

Final Technical Report
VOC and HAP Recovery Using Ionic Liquids

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Executive Summary

During the manufacture of wood composites, paper, and to a lesser extent, lumber, large amounts of volatile organic compounds (VOCs) such as terpenes, formaldehyde, and methanol are emitted to air. Some of these compounds are hazardous air pollutants (HAPs). The air pollutants produced in the forest products industry are difficult to manage because the concentrations are very low. Presently, regenerative thermal oxidizers (RTOs and RCOs) are commonly used for the destruction of VOCs and HAPs. RTOs consume large amounts of natural gas to heat air and moisture. The combustion of natural gas generates increased CO₂ and NO_x, which have negative implications for global warming and air quality. The aforementioned problems are addressed by an absorption system containing a room-temperature ionic liquid (RTIL) as an absorbent. RTILs are salts, but are in liquid states at room temperature. RTILs, an emerging technology, are receiving much attention as replacements for organic solvents in industrial processes with significant cost and environmental benefits. Some of these processes include organic synthesis, extraction, and metal deposition. RTILs would be excellent absorbents for exhausts from wood products facilities because of their unique properties: no measurable vapor pressure, high solubility of wide range of organic compounds, thermal stability to 200°C (almost 400°F), and immiscibility with water.

Room temperature ionic liquids were tested as possible absorbents. Four were imidazolium-based and were eight phosphonium-based. The imidazolium-based ionic liquids proved to be unstable at the conditions tested and in the presence of water. The phosphonium-based ionic liquids were stable. Most were good absorbents; however, cleaning the contaminants from the ionic liquids was problematic. This was overcome with a higher temperature (120°C) than originally proposed and a very low pressure (1 kPa). Absorption trials were conducted with tetradecyl(trihexyl)phosphonium dicyanamide as the RTIL. It was determined that it has good absorption properties for methanol and α -pinene, is thermally stable, and is relatively easy to synthesize. It has a density of 0.89 g/mL at 20°C and a molecular weight of 549.9 g/mol.

Trials were conducted with a small absorption system and a larger absorption system. Methanol, formaldehyde, and other HAPs were absorbed well, nearly 100%. Acetaldehyde was difficult to capture. Total VOC capture, while satisfactory on methanol and α -pinene in a lab system, was less than expected in the field, 60-80%. The inability to capture the broad spectrum of total organics is likely due to difficulties in cleaning them from the ionic liquid rather than the ability of the ionic liquid to absorb.

It's likely that a commercial system could be constructed to remove 90 to 100% of the gas contaminants. Selecting the correct ionic liquid would be key to this. Absorption may not be the main selection criterion, but rather how easily the ionic liquid can be cleaned is very important. The ionic liquid absorption system might work very well in a system with a limited spectrum of pollutants, such as a paint spray line, where there are not very high molecular weight, non volatile, compounds in the exhaust.

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Introduction

During the manufacture of wood composites, paper, and to a lesser extent, lumber, large amounts of volatile organic compounds (VOCs) such as terpenes, formaldehyde, and methanol are emitted to air. Some compounds are also hazardous air pollutants (HAPs). The air pollutants produced in the forest products industry are difficult to manage because the concentrations are very low. Presently, regenerative thermal oxidizers (RTOs and RCOs) are commonly used for the destruction of VOCs and HAPs. RTOs consume large amounts of natural gas to heat air and moisture. The combustion of natural gas generates increased CO_2 and NO_x , which have negative implications for global warming and air quality.

Other less common methods for removal of VOCs and HAPs include biofilters, activated carbon, silica gel, polymeric beads, or zeolites as adsorbents, and degradation with plasma (or corona), and ultraviolet light (UV). The temperature of the exhaust from wood products facilities can be high enough to inhibit the growth of microbes in biofilters, thus reducing the microbial degradation rate of VOCs. Biofilters are also difficult to operate because mill shutdowns disturb the life cycle of the microbes. Adsorption of VOCs and HAPs onto activated carbon, silica gel, polymeric beads, or zeolites is a non-selective process. Moisture from the gas will also be adsorbed onto these materials, thus lowering the efficiency of the removal of VOCs and HAPs. Moreover, fatty acids and resins will permanently block the adsorption sites for other VOCs and HAPs and make regeneration of the adsorbents difficult. Other techniques, such as degradation of VOCs and HAPs with plasma, corona, or uv are still in development. Any destructive method eliminates the possibility of chemical recovery.

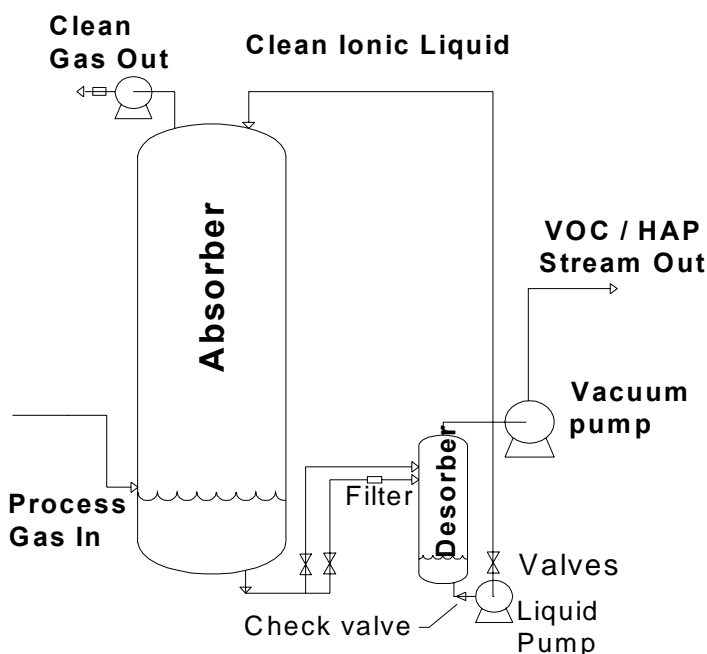
All of the aforementioned challenges are addressed by an absorption system containing a room-temperature ionic liquid (RTIL) as an absorbent. RTILs are salts, but are in liquid states at room temperature. RTILs, an emerging technology, are receiving much attention as replacements for organic solvents in industrial processes with significant cost and environmental benefits. Some of these processes include organic synthesis, extraction, and metal deposition. RTILs would be an excellent absorbents for exhausts from wood products facilities because of their unique properties:

- 1) no measurable vapor pressure, thus no loss of RTILs to the atmosphere. VOCs that are dissolved in the RTILs can be selectively and readily removed under reduced pressure.
- 2) high solubility of wide range of organic compounds. Thus, VOCs such as methanol, formaldehyde, and terpenes can be absorbed in RTILs. Prior work confirms the solubility of various polar and nonpolar organic compounds, such as methanol and formaldehyde, in an RTIL, [1-butyl-3-methylimidazolium][PF_6].

- 3) thermal stability to 200°C (almost 400°F) and high chemical inertness to VOC and HAPs. This means that the RTILs can be used at the temperatures of the exhausts without thermal and chemical degradation and subsequent pollution. The RTILs can be reused many times.
- 4) immiscible with water. Moisture in exhaust will not interfere with the absorption of VOCs and HAPs. Water from moisture condensation can be readily removed through phase separation or under reduced pressure.

A diagram of the proposed system is shown in Figure 1. The contaminated gas enters the bottom of the absorber and passes through the ionic liquid. Contaminates are absorbed into the ionic liquid and the clean gas passes out the top of the absorber. The ionic liquid is continuously taken from the bottom of the absorber, filtered to remove particulate contamination or dust, and then desorbed. The desorber is operated at a vacuum and a high enough temperature to remove the contaminants. This gives a concentrated stream of VOCs leaving the device in the gas phase and a clean ionic liquid that can be recycled to the top of the absorber. The VOC stream could be used for a product or a fuel.

A panel industry-wide savings of 31 billion ft³ per year (3.1×10^{13} BTU/yr) of natural gas would be achieved compared to using RTOs for control (based on Franklin Report to AFPA, Nov. 16, 2001). This is approximately a 60% reduction in natural gas (energy from fossil-based feedstock) compared to RTO control (also estimated from Franklin report). This does not include lumber kilns, if controls were ever to be required on them.. Electrical consumption will be less than an RTO because the pressure drop through the absorber will be 20% that of an RTO and we estimate panel industry-wide savings of 1,000,000 kWh/yr.



The recovered organic compounds would be present in **FIGURE 1. VOC capture device.** a high concentration and the stream would be combustible (but above the fuel). Therefore, energy would be recovered if the captured products are burned, for example, in a boiler. For the panel industry, this

stream would represent approximately 1.1×10^{12} BTUs annually if burned (estimated from mass in EPA AIRS Database for SICs 2493, 2436, and 2435).

