analysis was performed on all binders following the same procedure as outlined in the preceding sections. The IR absorption spectra for all recovered binders were compared with those of their replicates, as well as to the replicates of the virgin binders. These correlation coefficients are provided in Table 7.17 and 7.18 for both the AC-30 binder and the AC-20 binder respectively. The results of the correlation coefficients identify correlations between all spectra to be over 75%, which signifies good correlation between all binder samples tested. The results also show that the correlation coefficients between the virgin binder replicates provide higher coefficients with less variability when compared with the solvent-recovered samples. As for the binders recovered with the various solvents, the ranges of the correlation coefficients overlap closely between themselves, which indicate insignificant differences among the solvents.

Table 7.17: Correlation of FTIR Spectra of AC-30 Binder Recovered By Using Different Solvents

	Comparisons	Correlation
Correlations Between Virgin Binder Replicates	1-2	0.9013
	1-3	0.9224
	2-3	0.9164
Correlations Between EnSolv Replicates	1-2	0.8741
	1-3	0.8882
	2-3	0.8663
Correlations Between Reclaimed EnSolv Replicates	1-2	0.9136
	1-3	0.8434
	2-3	0.9131
Correlations Between TCE Replicates	1-2	0.9510
	1-3	0.9072
	2-3	0.9161
Correlations Between the Virgin Binder and the EnSolv Replicates	Virgin1 - EnSolv1	0.8821
	Virgin1 - EnSolv2	0.8420
	Virgin1 - EnSolv3	0.8822
	Virgin2 - EnSolv1	0.8642
	Virgin2 - EnSolv2	0.8171
	Virgin2 - EnSolv3	0.8754
	Virgin3 - EnSolv1	0.8529
	Virgin3 - EnSolv2	0.8390
Correlations Between the Virgin Binder and the Reclaimed EnSolv Replicates	Virgin1 - RE*1	0.8249
	Virgin1 - RE*2	0.9088
	Virgin1 - RE*3	0.8215
	Virgin2 - RE*1	0.8775
	Virgin2 - RE*2	0.9095
	Virgin2 - RE*3	0.8923
	Virgin3 - RE*1	0.8051
	Virgin3 - RE*2	0.8997
Virgin3 - RE*3	0.8726	

Note: RE* denotes the use of reclaimed EnSolv

Table 7.18: Correlation of FTIR Spectra of AC-20 Binder Recovered By Using Different Solvents

	Comparisons	Correlation
Correlations Between Virgin Binder Replicates	1-2	0.9360
	1-3	0.920
	2-3	0.9513
Correlations Between EnSolv Replicates	1-2	0.8619
	1-3	0.8930
	2-3	0.8502
Correlations Between Reclaimed EnSolv Replicates	1-2	0.8300
	1-3	0.8655
	2-3	0.9203
Correlations Between TCE Replicates	1-2	0.8474
	1-3	0.8953
	2-3	0.8569
Correlations Between the Virgin Binder and the EnSolv Replicates	Virgin1 - EnSolv1	0.8323
	Virgin1 - EnSolv2	0.8650
	Virgin1 - EnSolv3	0.8544
	Virgin2 - EnSolv1	0.8798
	Virgin2 - EnSolv2	0.7967
	Virgin2 - EnSolv3	0.8547
	Virgin3 - EnSolv1	0.8929
	Virgin3 - EnSolv2	0.8305
Virgin3 - EnSolv3	0.8823	
Correlations Between the Virgin Binder and the Reclaimed EnSolv Replicates	Virgin1 - RE*1	0.8637
	Virgin1 - RE*2	0.7966
	Virgin1 - RE*3	0.7808
	Virgin2 - RE*1	0.8109
	Virgin2 - RE*2	0.7583
	Virgin2 - RE*3	0.7231
	Virgin3 - RE*1	0.8452
	Virgin3 - RE*2	0.7951
Virgin3 - RE*3	0.8143	
Correlations Between the Virgin Binder and the TCE Replicates	Virgin1 - TCE1	0.9134
	Virgin1 - TCE2	0.7914
	Virgin1 - TCE3	0.8501
	Virgin2 - TCE1	0.8671
	Virgin2 - TCE2	0.8009
	Virgin2 - TCE3	0.8039
	Virgin3 - TCE1	0.8446
	Virgin3 - TCE2	0.7959
Virgin3 - TCE3	0.8395	