Reduced natural gas use would result in savings of \$257,000,000 per year in the panel industry based on the 2001 year gas prices (\$8.29/mft³ for commercial customers - <http://www.eia.doe.gov>). This would cause a significant increase in the competitiveness of the domestic industry. Additional savings would occur in other industry segments, such as lumber (if controls are required due to PSD or BART regional haze rules).

If the products are combusted, energy will be produced which can supply heat for the process. This is 1.1×10^{12} BTU/yr for the panel industry, the equivalent of \$9.1 million of natural gas. If products are recovered from the exhaust, the economic benefits will be greater.

Currently, electrostatic precipitators (ESPs) need to be operated ahead of RTOs to protect the ceramic from particulate and condensibles. This will probably not be necessary with the RTIL absorbent, eliminating a \$1,800,000 piece of equipment and the operating costs associated with it.

All of the over 38,326 tons/yr of VOCs released by the panel industry (EPA AIRS Database) could be controlled if this technology could replace RTOs. HAPs would also be controlled. The proposed technology reduces the panel industry's CO₂ emissions by 4.154 billion pounds per year compared to RTO control. In addition, there are no on-site NO_x emissions due to natural gas combustion. The combination of NO_x and VOC reduction will reduce ambient O₃, important in non attainment areas. The new technology would aid the industry in MACT requirements and states in meeting PSD and regional haze rules.

Background

Room temperature ionic liquids (RTILs) are salts that are liquids at room temperature. RTILs have many unique properties including high thermal stability, high electrical conductivity, and undetectable vapor pressure. Most RTILs are inert to various chemicals. Therefore, it has been demonstrated that RTILs can be used for the following applications: 1) as green solvents or reaction media for various chemical transformations (Blanchard et al. 1999; Branco and Afonso, 2001; Carmichael et al. 1999; Shelton, 2001), 2) as solvents for dissolution of cellulose (Rogers and Seddon, 2003; Swatloaski, 2002), 3) as electrolytes for various applications such as batteries (Kim et al. 2004), 4) as extraction agents for reduction of hazardous pollutants (Huddleston et al. 1998; Blanchard and Brennecke, 2001), and 5) as anti-electrostatic agents (Pernak et al. 2001; Li et al. 2004). Many other new applications of RTILs are being discovered. Parts of this background are taken from Wang (2005).

VOC and HAP Emissions from Wood Composite Industry

Wood-based composites are made from wood bonded together naturally or with synthetic adhesives using heat and pressure. The wood might be in the fibers, or may be larger particles, strands, veneer, or lumber. The nature of the wood raw material and the adhesive essentially determine the differentiated characteristics of the products. Wood-based composites may have more desirable properties than solid wood when processing variables are properly selected. Wood-based composites have become increasingly specialized in recent years and are used in wide ranging applications. At present, plywood, laminated veneer lumber (LVL), hardboard, particleboard, and oriented strand board (OSB) are the major wood-based panel products on the market [Forest Products Laboratory, 1999]. Adhesive bonding of wood components has played an essential role in the development and growth of the forest products industry and has been a key factor in the efficient utilization of our timber resource. However, manufacturing wood products especially results in VOC and HAP emissions.

VOC and HAP emissions have become a global issue due to their significant contribution to the air pollution and global warming. Compared to other chemical process, the amount of VOCs released per unit of wood products may be relatively small, but as a cumulative annual amount, the total VOC emissions are quite significant. According to the U.S. EPA, the total estimated VOCs released for the lumber and wood products industry is 41,423 short tons per year [Beakler, et al., 2005].

VOC emissions from wood processing are thought to be mainly from the extractive compounds in wood, especially in heartwood, and the adhesive and additive in composites. The extractable constituents of heartwood include tannins, resins, fats, waxes, oils and other aromatic compounds [Rice and Zibilske, 1999]. In general, the portion of total extracts in wood varies from 3 to 9 percent for temperate species [Rice and Zibilske, 1999]. Therefore, more VOCs are released during drying and manufacturing softwood species than hardwood species. HAPs, mainly methanol, are formed as the wood is heated during processing.

The adhesive is an important and necessary constituent for bonding wood elements together to form wood-based composite products. The thermosetting adhesives including phenol-formaldehyde (PF), ureaformaldehyde (UF), melamine-formaldehyde (MF), and isocyanate, are mostly used in manufacturing wood-based composite products in industry [Forest Products Laboratory, 1999]. These chemical components in adhesives are the potential sources for VOC and HAP emissions, especially formaldehyde [Beakler et al., 2005; Rice and Zibilske, 1999].

The sources of VOC and HAP emissions at wood product facilities are mainly drying, resin blending, pressing, and finishing [Barry et al., 1999]. However, dryers and presses are the most important sources of emissions because high temperature accelerates the emissions. Emissions are mostly caused by evaporation and thermal degradation. Evaporation plays a major role from ambient to 200 °C as VOCs are given off with the water vapor [Barry et

al., 1999]. Thermal degradation of wood components will contribute greatly to HAP emissions when temperature is increased above 200 °C due to breakdown of the less-thermally-stable hemicelluloses between 200 °C and 280 °C [Barry et al., 1999; McGinnis, 2001]. Formaldehyde will be a significant HAP when UF and PF resins are used and also can occur from the breakdown of wood components.

The actual composition of emissions from wood processing depends on the species of wood and processing conditions. Emissions from hardwood and softwood differ both in the nature and in the quantities of material evolved mainly due to their different extractive components [Rice and Zibilske, 1999]. Hardwoods emit principally degradation products that arise from the thermal breakdown of wood because the extractive content is small. These include VOCs, some of which are designated by the U.S. EPA as HAPs, such as methanol and formaldehyde [Otwell et al., 2000]. Softwoods can release a larger quantity of VOCs, most of which are terpenes and other wood extractives [Banerjee et al., 1998]. Because softwood wood tissue is also subject to thermal breakdown during processing like hardwood, they also emit the same breakdown products as hardwoods [Banerjee et al., 1998].

Research on VOCs from wood processing has mostly centered on softwood species for two primary reasons. First, softwood species comprise over 83 percent of the lumber dried in the United States [McDonald et al., 2002]. Nearly all solid structural lumber products, as well as most engineered wood products (i.e., plywood and other structural composite products), used in construction are derived from softwood species [Forest Products Laboratory, 1999; McDonald et al., 2002]. And second, softwoods generally contain larger amounts of extractive material than hardwoods. Smaller total amount of VOCs and HAPs are likely from hardwood processing.

Processing conditions, such as moisture content, wood particle size, temperature, pressure, storage time of the raw material, types of adhesives and additives also play significant roles in determining the VOC and HAP emissions from the manufacturing of wood-based composite products [Banerjee et al., 1998].

Although the VOC composition changes with both species and drying conditions, methanol and formaldehyde are the two major HAPs emitted from both hardwood and softwood. Among the HAPs emitted, methanol, formaldehyde, acetaldehyde, acrolein, phenol and propionaldehyde are the HAPs of most concern to the EPA [Heinold and Hunt, 2003]. α -pinene and β -pinene are the most notable VOCs released from most softwoods and α -pinene can be oxidized by air to ringed compounds with aldehydes, ketones and hydroxyl groups [Milota et al., 2000; Heinold and Hunt, 2003]. As a result, 25 or 30 compounds in the terpene family might be detected in dryer exhaust [Punsuvon, 1994]. Nonterpene VOCs emitted from wood include acids such as formic, acetic and propionic. Total organic emissions from softwood lumber are 0.25 to 3 pounds per 1,000 board feet and 0.5 to 4 pounds per oven-dry ton are released from dryers [Milota, 2000]. In the late 1990s, the National Council of the Paper Industry for Air and Stream Improvement (NCASI) tested emissions at 29 wood product mills to provide emissions data which could be used by the

industry and EPA in the development of the Maximum Achievable Control Technology (MACT) rule [National Council for Air and Stream Improvement, 1999]. Concentrations measured during this study are listed in Table 1. The major VOCs, methanol, α -pinene and formaldehyde, are all emitted at low concentrations.

Table 1. The concentrations of some VOCs mainly based on emissions from press and dryer [NCASI, 1999].

VOCs&HAPs Products	Methanol (ppm)	α -pinene (ppm)	Formaldehyde (ppm)	THC (ppm)	Temp. (°F)
OSB	2.0-90	7.8-50	2.4-45	130-1200	100-190
Plywood	5.5-21.7	66.6-249	4.4-20.8	1814-5090	290-330
Particleboard	4.5-110	13-15	1.1-43	120-800	140

Regulations for VOC and HAP Emissions from Industry

Environmental concerns arise because VOCs are potential precursors for photochemical formation of ozone, other atmospheric oxidants, and aerosols in troposphere. Some VOCs deplete ozone in the stratosphere and some such as formaldehyde, are known or suspected to have adverse effects on human health [Harley and Cass. 1994]. These factors have resulted in strict regulations by U.S. EPA and State Agencies for VOC and HAP discharges. The wood-based panel industry is facing a new challenge, the further abatement of VOCs and HAPs, and is searching for novel techniques for reducing VOCs and HAPs.