Note: RE* denotes the use of reclaimed EnSolv

7.8 Conclusions

To evaluate the effects of solvents on asphalt binders, asphalt samples were completely dissolved in each of the test solvents and recovered so that the physical properties of the recovered binders could be tested and compared. The recovery times of the binders were recorded, for each solvent, and the results indicated that the recovery time using EnSolv and reclaimed EnSolv were consistently faster than that using TCE. This reduction in recovery time was consistent for both asphalt binders tested and also agree with the findings of the first part of this study previous research studies.

The results of the penetration test indicated that for the most part, TCE and reclaimed EnSolv gave similar results as the virgin material. Although slight differences between these two solvents did occur, they did not seem significant when compared to the variability of the test itself. As for the binders recovered using EnSolv, the results indicated that hardening of the samples did occur during the recovery of both tested binders.

For the Brookfield viscosity tests, some variability was found between the results, but a similar trend to the penetration results was found. The hardening of samples caused during the recovery of the EnSolv binder was again confirmed by the viscosity test. The viscosity of the EnSolv-recovered binders (for both binders tested) were significantly higher when compared to the virgin material.

The results of the DSR test continued to confirm the hardening of the recovered binders using EnSolv. For both binders tested, and at both temperatures tested, the EnSolv recovered samples were found to be statistically different when compared to the virgin material. The increase in $G^*/\sin(\delta)$ at high temperatures and $G^*\sin(\delta)$ at

intermediate temperatures identify hardening of the EnSolv-recovered binders. As for the reclaimed EnSolv and the TCE, the results indicated that there was no significant difference between these samples and the virgin material.

The results from the BBR test have indicated that, for the most part, the stiffness and the rate at which creep changes with time were not affected by having the binders dissolved and recovered in any of the solvents. The results of this test indicated that binders recovered from all three solvents were similar to the properties of the virgin material, for both binders tested.

Finally, the FTIR spectra, for all samples, were analyzed to identify if the hardening that has been previously determined was caused by oxidation. As previously mentioned the FTIR spectrum (within the range of 1500 cm^{-1} and 2000 cm^{-1}) should detect the formation of several functional groups (including carboxylic acids, ketones, and anhydrides), that are formed as a result of oxidation. The results of the FTIR analysis indicated that all samples scanned had similar chemical compositions and that no signs of oxidation had occurred during the recovery of the EnSolv samples, or in the recovery of any of the samples using reclaimed EnSolv or TCE. Thus, the hardening observed in the EnSolv recovered samples must have been caused by some other mechanism, such as loss of volatiles.

CHAPTER 8 COMPOSITIONAL ANALYSES OF ENSOLV AND RECLAIMED ENSOLV

8.1 Introduction

Independent compositional analyses of EnSolv were performed by Dr. Hua Chee Ooi and Mr. Stephan Audetat of the Department of Chemistry at the University of Florida. Similar analyses were also performed on the reclaimed EnSolv used in this study. This chapter includes two reports by these two chemists on the results of the analyses and their comments on the health and safety aspects of EnSolv.

8.2 Report on the Composition and Safety Aspects of EnSolv

8.2.1 Analysis Results

EnSolv is a commercial product of Enviro Tech International Inc. A sample was analyzed to confirm whether the composition matched that reported by the supplier. The analysis was conducted using GC-MS (gas chromatography - mass spectrometry) and ^1H nmr spectroscopy.

GC-MS Analysis (gas chromatography - mass spectrometry)

The GC was run using a Finnigan GCQ with a 30 m fused silica capillary column from J&W Scientific (DB5-MS), and an ion trap MS detector. The neat sample was injected.