Air pollution concerns have existed since coal was burned as fuel 500 years ago. However, the first air pollution control regulation in the United States, the Air Pollution Control Act, was not developed until 1955 [U.S. EPA, 1999]. This Act required the U.S. Public Health Service to assist communities in reducing the formation of photochemical smog. Clean Air Acts (CAA) in 1963 and 1967 provided for a better understanding through research. The U.S. EPA was created in 1970 by executive order [U.S. EPA, 1999]. A Clean Air Act, also passed in 1970 and amended in 1977, authorized the EPA to establish the National Ambient Air Quality Standards (NAAQS) for seven criteria pollutants including particulate matter, VOCs, sulfur oxides, nitrogen dioxide, carbon monoxide, ozone, and lead. Also, The CAA directed each state to develop a state implementation plan to achieve the NAAQS. The 1990 amendments to the CAA used approaches for reducing pollution that were different from the past legislation in that market-based principles and emission banking and trading were introduced [U.S. EPA, 1999]. Another result of the 1990 CAA are uniform standards that regulate the release of HAPs from many industries. These are known as the Maximum Achievable Control Technology (MACT) regulations [U.S. EPA, 2005]. The MACT rule for the wood industry provides for six compliance options. Add-on control technologies must be used on certain types of dryers and presses at major sources

to reduce total hydrocarbon (THC) emissions by 90 percent, reduce methanol emissions by 90 percent, reduce formaldehyde emissions by 90 percent, limit the concentration of THC in the outlet of the add-on control device to 20 parts per million by volume dry basis (ppmvd), limit the concentration of methanol in the outlet of the add-on control device to 1 ppmvd, or limit the concentration of formaldehyde in the outlet of the add-on control device to 1 ppmvd [Willingham, 2003; Federal Register, 2004]. Technologies capable of treating low concentration gas streams are needed due to these stringent regulations.

Control Technologies for VOC and HAP Emissions

As mentioned previously, RTOs, RCOs, biofiltration and absorption are most commonly used control technologies for VOC and HAP emissions in wood-based panel industry. Both the advantages and disadvantages are discussed below.

RTOs and RCOs

Thermal oxidation (TO), or thermal incineration, is the process of oxidizing combustible materials using a high temperature for sufficient time to convert the pollutants to carbon dioxide and water [Moretti, 2002; Hunter and Oyama, 2000]. Processing conditions such as time, temperature, turbulence (for mixing), and the amount of oxygen significantly affect the rate and efficiency of the combustion process [Moretti, 2002; Forest Products Laboratory, 2005]. Operating temperatures range from 650°C to 1100°C (1200-2000°F) and gas residence times are typically 1 second or less [Moretti, 2002]. Natural gas is used as fuel.

Regenerative thermal oxidation (RTO) units are distinguished from thermal oxidation only by their ability to recover heat at high efficiency. A RTO uses a high-density media such as a ceramic-packed bed which is still hot from a previous cycle to preheat an incoming waste gas stream containing VOCs and HAPs [Moretti, 2002]. Therefore, RTOs generally have lower fuel requirements because of higher energy recovery (up to 95%) compared to TOs.

Regenerative catalytic oxidations (RCOs) operate similarly to RTOs. The primary difference is the use of a catalyst, which has the effect of increasing the oxidation reaction rate, thus allowing the reaction to occur at a lower temperature than is required for thermal ignition [Hunter and Oyama, 2000; Forest Products Laboratory, 2005]. The maximum operating temperature ranges from 540°C to 675°C (1,000-1,250°F) for RCOs. RCOs, therefore, use less energy than RTOs [Moretti, 2002; Hunter and Oyama, 2000]. In general, metal oxides or precious metals, such as platinum and palladium are used as catalysts for VOC or HAP abatement and they have a longer service life and are more resistant to poisoning and fouling than less-expensive base-metal catalysts, such as manganese dioxide [Moretti, 2002].

RTOs and RCOs are proven to be a method for destroying VOC/HAPs, with destruction efficiencies up to 99.9999% [Moretti, 2002]. They can be used to reduce emissions from almost all VOC and HAP sources, including process exhaust vents, storage tanks, treatment, and storage and disposal facilities. However, they are not well-suited to exhaust streams with highly variable flowrates, which cause the combustion chamber temperature to fall and the destruction efficiency to drop [Moretti, 2002; Forest Products Laboratory, 2005].

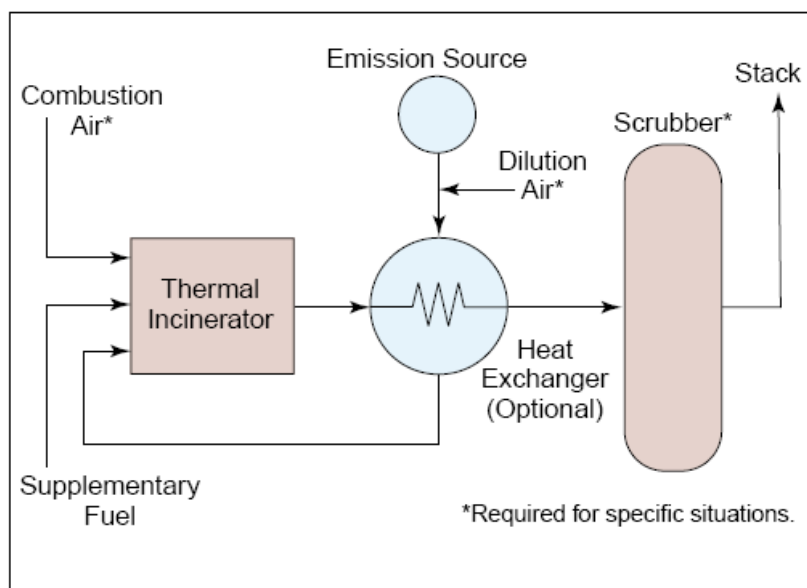


Figure 2. A thermal oxidizer incorporates regenerative energy recovery [Moretti, 2002].

Biofiltration

Biofiltration utilizes microbes to breakdown VOCs and HAPs and thus offers an environmentally attractive alternative to RTOs and RCOs [Pond, 1999]. The key component of a biofiltration system is a bed, made of natural materials such as soil and bark that is maintained at high humidity by continuously supplying water through sprayers [McGinness, 2000]. The moisture level is very important to the proper functioning and efficiency of a biofilter because the degradation processes of VOCs or HAPs are exothermic and tend to dry the filter beds. Typically, the organic pollutants in the waste gas stream dissolve in water and then are converted by microorganisms to water and carbon dioxide in the biolayer. The type of microorganism used depends on the type of VOCs/HAPs treated.

In general, water-soluble, oxygenated compounds with low molecular weight are good candidates for biofiltration. Aldehydes, ketones, alcohols, ethers, esters and organic acids degrade rapidly in biofilters. However, halogenated hydrocarbons and polyaromatic

hydrocarbons do not. For easily degradable compounds, removal efficiencies have been demonstrated to be greater than 90% [Moretti, 2002].

Other less common methods for removal of VOCs and HAPs include adsorption, which employs activated carbon, silica gel, polymeric beads, or zeolites as adsorbents, and degradation with plasma (or corona), and ultraviolet light (UV) [Hunter and Oyama, 2000]. Adsorption of VOCs and HAPs onto activated carbon, silica gel, polymeric beads, or zeolites is a non-selective process. Moisture from the gas will also be adsorbed onto these materials, thus lowering the efficiency of the removal of VOCs and HAPs [Milota and Li, 2001]. Moreover, large molecular compounds such as fatty acids and resins will permanently block the adsorption sites and make regeneration of the adsorbents difficult. Other techniques, such as degradation of VOCs and HAPs with plasma, corona, or UV are still in development.

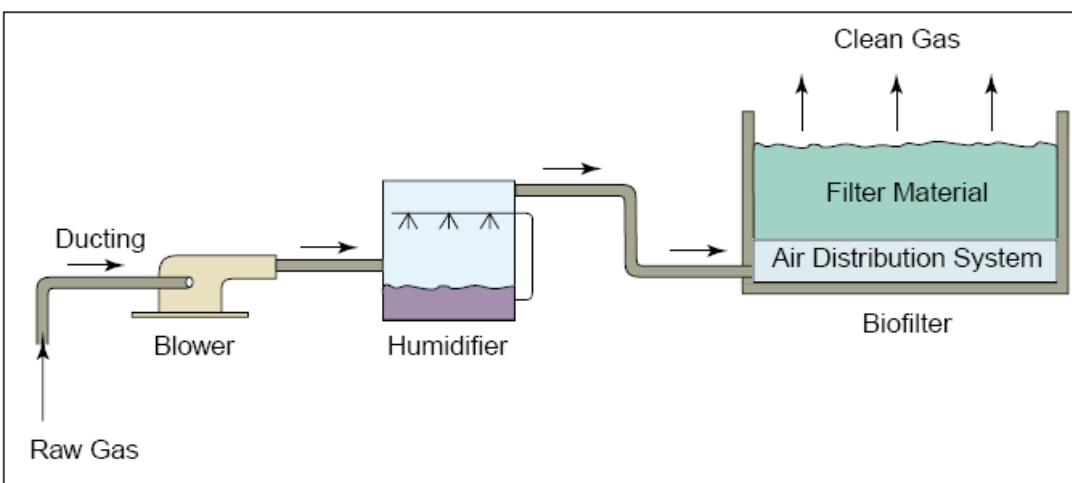


Figure 3. Biofiltration system [Moretti, 2002].

Absorption

Gas absorption or scrubbing is the unit operation in which one or more soluble components of a gas mixture are dissolved in a liquid. The absorption may be a purely physical phenomenon or may involve reaction among the constituents in the liquid solution. The reverse operation, called stripping or desorption, is employed to transfer one or more volatile components from liquid mixture into a gas [Perry et al, 1997]. Absorption systems are often used to separate gaseous streams containing high concentrations of organics, especially water-soluble compounds such as methanol, ethanol, isopropanol, butanol, acetone, and formaldehyde. It is widely used to abate VOC and HAP emissions from industry, especially for natural gas purification [Moretti, 2002; Hunter and Oyama, 2002].

However, several factors limit the use of absorption as the primary control technique for VOCs and HAPs recovery. One factor is the availability of a suitable solvent for the VOCs and HAPs. To date, water and high boiling point mineral oils or other petroleum oil are most common used. Another factor is the availability of vapor/liquid equilibrium data, usually as Henry's Law Constants, for the specific organic/solvent system are necessary for the design of absorber systems. However, they are not readily available for uncommon organic compounds. In addition, the desorption efficiency and disposal of pollutants from absorbents have to be considered to avoid creating a second contaminated stream. In most cases, VOC/HAP is desorbed from the absorbent at elevated temperatures and/or under vacuum so that the scrubbing liquid containing the VOCs and HAPs is regenerated for reuse again. The VOC or HAP is then recovered as a liquid in a condenser.

Issues Associated with Destruction Technologies

Sauer et al. [36] investigated the environmental tradeoffs associated with various emission control technologies currently used in the wood products industry. They concluded that the use of RTOs and RCOs resulted in greater life cycle burdens for energy, solid waste, greenhouse gas, CO, NO_x, SO_x, and other emissions even though VOC and HAP emissions and particulate emissions were reduced efficiently by RTO and RCO destruction technologies. In addition, RTOs and RCOs need high capital costs, high installation costs, high utility operating costs and high maintenance costs, for moving parts and catalysts [McGinness, 2000; FPL, 2005].

Biofiltration creates no green house gases due to the combustion of fuel. It is an environmentally benign technology for VOC and HAP destruction. However, the biofilter bed lifetime is limited to two to five years even though occasional washing of the bed can extend its life in some cases [Moretti, 2002; Sauer et al, 2002]. In addition, the temperature of the exhaust from wood products facilities can be high enough to inhibit the growth of microbes in biofilters, thus reducing the rate at which microbial degradation of the VOCs occurs. Biofilters are also difficult to operate because mill shutdowns disturb the life cycle of the microbes [FPL, 2005; Sauer et al, 2002].

Any destructive treatment, such as RTOs, RCOs, and biofiltration, eliminates the possibility of chemical recovery [McGinness, 2000]. The absorption of VOCs and HAPs into solvents could be a reversible process and permit chemical recovery. Presently, much research is focused on scrubbing of waste gases using selective solvents [Via et al, 1999; Hadjoudj, 2004]. The commonly used absorbents such as high-boiling mineral oils and petrol oils produce VOC emissions at high operating temperature [Hadjoudj et al. 2004]. This limits their use for absorption in industry. Therefore, solvents with negligible vapor pressure, thermal and chemical stability, and high solubility to large range of VOCs are desirable for the absorption technology of the future.

Room Temperature Ionic Liquids

Room temperature ionic liquids (RTILs) are organic salts that are liquids at ambient temperature. In the early 1990s, the first air- and water-stable ionic liquids with hexafluorophosphate and tetrafluoroborate anions were prepared [Forsyth et al., 2004]. In recent years, RTILs have received increased attention. Due to their unique physicochemical properties, RTILs appear to be attractive replacements for traditional organic solvents. RTILs are referred to be "green" designer solvents [Dupont et al., 2000; Rogers and Seddon, 2003; Earle and Seddon, 2000]. Although imidazolium based ILs are the most widely available, pyridinium-, ammonium-, and phosphonium-based ILs are also in use [Del Sesto et al., 2005]

A typical chemical structure of a RTIL is shown in Figure 4. Properties of RTILs such as melting point, viscosity, and absorption capacity of VOCs vary with the chemical structure. For example, the chain length of the alkyl group (R- in Figure 4) will significantly affect the melting point (Holbrey and Seddon 1999). The nature of the anion pair $[PF_6^-]$ also greatly affects the absorption capacity for organic vapors (Liang et al, 2002). Significant changes in properties with small changes in the chemical structure mean that an RTIL can be tailored for a specific purpose, such as VOC and HAP absorption.

Properties and Applications

RTILs offer a variety of physicochemical properties that make them attractive replacements for traditional organic solvents. Some of these properties are common to all ionic liquids. The negligible vapor pressure of RTILs is very desirable in many applications, especially at high temperature. This property is significant when addressing the health and safety concerns associated with many traditional solvents. Negligible vapor pressure means solvent evaporation is eliminated, reducing the need for respiratory protection and exhaust systems. Furthermore, their non-volatility allows RTILs to be used at elevated vacuum and temperature without loss. A range of separation techniques such as distillation and vacuum stripping could be used to recycle used RTILs. These are not possible when using low-boiling organic solvents [Blanchard and Brennecke, 2001].

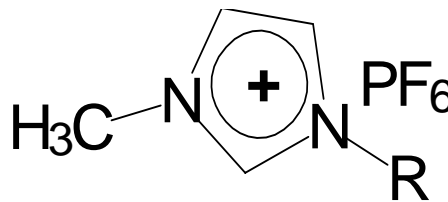


FIGURE 4. Ionic liquid

The ability to dissolve a wide range of organic and inorganic compounds makes RTILs excellent solvents. This is important when dissolving disparate combinations of compounds. Presently, research using RTILs as solvents has been focused on homogeneous catalysts because reactions tend to proceed faster and with more control when they take place in solution [Seddon, 1997; 2001]. RTILs dissolve both the reactants and catalysts, which make reactions more efficient. The easy recycling of catalyst and byproducts is a further benefit.

Generally, RTILs remain as liquids to 300 °C and have high thermal stability. Most traditional solvents will either freeze or boil across such a large temperature range [Milota and Li, 2001]. This wide range of thermal stability allows for tremendous kinetic control of chemical process. Meanwhile, it is also very important for temperature-dependent separation techniques such as extraction and crystallization. For example, a natural product can be extracted into an IL at 150 °C and precipitated by cooling to room temperature [Forsythe et al., 2004].

Another fundamental property of RTILs is ion conductivity, which makes them good electrolytes. RTILs can be used to replace the traditional solvent-based electrolytes, which are prone to corrosion, leakage, volatility, and flammability. Other advantageous properties that RTILs offer over traditional solvents include enhanced enzyme lifetime, improved chemo-selectivity even for heterogeneous reaction, easier catalyst recovery, and recycling as reaction solvents or media [Brennecke and Maginn, 2001; Forsyth et al., 2004].

Based on these unique properties, RTILs still have many other potential applications besides reaction solvents. RTILs can be used as absorbents for gas separations. Many RTILs are hygroscopic and thus can efficiently remove water vapor from a gas stream [Anthony et al., 2001; 2002]. CO₂ has remarkably high solubility in some RTILs [Blanchard and Brennecke, 2001; Anthony et al., 2001]. Therefore, RTILs may be desirable absorbents for VOCs and HAPs. Many RTILs are excellent solvents for a wide variety of both polar and nonpolar compounds [Blanchard and Brennecke, 2001]. This property allows for RTILs potential absorbents for both polar and nonpolar compounds.