Due to the varying ionization potentials of the different compounds present, integration of the area under the peaks in the GC trace is not an accurate method for a quantitative analysis of the mixture.

The GC-MS analysis confirmed the presence of the following compounds:

- (i) 1-bromopropane [CAS # 106-94-5]
- (ii) 1,3-dioxolane [CAS # 646-06-0]
- (iii) 1,2-epoxybutane [CAS # 106-88-7]

The GC-MS analysis indicated the potential presence of:

- (i) Isomers of bromo-fluorobenzene

¹H nmr spectroscopy

The ¹H nmr spectrum was recorded by using a Varian Inova 500 MHz nmr spectrometer in a deuteriochloroform solution (concentration 5 mg/ml), using tetramethylsilane as the internal standard.

The ¹H nmr spectrum allowed for a more quantitative assessment of the components in the sample (please note that the error is *ca.* ±1%). The ¹H nmr spectrum analysis confirmed the presence of the following compounds :

- | | | |
|-------|----------------------------------|--------------------|
| (i) | 1-bromopropane [CAS # 106-94-5] | 88 wt% |
| (ii) | 1,3-dioxolane [CAS # 646-06-0] | 5 wt% |
| (iii) | nitromethane [CAS # 75-52-5] | <1 wt% |
| (iv) | 1,2-epoxybutane [CAS # 106-88-7] | <1 wt% |
| (v) | unidentified compound(s) | 6 wt% ^a |

^a Assuming a MW of 140.

Although isomers of bromo-fluorobenzene were observed in the GC-MS analysis, they were not detected in the ^1H nmr spectrum, which indicates that they are present in very small (<1%) quantities.

The unidentified compounds are most likely to be terpenes, which are described in the patents taken out on EnSolv.¹

Comparison with Published Data

It is interesting to note that as of 20 June 2000, the MSDS available for EnSolv only identifies two components.²

- (i) 1-bromopropane (>90.5 wt%)
- (ii) 1,3-dioxolane (<3.00 wt%)

Both of these compounds have been identified by GC-MS and ^1H nmr spectroscopic analysis.

This is in contrast to the previously issued MSDS (issued 16 February 2000) which stated the components of EnSolv were:

- (i) 1-bromopropane
- (ii) 1,3-dioxolane
- (iii) nitromethane
- (iv) 1,2-epoxybutane

Conclusion

The sample analyzed is reasonably consistent with the composition of EnSolv as reported in the MSDS prepared by Enviro Tech International Inc.

8.2.2 Health and Safety Issues

Extensive toxicity studies have been conducted on trichloroethylene. Unfortunately the same cannot be said of 1-bromopropane, which is the main component of EnSolv. This compound is currently being evaluated by the EPA.³

Toxicity

Trichloroethylene

TLV-TWA (ACGIH) 50 ppm⁴⁻⁷

STEL-TWA (ACGIH) 100 ppm⁴⁻⁷

1-Bromopropane

To the best of our knowledge, no exposure limits have been set by the ACGIH or OSHA.

WEG-TWA (Enviro Tech) 100 ppm (recommended)²

1,3-Dioxolane

TLV-TWA (ACGIH) 20 ppm⁵

1,2-Epoxybutane

To the best of our knowledge, no exposure limits have been set by the ACGIH.

PEL (Aldrich) 400 ppm (recommended)⁵

Nitromethane

TLV-TWA (ACGIH) 20 ppm⁴⁻⁷

Carcinogenicity

Trichloroethylene

ACGIH: Class A5 - not suspected of causing cancer in humans.⁵⁻⁷

State of California: carcinogen⁵⁻⁷

IARC: Group 2A - possibly carcinogenic to humans.⁵⁻⁷

NIOSH: occupational carcinogen.⁶

OHSA: possible select carcinogen.⁶

1-Bromopropane

The carcinogenicity of 1-bromopropane has yet to be fully investigated.