RTILs are typically comprised of combinations of bulky organic cations and organic or inorganic anions, invariably possessing a high degree of asymmetry that frustrates packing and thus inhibits crystallization. This explains the fact that RTILs are liquid instead of solid at room temperature as other conventional salts such as sodium chloride [Brennecke and Maginn, 2001]. Generally, anions that form RTILs are weakly basic organic or inorganic compounds that have a diffuse negative charge [Brennecke and Maginn, 2001]. Anions have a strong influence on the viscosity of RTILs, though factors affecting the viscosity are still poorly understood [Brennecke and Maginn, 2001; Brennecke and Maginn, 2001; Anthony et al., 2005]. Also, anions dramatically affect water miscibility. Subtle changes in the nature of the anion, such as a change from the tetrafluoroborate [BF₄⁻] to the hexafluorophosphate anion [PF₆⁻] can significantly change the hydrophilicity. Anion [BF₄⁻] is more hydrophilic than [PF₆⁻] [Anthony et al., 2001].

Both the cations and the substituent groups (R-group) on cations have important effects on the physicochemical properties of RTILs. However, the selection of different anions has a more significant and wide-ranging effect on the properties of RTILs than does a variation in cation and R-group [Forsyth et al., 2004; Anthony et al., 2005]. Generally, cations that produce low melting points are organic species with high asymmetry.

RTILs as "green designer" solvents

RTILs have been described as green designer solvents, where "green" means environmental friendly properties and "designer" indicates that their properties can be adjusted to suit the specific requirements of a particular process [Brennecke and Maginn, 2001; Earle and Seddon, 2000]. Physicochemical properties such as melting point, viscosity, density, hydrophobicity and solvation can be varied at will by simple changes to the structure of cations, R-group, and anions [Earle and Seddon, 2000; Rogers and Seddon, 2002]. Generally, the melting points of RTILs increase with increasing substituent chain length [Fredlake et al., 2002; Tokuda et al., 2005]. Meanwhile, with an increase in the number of carbon atoms in alkyl chain, viscosity initially decreases from methyl- to ethyl- group and then increases with further increase in the alkyl chain length [Tokuda et al., 2005]. In addition, 1-octyl-3-methylimidazolium tetrafluoroborate will accept more water than 1-butyl-3-methylimidazolium hexafluorophosphate because the anion $[\text{BF}_4]^-$ is more hydrophilic [Anthony et al., 2001].

As shown in Figure 5, the various combinations of cations, substituents, and anions promise a wide range of tunable properties for specific applications. To date, numerous attempts including combinations of new anions, cations and substituents have been made to prepare novel RTILs and understand their characteristics.

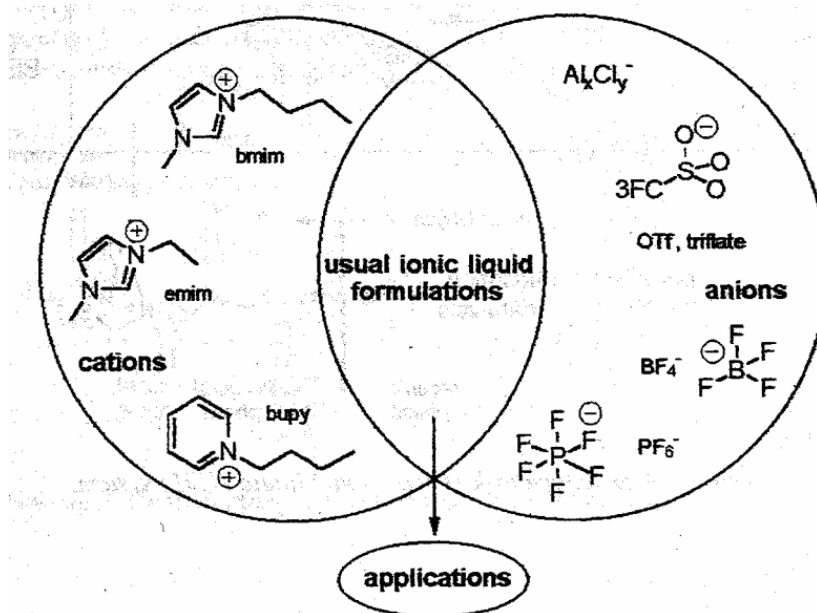


Figure 5. Formulations of a variety of RTILs by different cations, anions, and substituents (Rogers and Seddon, 2002) .

Incorporating a capacity for selective interactions with substrates can create task-specific ILs capable of accomplishing specific tasks. Bates et al. [2002] successfully designed a task-specific IL (TSIL) which could readily and reversibly sequester CO_2 . Moreover, some new TSILs have proven useful in both synthesis and separation applications [Rogers and Seddon, 2002, 2005].

Imidazolium-based RTILs

RTILs based on imidazolium salts with anions such as $[BF_4^-]$ and $[PF_6^-]$ exhibiting a wider range of chemical and electrochemical applications, are a major breakthrough in the chemistry of ionic liquids [Rogers and Seddon, 2002]. Based on the number of R-groups on the cation, imidazolium-based ILs can be categorized into three types including monosubstituted, disubstituted, and trisubstituted imidazoliums. The major structures for these are shown in Figure 6.

Salts based on the 1,3 dialkylimidazolium cation represent the largest group of room temperature ionic liquids currently available because they are easily prepared and synthesized and have attractive properties [Holbey and Seddon, 1999]. Fredlake et al

[2004] investigated the thermophysical properties of 13 imidazolium-based RTILs and provided fundamental understanding for the design of this type of RTIL. The physical and electrochemical properties of air-stable 1,3-dialkyl imidazolium-based RTILs have been extensively studied for their application as reaction media and electrolytes for batteries [Brennecke and Maginn, 2001]. These imidazolium-based RTILs possess several properties such as non-volatility, non-flammability, and high thermal and electrochemical stability, which make them attractive alternatives to traditional volatile solvents and nonaqueous electrolytes. Visser et al. [Rogers and Sedddon, 2002] has studied the characterization of hydrophilic and hydrophobic imidazolium-based RTILs as alternatives to VOCs for liquid-liquid separations, providing detailed knowledge of the solvents' physical properties for RTILs comprised of the 1,3 dialkylimidazolium cation.

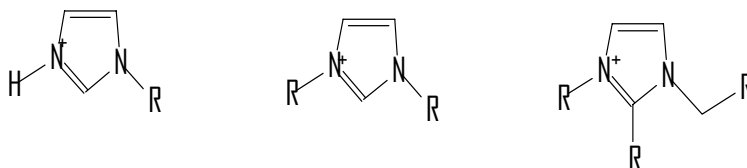


Figure 6. The structures of monosubstituted, disubstituted, and trisubstituted imidazoliums.

Phosphonium-based RTILs

Phosphonium-based RTILs are comprised of tetraalkylphosphonium, $([PR_1R_2R_3R_4]^+)$ as cations and various anions such as cyanide dicyanamide $(N(CN)_2)$ or sulfonate derivatives [Merck, 2005]. The alkyl groups, R_n , generally are large and not all the same as shown in Figure 7.

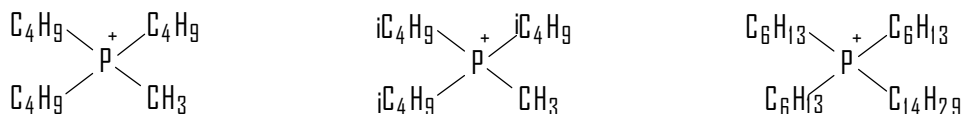


Figure 7. The typical cation structures of phosphonium-based RTILs.

The numerous RTILs that can be synthesized using various R-groups and anions increase the fine tunability of the resulting properties such as their melting point, viscosity and electrochemical properties. The large phosphonium cations can combine with relatively large anions to make viscous but free flowing liquids [Del Sesto et al., 2005]. The phosphoniums lack the weakly acidic ring protons, which are more common in imidazolium cations - a limitation when strongly basic anions are used, therefore, the quaternary phosphonium salts have been reported to be more chemically stable than nitrogen-based cations [Del Sesto et al., 2005].

Although the phosphonium-based RTILs have not received as much attention as the more common imidazolium and other nitrogen-containing RTILs, they have been used extensively in several areas of chemistry for many years, such as catalysis, phase transfer reactions, and extractions [Karodia et al., 1998; Chen et al., 2002]. A number of these phosphonium salts with desired anions were synthesized with nearly all being liquids at and well below room temperature. They are stable up to 400 °C in some cases [Del Sesto et al., 2005].

Recovery of VOCs and HAPs using RTILs as Absorbents

RTILs as absorbents

Due to their unique physiochemical properties, RTILs have the potential to be media in separation technologies. RTILs have been used as solvents for liquid-liquid extraction, gas-liquid extraction, and gas separation [Brennecke and Maginn, 2001; Forsyth et al., 2004; Anthony et al., 2002; Rogers and Seddon, 2002]. There is increased interest in using ionic liquids to replace volatile organic solvents for gas separations.

Scovazzo et al. [Rogers and Seddon, 2002] successfully separated CO₂ from N₂ using RTIL B_{mim}PF₆. Anthony et al. [Anthony et al., 2002] reported the solubility of carbon dioxide, ethylene, ethane and methane in B_{mim}PF₆ and concluded that CO₂ was quite soluble in B_{mim}PF₆ followed by ethylene, ethane, and methane. This study is very important in evaluating RTILs as media for reactions involving gases. Baltus et al. [2004] obtained the Henry's constants of CO₂ in nine different ionic liquids which help in understanding the role of chemical structure on the separation capabilities of RTILs. CO₂ has notably greater solubility in the ionic liquid having the fluorine-substituted anion as compared to the corresponding ionic liquid with a nonfluorinated anion.

Crosthwaite et al. [2004] studied the liquid phase behavior of imidazolium-based ionic liquids with alcohols and concluded that the effect of alkyl chain length on the cation and the choice of anion have significant effects on the solubilities of alcohols due to the coulombic and van der Waals interaction between the RTILs and alcohols. B_{mim}BF₄ is completely miscible with methanol and ethanenitrile [Crosthwaite et al., 2004]. With regard to the waste gases from wood composite industry, methanol is an important pollutant. Therefore, these studies about the relationships between RTILs and alcohol indicated that RTILs might be good absorbents to VOCs and HAPs.

Effect of water

Although water is stable, some RTILs are hygroscopic, so the uptake of water vapor in RTILs is an important concern [Anthony et al., 2001]. The presence of water may significantly change the properties of RTILs such as viscosity, density, and ion conductivity. Seddon et al. [2000] pointed that the anion has a greater effect on water miscibility compared to the alkyl chain length on the cation.

Exhaust gases from the wood dryers and presses normally have a high moisture content. Water can be present in RTILs due to ineffective drying or due to absorption from the ambient air. The presence of water in RTILs is a concern because it may alter their ability to absorb VOCs and HAPs.

Recycling of used RTILs

An RTIL used for adsorption system must be recycled or a contaminated liquid stream is created. RTILs have no measurable vapor pressure, which allows for the separation between RTILs and contaminants using distillation and vacuum with negligible loss [Anthony et al., 2001]. Ionic liquid/organic mixtures can be separated by application of CO₂ at pressures that induce a phase split, thereby providing a means of recovering the ionic liquid from mixtures used in an extraction process [Blanchard and Brennecke, 2001]. Bates et al. desorbed CO₂ from RTIL upon heating 80-100 °C for several hours under vacuum [Bates et al., 2002].

Solid phase Microextraction and Gas Chromatography

Solid Phase Microextraction (SPME) is an innovative technology that allows solventless sampling of volatiles and semivolatiles from a wide variety of matrices. It has been used to measure drugs and their metabolites in body fluids, volatile organic compounds in liquids, and explosive residues from solid samples [Vu et al., 2000]. The tool for SPME is a fiber coated with a liquid (polymer), a solid (sorbent), or a combination of both. The fiber coating removes the compounds from a sample by absorption in the case of liquid coatings or adsorption in the case of solid coatings. Compared to conventional sample preparation techniques, SPME provides fast, easy to use, and inexpensive sampling, and eliminates the use of organic solvents [Rocha et al., 2001]. The first application of SPME was to evaluate pollutants in water [Rocha et al., 2001]. To date, SPME has been successfully applied in numerous environmental, food, flavor, pheromone, pharmaceutical, clinical and forensic applications, and especially for quick screening of the volatile composition of a various range of products. Koziel et al. [2000] pointed out that SPME is the fastest extraction technique for air sampling at typical airborne VOC concentrations. Presently, the poly(dimethylsiloxane) (PDMS) coating is one of the most widely used coatings for extracting volatile analytes from environmental samples via absorption [Koziel et al., 2000]. The sensitivity of solid (or mixed-phase) SPME coatings, such as divinylbenzene

(PDMS/DVB) and Carboxen/PDMS, are much higher compared to PDMS for extracting VOCs.

SPME can be used in conjunction with gas chromatography (GC) as an innovative analytical method. The analytes are extracted from a variety of matrixes by partitioning them from a liquid or gas sample onto a stationary SPME adsorbent. The extracted analytes can be thermally desorbed in the injector of the GC and subsequently swept onto the column where they are separated [Sostaric et al., 2000]. The technique has been successfully used for the analysis of a wide range of volatile and semivolative components, where the traditional sample preparation methods, such as steam distillation and direct solvent extraction, are time-consuming and difficult to operate.

Sostaric et al. [2000] found the SPME-GC technique to be suitable for analyzing the volatile components that exist in vanilla extracts and flavorings. Spinhirne et al. [2004] analyzed the VOCs in bovine breath using the SPME-GC method, and showed it to be a useful diagnostic tool for animals and humans. The concentrations of some VOCs such as acetic acid and formaldehyde from particleboard, medium density fibreboard (MDF), and engineered wood also have been studied. Lattuati-Derieux et al. [Lattuati-Derieux et al., 2004] investigated the VOCs from paper materials by the SPME-GC technique and he concluded that SPME was a non-destructive, non-contact method, which seemed especially suitable for investigating volatile compounds emitted.

Henry's Law Constant

Chemical transfer of the environmental contaminants plays a key role in the control and reduction of contaminants. The solubility of a gas in an aqueous phase depends on temperature, the partial pressure of the gas over the liquid, the properties of the liquid and of the gas. The gas-liquid partitioning equilibrium constant, better known as the Henry's constant (K or H) is a crucial parameter in order to determine the solubility of chemicals into aqueous phase [Perry et al, 1997]. There are several ways of describing the Henry's law constant. Usually, it is defined as:

$$K_H = P_g / C'_L \quad (\text{atm} \cdot \text{L} / \text{mol}) \quad (1)$$

or

$$H = C_g / C_L \quad (\text{dimensionless}) \quad (2)$$

where

- P_g = partial pressure
- C'_L = concentration of contaminant in liquid (mole/L)
- C_g = concentration of contaminant in gas (mole/mole)
- C_L = concentration of contaminant in liquid (mole/mole)

Based on expressions (1) and (2), Henry's constant is inversely proportional to gas solubility, which means a high value of H corresponds to the low gas solubility into the liquid phase. Therefore, the solubility of contaminants into each RTIL can be determined by measuring the Henry's constants.

The laws of thermodynamics (Van't Hoff equation) predict that Henry's law constant varies with temperature and pressure. At a constant pressure, the temperature dependence of Henry's law constant can be expressed as equation 3 [Robbins et al., 1993]

$$H_i = \exp (B_{Hi}/T - A_{Hi}) \quad (3)$$

where T is the absolute temperature (K) and B and A are constants depending on the nature of solvent-solute combination. Over a narrow temperature range in which the heat of vaporization of the solute from solvent remains constant, there is a linear relationship between the natural logarithm of the Henry's law constant for a given compound and the reciprocal of the absolute temperature [Robbins et al., 1993].

Project Objectives

The objectives of this project were to:

- Synthesize RTILs and optimize their chemical structures for a VOC/HAP absorption process.

- Evaluate of the solubility and removal of VOC compounds in the synthesized RTILs and determine other chemical and physical properties important for absorption.

- Construct a continuous prototype absorption system using the RTIL most suited for VOC removal.

- Using the prototype, determine the ability of the RTIL to clean exhaust during long-term trials on wood dryer and press exhaust.

Experimental Approach

The project was approached in three phases. In phase one, 12 ionic liquids were evaluated for suitability as absorbants. In the second phase, one RTIL was selected for further study and a continuous, portable prototype absorption system was designed and constructed. Clean air contaminated with methanol and α -pinene and gas from a lumber kiln were used to test the system. An industrial source was also tested. In the third phase, a larger continuous absorption system was constructed, tested in the lab, and then tested on a veneer dryer and a particleboard press over a period of four weeks to determine the operating efficiency and the potential for problems related to longer-term operation.

Phase one, Selecting ionic liquids

Start up was problematic because of personnel. We brought one (of the two proposed) students on board within a few months of project initiation. While this individual had excellent credentials, there were numerous problems that resulted in dismissal. We had difficulty locating a second student. The second student did not come on board for over a year after the project started. It became clear that we would not accomplish the project objectives with students. In July of 2004, we hired a research assistant to work half-time on the absorption project. This accelerated the project considerable. A second half-time research assistant was hired to do organic synthesis. With the addition of these two non-student employees, we acquired the necessary skills to accomplish the project objectives in a more timely fashion. Nevertheless, these start up problem set us behind our proposed timeline.