1,3-Dioxolane

The carcinogenicity of 1-bromopropane has yet to be fully investigated.

1,2-Epoxybutane

IARC: Group 2B - possibly carcinogenic to humans.⁵

Nitromethane

State of California: carcinogen^{6,7}

Flammability*Trichloroethylene*Fp (°C)⁴⁻⁷: None.

Not flammable.

*1-Bromopropane*Fp (°C)⁷: 22.Fp (°C)⁴: 25.Fp (°C)⁶: 69.Fp (°C)⁵: 109.*1,3-Dioxolane*Fp (°C)⁴⁻⁶: -6.

Highly flammable

*1,2-Epoxybutane*Fp (°C)^{4,5}: -12.

Highly flammable

*Nitromethane*Fp (°C)⁴⁻⁷: 35.

Flammable

The reported flash point of 1-bromopropane, which is the major component of EnSolv, varies considerably. Independent determination of the flash point of EnSolv by Factory Mutual Research Corporation of Norwood, MA, showed however that EnSolv does not possess a flash point. As a safety precaution though, it would be wise to keep EnSolv away from sources of heat and ignition.

Conclusions

From the information available, EnSolv appears to be a viable alternative to trichloroethylene. The material should however still be considered as hazardous, and appropriate precautions should be exercised during its storage, transportation, handling and use. Inhalation, ingestion and contact with the skin of EnSolv should be avoided.

8.2.3 Summary of Analysis

Compound	Present in ^1H nmr spectrum	Present in GC-MS	%wt from ^1H nmr spectrum
1-Bromopropane CAS # 106-94-5 $\text{C}_3\text{H}_7\text{Br}$ MW: 122.99 bp ($^\circ\text{C}$): 71	YES	YES	88
1,3-Dioxolane CAS # 646-06-0 $\text{C}_3\text{H}_6\text{O}_2$ MW: 74.08 bp ($^\circ\text{C}$): 74-75	YES	YES	5
Nitromethane CAS # 75-52-5 CH_3NO_2 MW: 61.04 bp ($^\circ\text{C}$): 101	YES	NO	<1
1,2-Epoxybutane CAS # 106-88-7 $\text{C}_4\text{H}_8\text{O}$ MW: 72.11 bp ($^\circ\text{C}$): 63	YES	YES	<1
Unidentified Compounds (Perhaps Terpenes) MW: Approx.140	YES	Perhaps	6
1-Bromo-2-fluorobenzene CAS # 1072-85-1 $\text{C}_6\text{H}_4\text{BrF}$ MW: 175.00 bp ($^\circ\text{C}$): 155-157	NO	Perhaps	N/A
1-Bromo-3-fluorobenzene CAS # 1073-06-9 $\text{C}_6\text{H}_4\text{BrF}$ MW: 175.00 bp ($^\circ\text{C}$): 149-151	NO	Perhaps	N/A
1-Bromo-4-fluorobenzene CAS # 460-00-4 $\text{C}_6\text{H}_4\text{BrF}$ MW: 175.00 bp ($^\circ\text{C}$): 150	NO	Perhaps	N/A

8.3 Report on the Composition of Reclaimed EnSolv

8.3.1 Analysis Results

EnSolv is a commercial product of Enviro Tech International Inc. An analysis was undertaken to determine the composition of a sample of EnSolv which had been used to dissolve asphalt, and which was subsequently recovered by distillation from the asphalt solution (so called reclaimed EnSolv). The analysis was conducted using GC-MS (gas chromatography - mass spectrometry) and ^1H nmr spectroscopy.

GC-MS Analysis (gas chromatography - mass spectrometry)

Reclaimed EnSolv

The GC was run using a Finnigan GCQ with a 30 m fused silica capillary column from J&W Scientific (DB5-MS), and an ion trap MS detector. The neat sample was injected.

Due to the varying ionization potentials of the different compounds present, integration of the area under the peaks in the GC trace is not an accurate method for a quantitative analysis of the mixture.