Measuring Techniques

Gas concentration: A method was needed to measure concentrations in the gas phase. We initially worked with solid phase micro extraction (SPME) and gas chromatography (GC) to measure concentrations in the gas phase. Early in the project we determined that the results were very inconsistent and that our current GC was not suitable for the task. It was quite old and we replaced it. This was an additional set back.

Eventually, the SPME method was abandoned in favor of direct gas injection. The SPME was too sensitive for our needs and difficult to calibrate when multiple chemicals were in the gas stream and samples were taken at higher temperature.

Liquid concentration: It was not practical to inject ionic liquid into the GC to measure liquid concentrations. The high boiling points of the ionic liquids causes them to not evaporate in the GC injector. Thus we used headspace analysis to determine liquid concentrations in the ionic liquids tested. Standards were made by mixing known amounts of methanol or alpha pinene into ionic liquid. The method developed then consisted of putting ionic liquid into a 10 mL vial, sealing with a septa top, rotating for several hours, and placing the

vial in a heating block at 60°C. After the gas and liquid phases were allowed to come to equilibrium in the heating block for several hours, a 2-mL gas sample was removed with a heated syringe and injected into the GC. The peak areas for samples with unknown concentrations were compared to the peak areas for the standards to determine the concentration in the liquid.

Sample Gas Generation

A method was developed for making gas mixtures of known concentrations to serve as standards for gas chromatography and to place in contact with the ionic liquids to determine equilibrium coefficients. In the first attempt at this, we first generated mixtures at various concentrations by first creating a large, relatively concentrated sample that could be made by liquid mass and gas volume. Large (100 to 200L) Tedlar® bags were used for this and an extra GC injector port was modified to vaporize the liquids as they were injected into the bag. These were then diluted by mixing to make samples at lower concentrations. This approach did not work because the SPME was highly sensitive to unwanted contaminants in the Tedlar® bags. Even new, clean, bags filled with clean air gave numerous peaks on the GC. We therefore abandoned this approach.

Instead we developed a gas mixing system capable of continuously generating a continuous supply of gas with known concentrations of the desired contaminants (Figure 8). The system used permeation tubes to provide gas with known impurities. The permeation tubes emit the impurities at a known rate at a certain temperature and we controlled the airflow rate to make the desired concentration. We used the permeation tubes for methanol. An old GC oven was used for temperature control. To add α -pinene to air, a series of four midjet impingers containing α -pinene were set up and gas was bubbled through the midjet impinger. The impingers were held at a predetermined temperature. When the gas exited the impingers it was saturated with α -pinene at the impinger temperature in a water bath. This was then mixed with the gas containing methanol to obtain a gas with two components. Humid gas was generated by adding a third stream to the mixture. Impingers were also used in this stream, except they contained water. Average concentrations in the gas could be verified based on the weight loss of the permeation tube or impingers over an extended time period. Transfer lines were heated to prevent condensation.

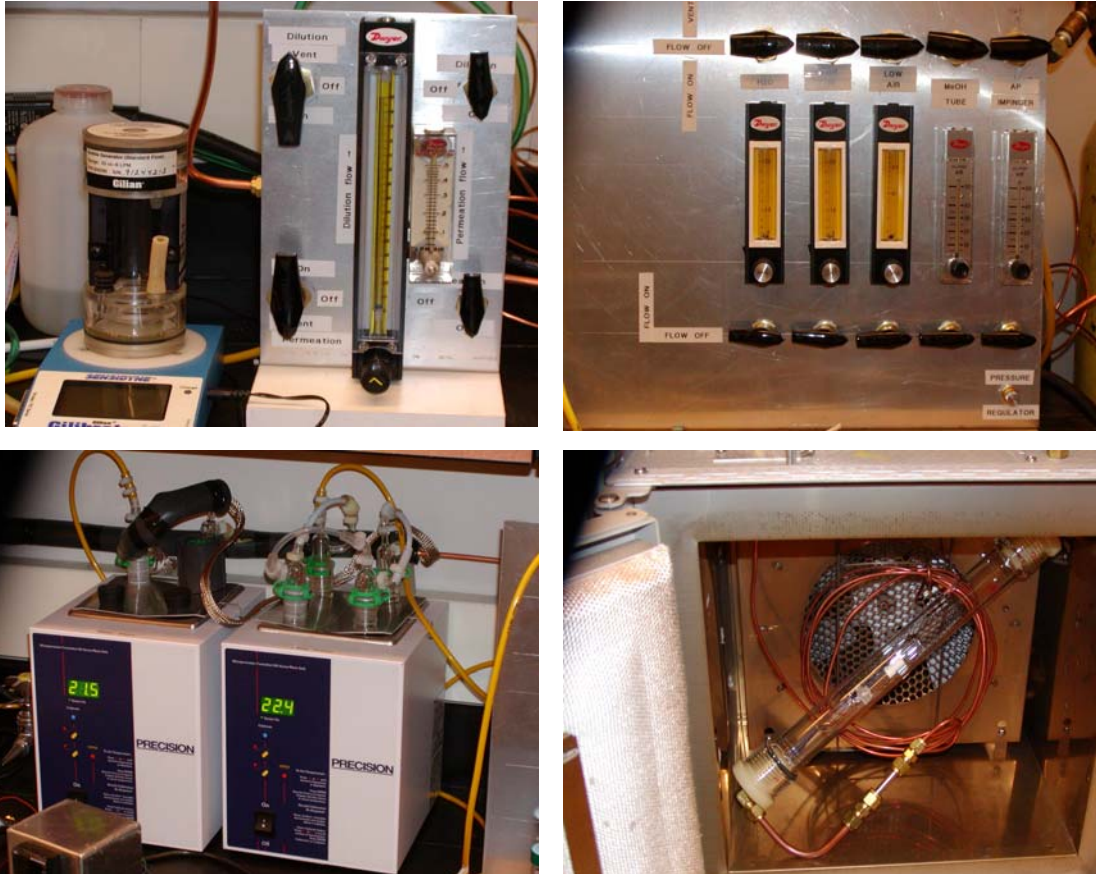


Figure 8. Gas mixing device. Permeation tube in temperature-controlled oven (lower right). Impingers in water bath (lower left). Panel for controlling gas flows (upper right). Panel for dilution gas (upper left).

Henry's Law for the Ionic Liquids

Methanol was selected to represent a low molecular weight, polar compound. It is a common HAP in many wood dryer and press exhaust streams. α -pinene was selected to represent a higher molecular weight, nonpolar compound. α -pinene and similar compounds occur naturally in many species, especially the pines. Methanol and α -pinene were purchased from Aldrich (Milwaukee, WI). Imidazolium-based RTILs [OMIN][PF₆], [HMIN][PF₆], [BMIN][PF₆], and [BMIN][BF₄] (Table 2) were purchased from Solvent Innovation GmbH (Köln, Germany). The phosphonium-based RTILs (Table 2) were synthesized in our laboratory except samples of TTPP, TTPC, and TBPT were obtained from Cytec, Inc (West Patterson, NJ).

Table 2. Names, abbreviations, and properties of ionic liquids tested.

Ionic Liquid	Abbreviation	MW	Density at 20°C
		g/mol	g/mL
1-butyl-3-methyl-imidazolium hexafluorophosphate	BMIM-PF ₆	284.2	1.38
1-hexyl-3-methyl-imidazolium hexafluorophosphate	HMIM-PF ₆	312.4	1.28
1-octyl-3-methyl-imidazolium hexafluorophosphate	OMIM-PF ₆	340.3	1.25
1-butyl-3-methyl-imidazolium tetrafluoroborate	BMIM-BF ₄	226.0	1.20
Tetradecyl(trihexyl)phosphonium bis 2,4,4 trimethylpentyl phosphinate	TTPP	733.3	0.89
Trihexyltetradecylphosphonium sulfate	THPSO ₄	602.6	0.95
Tetrabutylphosphonium dodecylbenzenesulfonate	TPD	584.9	0.98
Tributyltetradecylphosphonium dodecylbenzenesulfonate	TBPD	725.2	0.95
Trihexyltetradecylphosphonium dodecylbenzenesulfonate	THPD	809.3	0.93
Tetradecyl(trihexyl)phosphonium dicyanamide	TTPC	549.9	0.89
Hexadecyltributylphosphonium dicyanamide	HDPC	494.8	0.93
Triisobutyl(methyl)phosphonium tosylate	TBPT	388.5	0.89

Two techniques were used to determine the Henry's Law constant for methanol and α -pinene in the ionic liquid. In one technique a gas containing contaminants was bubbled through the ionic liquid. In the other technique an ionic liquid containing contaminants was brought into equilibrium with clean air.

Impinger technique for determination of Henry's Law constants: A gas with known concentrations of solutes in air was made using the gas generation equipment described above. The desired solute concentrations in the final mixed gas stream were achieved by adjusting the air flow rates of each air stream (air containing methanol, α -pinene, or water) and the temperatures. Concentrations in the gas phase were verified based on the weights of methanol and α -pinene evaporated.