The GC-MS analysis confirmed the presence of the following compounds:

- (i) 1-bromopropane [CAS # 106-94-5]
- (ii) 1,3-dioxolane [CAS # 646-06-0]
- (iii) 1,2-epoxybutane [CAS # 106-88-7]

The GC-MS analysis indicated the potential presence of:

- (i) Isomers of bromo-fluorobenzene
- (ii) Toluene [CAS # 108-88-3]

Comparison with the results obtained from a fresh sample of EnSolv (analyzed previously)

Every significant peak at a given retention time could be found in both samples of fresh and reclaimed EnSolv. The areas under the respective peaks in the GC-trace vary between the two samples, but as mentioned above, due to the nature of the ionization technique, this does not necessarily indicate a difference in the composition of the material analyzed.

¹H nmr spectroscopy

Reclaimed EnSolv

The ¹H nmr spectrum was recorded by using a Varian Inova 500 MHz nmr spectrometer in a deuteriochloroform solution (concentration 5 mg/ml), using tetramethylsilane as the internal standard.

The ¹H nmr spectrum allowed for a more quantitative assessment of the components in the sample (please note that the error is *ca.* ±1%). The ¹H nmr spectrum analysis confirmed the presence of the following compounds :

(i)	1-bromopropane [CAS # 106-94-5]	89 wt%
(ii)	1,3-dioxolane [CAS # 646-06-0]	4 wt%
(iii)	nitromethane [CAS # 75-52-5]	<1 wt%
(iv)	1,2-epoxybutane [CAS # 106-88-7]	<1 wt%
(v)	unidentified compound(s)	6 wt% ^a

^a Assuming a MW of 140.

Although isomers of bromo-fluorobenzene were observed in the GC-MS analysis, they were not detected in the ^1H nmr spectrum, which indicates that they are present in very small (<1%) quantities. There was also no evidence of toluene in the sample. It should be noted that toluene may be a common contaminant in a chemical laboratory.

The unidentified compounds are most likely to be terpenes, which are described in the patents taken out on EnSolv.¹

Comparison with the results obtained with a fresh sample of EnSolv (analyzed previously)

The ^1H nmr spectra of the fresh and reclaimed samples of EnSolv are very similar. As can be seen from the percentage composition breakdown, the amount of 1-bromopropane has increased by 1%, while that of 1,2-epoxybutane has decreased by 1%. Please note that these changes are not really significant, as the error associated with this form of analysis is *ca.* $\pm 1\%$.

Conclusion

The analysis of the reclaimed sample of EnSolv indicates that it is not significantly different from the fresh sample of EnSolv which was previously analyzed.

8.3.2 Summary of Analysis

Compound	Present in ¹ H nmr spectrum		Present in GC-MS		%wt from ¹ H nmr spectrum	
	Fresh	Reclaimed	Fresh	Reclaimed	Fresh	Reclaimed
1-Bromopropane CAS # 106-94-5 C ₃ H ₇ Br MW: 122.99 bp (°C): 71	YES	YES	YES	YES	88	89
1,3-Dioxolane CAS # 646-06-0 C ₃ H ₆ O ₂ MW: 74.08 bp (°C): 74-75	YES	YES	YES	YES	5	4
Nitromethane CAS # 75-52-5 CH ₃ NO ₂ MW: 61.04 bp (°C): 101	YES	YES	NO	NO	<1	<1
1,2-Epoxybutane CAS # 106-88-7 C ₄ H ₈ O MW: 72.11 bp (°C): 63	YES	YES	YES	YES	<1	<1
Unidentified Compounds (Perhaps Terpenes) MW: Approx.140	YES	YES	Perhaps	Perhaps	6	6
1-Bromo-2-fluorobenzene CAS # 1072-85-1 C ₆ H ₄ BrF MW: 175.00 bp (°C): 155-157	NO	NO	Perhaps	Perhaps	N/A	N/A
1-Bromo-3-fluorobenzene CAS # 1073-06-9 C ₆ H ₄ BrF MW: 175.00 bp (°C): 149-151	NO	NO	Perhaps	Perhaps	N/A	N/A
1-Bromo-4-fluorobenzene CAS # 460-00-4 C ₆ H ₄ BrF MW: 175.00 bp (°C): 150	NO	NO	Perhaps	Perhaps	N/A	N/A
Toluene CAS # 108-88-3 C ₇ H ₈ MW: 92.14 bp (°C): 111	NO	NO	Perhaps	Perhaps	N/A	N/A

8.3.3 Glossary

TLV	Threshold Limit Value. - An ACGIH recommended concentration of a substance to which most workers can be exposed without adverse effect.
TWA	Time Weighted Average. - A normal 8 h workday or 40 h workweek.
STEL	Short Term Exposure Level. - The maximum concentration to which workers can be exposed for up to 15 min, provided that no more than 4 exposures per day are permitted, with 60 min between exposures, and provided that the daily TWA is not exceeded.
CL	Ceiling Level - The concentration threshold of a substance that should never be exceeded.
PEL	Permissible Exposure Level
WEG	Workplace Exposure Guideline
Fp	Flash Point - The lowest temperature at which vapors of a volatile combustible substance will sustain combustion in air when exposed to a flame.
ACGIH	American Conference of Government Industrial Hygienists
IARC	International Agency for Research on Cancer
NIOSH	National Institute for Occupation Safety and Health USA
OHSA	Standards outlined under the Occupational Health and Safety Act of 1970, USA.

8.3.4 References

1. EnSolv patents.
 - a) Clark; L. A. US Patent 5,616,549, December 29, 1995
http://www.ensolv.com/First_Patent.htm
 - b) Clark; L. A. US Patent 5,824,162, March 28, 1997
http://www.ensolv.com/Second_Patent.htm
 - c) Clark; L. A. and Priest; J. L. US Patent 5,938,859, November 10, 1997.
http://www.ensolv.com/Third_Patent.htm
2. New EnSolv MSDS (Updated June 20, 2000)
http://www.ensolv.com/EnSolv_MSDS.htm
3. EPA documents, focusing on 1-bromopropane
http://www.ensolv.com/PDF/2103_SNAP_Federal_Register21899.pdf
http://www.ensolv.com/PDF/2102_SNAP_EPA_Slide_Presentation.pdf
4. 'The dictionary of substances and their effects', 2nd Edn (Ed. S. Gangolli) (Royal Society of Chemistry: Cambridge 1999).
5. Aldrich MSDS (requires Login, use pull down menu to select MSDS)
<http://www.sigma-aldrich.com>
6. Fisher Scientific - ACROS MSDS (search for chemical, then locate MSDS)
<http://www3.fishersci.com>
7. Mallinckrodt - Baker MSDS (search for chemical, then locate MSDS)
<http://www.mallchem.com/cgi-bin/pasi.pl?Begin>

CHAPTER 9

CONCLUSIONS

9.1 Solubility of Asphalt Binders in EnSolv

The results of standard asphalt solubility test (ASTM D 2042) using EnSolv and TCE indicated that EnSolv is not statistically different from TCE in 7 out of 10 sets of tests. In the three sets of tests that EnSolv was statistically different, the maximum difference of the means of the results for TCE and EnSolv was 0.114%. In all cases, the differences were all within the allowable variation as specified in the ASTM Standard D 2042 for the Solubility Test between laboratories. This difference is so small that there is no practical significance between the two solvents; therefore, EnSolv could be a suitable replacement for TCE in the standard solubility test. In addition, the study showed that no modifications to the current test procedure are necessary when using EnSolv.

9.2 Extraction of Asphalt Binders from Mixtures

The extraction procedure was performed using two different set-ups, a small unit (1000-gram) and a large unit (2000-gram). This study evaluated both set-ups and concluded that the larger set-up provides a faster, less complicated extraction. In addition, it allows for more mixture to be extracted at one time.

The results from the extraction test indicated that from the standpoint of asphalt content and extraction time, EnSolv and reclaimed EnSolv could be suitable replacements

for TCE for ASTM D 2172, Method B. The testing methods are applicable for the use of both solvents. In addition, the use of EnSolv and reclaimed EnSolv reduce the time required for extraction.

The only problem encountered in the Reflux extraction test was the extraction of the crumb rubber modified mixture. These problems included the extended length of time required to complete the procedure, problems of clogging in the filter and excessive rubber remaining in the extracted solution due to spilling. Using a three-layer filter paper system, which was suggested by the FDOT, solved all of these problems. This system consisted of three layers of towel like paper with thread woven through it. This modification enabled the extraction process to be completed in the time allowed with no complications. In addition, this filter system may also enable a more accurate determination of asphalt content.

An additional study of the three-layer filter system was performed on a laboratory conventional mix. In this study, it was found that there was no noticeable difference in the required extraction time between the two different filters, which was noticed in the crumb rubber modified mix.

9.3 Recovery of Asphalt Binders from Solution

Two different asphalt recovery procedures using the rotavapor, the ASTM and the FDOT proposed procedure were investigated. The results from the FDOT proposed recovery procedure indicated that the time required for the complete recovery of the asphalt binder in solution was less than the time required for the ASTM recovery

procedure with any of the solvents investigated. The FDOT method was also easier to perform.

When the solvents were compared, the results of the recovery methods indicated that the binders recovered from EnSolv and reclaimed EnSolv were recovered faster than those recovered from TCE. There were no modifications necessary for either of the recovery procedures when using EnSolv or reclaimed EnSolv as a replacement solvent for TCE; therefore, EnSolv and reclaimed EnSolv could be suitable replacements for TCE in the extraction and recovery process.

9.4 Properties of Recovered Binders

The recovered binders were tested to determine if each combination of solvent and recovery method would yield the results as TCE using the ASTM Standard Method. The tests performed on these binders included Penetration, Brookfield Viscosity, Dynamic Shear Rheometer, Bending Beam and FTIR Spectral Analysis. The results from these tests were analyzed using the Student's t-test.

The results from the penetration test on the recovered binder indicated that in all but one case, EnSolv and reclaimed EnSolv were not significantly different from TCE. In addition, the FDOT proposed recovery method was not significantly different from the ASTM method. In all cases, the differences between the means compared were all within the allowable variation of test results as specified in the precision statement for the recovery test (ASTM D 5404).

The results of the viscosity test on the recovered binder show that there was no significant difference between the EnSolv, reclaimed EnSolv and TCE. There is also no

significant difference between the FDOT proposed and the ASTM recovery method. Once again, in all cases, the differences between the means were all within allowable variation of test results as specified in ASTM D 5404.

Although there was no significant difference in the results of the binder viscosity tests, it should be noted that when the binders were heated for testing, the binders recovered from the EnSolv and reclaimed EnSolv had a slight odor indicating the possibility of residual solvent. This is not an uncommon occurrence in the recovery process. In fact, this problem has even been noted to occur occasionally when using TCE. For the properties studied, the possibility of residual solvent has shown no effects, but it would be necessary to investigate this in future studies.

In the study of the two different types of filter paper, it was determined that there was no significant difference in the penetration and viscosity results.

The DSR values of $G^*/\sin\delta$ (at 60 and 64° C) and $G^*\sin\delta$ (at 25° C) were analyzed. In all but two cases, there was no significant difference in the results from the DSR when comparing each solvent and recovery method with the ASTM recovery method when using TCE for extraction.

The use of EnSolv and reclaimed EnSolv for the purpose of asphalt extraction and recovery from asphalt mixtures has been found to perform equally to TCE. No significant difference was found in the binder properties tested between samples recovered using TCE and the samples recovered with EnSolv and reclaimed EnSolv, although a significant reduction in time was observed.

Furthermore, this evaluation has also determined that the FDOT proposed recovery method could also be used as a suitable replacement for the existing ASTM

standard recovery method. Once again, no significant difference was found between any of the solvent-mixture combinations when compared to the ASTM standard recovery method using TCE as the solvent.

9.5 Evaluation of the Effects of Solvents on Recovered Binders

When an asphalt binder is dissolved in a solvent (TCE or EnSolv) and then recovered, the properties of the recovered binders were observed to have higher variability as compared to the tested properties of the virgin asphalt. This increase in variability was anticipated as the solvent and the recovery procedure added sources of variability.

It was observed that dissolving a virgin binder in EnSolv caused a significant hardening of the binder. However very little binder hardening was observed when the reclaimed EnSolv was used. Where extraction and recovery were performed on asphalt binders, which had previously undergone short-term aging (as in the plant mixtures), little difference was observed between EnSolv and reclaimed EnSolv.

The results indicate that EnSolv can be used to extract and recover binders which have undergone some aging, such as from a plant mix or RAP. For extraction and recovery of asphalt, which has not undergone any aging, the use of a reclaimed EnSolv can result in lesser effects on the binders.

9.6 Composition of EnSolv and Reclaimed EnSolv

Results of GC-MS Analysis (Gas Chromatography – Mass Spectrometry) and ¹H nmr (nuclear magnetic resonance) spectroscopy on EnSolv indicated its composition to

be reasonably consistent with that as reported in the MSDS prepared by Enviro Tech International Inc. The MSDS available for Ensolv, dated June 20, 2000, only identifies the following two components:

- (i) 1-bromopropane (>90.5 wt%)
- (ii) 1,3-dioxolane (<3.00 wt%)

The ^1H nmr spectrum analysis on an EnSolv sample confirmed the presence of the following compounds :

- | | | |
|-------|--------------------------|--------|
| (i) | 1-bromopropane | 88 wt% |
| (ii) | 1,3-dioxolane | 5 wt% |
| (iii) | nitromethane | <1 wt% |
| (iv) | 1,2-epoxybutane | <1 wt% |
| (v) | unidentified compound(s) | 6 wt% |

The similar analyses on the reclaimed Ensolv indicated that it was not significantly different from the fresh Ensolv. The ^1H nmr spectrum analysis on a sample of reclaimed EnSolv confirmed the presence of the following compounds :

- | | | |
|-------|--------------------------|--------|
| (i) | 1-bromopropane | 89 wt% |
| (ii) | 1,3-dioxolane | 4 wt% |
| (iii) | nitromethane | <1 wt% |
| (iv) | 1,2-epoxybutane | <1 wt% |
| (v) | unidentified compound(s) | 6 wt% |

From the health and safety information available, Ensolv appears to be a viable alternative to trichloroethylene. The material should however still be considered as hazardous, and appropriate precautions should be exercised during its storage,

transportation, handling and use. Inhalation, ingestion and contact with the skin of Ensolv should be avoided.

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APPENDIX
INFORMATION FOR MARSHALL, SUPERPAVE AND CRUMB RUBBER
MODIFIED MIXTURES

Table A.1: Information for the Marshall Mixture

Type of Mix	S-III Recycle
Road	SR-91
Plant Location	Ft. Pierce, Florida
Materials	
Crushed RAP	
S-1-B Stone	
Screenings	
Local Sand	
Asphalt Content	7.00%

Table A.2: Information for the Superpave Mixture

Type of Mix	19.0 mm Recycle
Road	SR-8
Plant Location	Shalimar, Florida
Materials	
Milled Material	
#67 Granite	
#89 Granite	
W-10 Granite	
M-10 Granite	
Asphalt Content	4.70%

Table A.3: Information for the Crumb Rubber Modified Mixture

Type of Mix	FC-2 with GTR
Road	SR-580
Plant Location	Tampa, Florida
Materials	
#789-B Granite	
#105-A Screenings	
Asphalt Content	4.70%