The air with methanol, α -pinene, water, or a combination as solutes was bubbled at a rate of approximately 100 mL/min through 25 mL of RTIL in a midjet impinger. The air was preheated to 30°C and the impinger was immersed in an oil bath maintained at 30°C. The inlet gas concentrations were 80 and 300 ppmv for methanol and α -pinene, respectively.

The mixed gas was bubbled through the RTIL for at least 24 hours. Prior experiments determined this time was sufficient for equilibrium to be reached. The long time was not due to slow kinetics. The low concentration in the gas and the high capacity of the RTIL to absorb resulted in nearly 100% of the solutes in the gas transferring to the liquid during the first few hours. After equilibrium was reached, four 2-mL liquid samples were placed in 4-

mL vials, thermally equilibrated to 30°C. After eight hours the concentration of solutes in the RTILs were measured by headspace analysis. A solid phase microextraction (SPME) fiber coated with 75 μm carboxenTM-polydimethylsiloxane (Supelco, P325408) was exposed to the vial headspace for 20 minutes, then immediately desorbed in the GC injector port. The liquid phase concentrations were determined by comparing the GC peak areas for methanol and α -pinene to those from gravimetrically-prepared standards handled in an identical manner.

Vial technique for determination of Henry's Law constants: Liquid solutes were mixed with the RTILs and the headspace gas was allowed to come to equilibrium. Methanol or α -pinene was mixed gravimetrically with 0.8 mL of RTIL in 4-mL vials and capped with septa. Vials containing both methanol and α -pinene were also prepared as were vials containing 20,000 ppmw (2% by weight) water plus the solutes. The solute concentrations in the liquid phase (Table 3) and were chosen so that the concentrations in the gas phase would be similar for all experiments after equilibration at 30, 60, or 90°C. This was done to minimize variability in the analytical technique. The resulting methanol concentrations in the gas phase ranged from 35 to 330 ppmv and α -pinene from 70 to 700 ppmv. For most samples the gas phase concentrations were between 60 to 120 ppmv and 150 to 300 ppmv for methanol and α -pinene, respectively. A minimum of three replicates were done for each condition with six replicates for some samples.

The vials were rotated at eight rpm for a minimum of eight hours in a test tube shaker to assure complete mixing, then placed for a minimum of eight hours in a temperature-controlled aluminum sample block. This period was deemed adequate based on preliminary work. The block was controlled to 30, 60, or 90°C, the range of expected temperatures for exhaust at wood products facilities.

Table 3. Approximate concentrations for methanol and α -pinene mixed into ionic liquids for experiments at each temperature. Values are ppm by weight.

Ionic Liquid	Methanol			α -pinene		
	30°C	60°C	90°C	30°C	60°C	90°C
TTPP	3500	900	400	14350	3500	1780
THPSO ₄	370	98	25	5975	1600	350
TPD	147	38	11	3600	940	400
TBPD	300	75	30	7500	1875	750
THPD	167	42	17	11250	2813	125
TTPC	97	29	8	3750	1125	375
HDPC	260	54	9	6000	1181	275
TBPT	183	27	12	2250	643	225

The gas phase concentrations of the solutes in the vial headspace were determined by gas chromatography with a flame ionization detector (GC-FID). A 1 mL gas-tight syringe was stored at 33 kPa absolute pressure and 60°C to remove contamination. It was used to draw a 0.2 mL gas sample from the vial headspace and inject it into the GC. The GC responses to the methanol and α -pinene in the gas injection were converted to concentrations using response factors obtained by injecting 1 μ L of dichloromethane containing 4, 40, or 400 mg/L of methanol and α -pinene. Solution injections were made daily to check for drift in the response factors. The GC was operated with a 60 m long, 0.53 mm inside diameter, type 624 fused silica capillary column. The carrier gas was helium at 40 cm/sec. The oven temperature ramped from 45°C to 200°C over 10 minutes. The injection port was held at 200°C and contained a 2mm inside diameter glass liner. The FID was held at 250°C and used hydrogen at 47ml/min, air at 400ml/min, and makeup helium at 25ml/min.

Because some solute leaves the liquid phase during equilibration, the concentrations of methanol and α -pinene in the liquid phase after the vials reached equilibrium were recalculated based on the as-mixed concentration, measured headspace concentration, and headspace volume.

Determining Henry's Law Constant: Henry's constants [H , ($\text{mol}_{\text{solute}}/\text{mol}_{\text{gas}}$) / ($\text{mol}_{\text{solute}}/\text{mol}_{\text{liquid}}$)] were calculated as

$$H = \frac{C_v}{C_L}$$

where C_v ($\text{mol}_{\text{solute}}/\text{mol}_{\text{gas}}$) and C_L ($\text{mol}_{\text{solute}}/\text{mol}_{\text{liquid}}$) are the mole fractions of solute in gas and liquid phases, respectively.

For each RTIL, the dependence of Henry's Law constant on temperature (T , K) was expressed as

$$H = e^{(A / T + B)}$$

where A and B are constants. The constants were determined by linear regression of $\ln(H)$ versus $1/T$ for each solute-solvent combination.

The effect of the presence of other solutes, α -pinene and water for methanol and methanol and water for α -pinene, on Henry's Law constant was evaluated using an analysis of variance with temperature as a covariate and a Tukey multiple comparison test at the $\alpha=0.05$ level (SAS Institute, 1988).

Henry's Law constants can be calculated from physicochemical data; however, the properties of the RTILs are not well defined. They are measured by several techniques and considerable differences can arise due to the technique (Rathbun 1998), especially at low values of Henry's Law constant. Batch stripping requires control of the incoming air in addition to the gas and liquid. Being a dynamic technique it is more subject to error (Dewulf et al. 1999) than static techniques. Henry's Law constant is often measured using a variable volume technique (Poddar and Sirkar 1996). The solvent containing solute is pipetted in different amounts into two vials. After equilibrium, gas samples from the vials' headspaces are injected into a chromatograph. The method is convenient because the Henry's Law constant can be determined from the peak areas and gas to liquid ratios without knowing the actual headspace concentrations (no gas chromatograph calibration). We were unable to use this technique, however, because the Henry's Law constants for the RTILs were very low. Thus, the liquid phase contained a large amount of solute and its concentration remains essentially unchanged during equilibration in the vial regardless of the volume of liquid pipetted into the vial. Dewulf (1999) presents a similar technique, equilibrium partitioning in closed systems (EPICS) combined with solid phase micro extraction, which applies to Henry's Law constants as low as $0.3 \text{ (mol}_{\text{solute}}/\text{mol}_{\text{gas}})/(\text{mol}_{\text{solute}}/\text{mol}_{\text{liquid}})$ however, our data were still an order of magnitude lower than this.

The direct approach to Henry's Law constants, used for most of this work, is measurement of the concentrations in the gas and liquid phases. We compared data from our technique to data presented by Poddar and Sirkar (1996) for methanol in Paratherm™ (Dow Chemical). Paratherm is similar to a mineral oil. Replicating the variable volume technique we obtained a value for Henry's Law constant within 10% of that published by Poddar and Sirkar. By a direct calculation technique on the same data, our values were 80% higher than published. This prompted further verification of the technique.

The syringe injection technique was tested using known concentrations of methanol and α -pinene in air (generated as described for impinger method) sampled directly from the gas generation apparatus (not from a vial). The minimum gas phase concentration was 97% of what was expected based on a gravimetric calculation. A concern with the vial technique is adsorption of solute onto the glass vial. We added gas of known concentration to empty vials. The measured gas concentrations were approximately 85% of what would have been expected with no adsorption onto the glass. The moles adsorbed, however, are a very small fraction of what is contained in the vial during experiments with liquid present. In the 3-phase system (glass, gas, and RTIL) the solute in the gas and RTIL still remain in equilibrium according to Henry's law and there is ample solute in the liquid so that adsorption onto the glass has less than a 0.5% effect on Henry's Law constants.

We also compared the values obtained from the vial technique to the impinger technique for two RTILs, TTPC and TBPT. The values obtained from the vial technique were 97% and 119% of the values obtained by the impinger technique for methanol and 123% and 49% for α -pinene, respectively. While the two techniques may differ somewhat, we considered these differences acceptable. Based on all the evidence we concluded that

there is not a large systematic error associated with the vial technique and it should produce reliable values for Henry's Law constants. The vial technique is advantageous because many samples can be equilibrated simultaneously, compared to one sample per day using the impinger technique. It also eliminates the need to generate large quantities of gas with known concentrations of solutes.

Henry's Law Constant for imidazolium-based RTILs: [OMIN][PF₆], [HMIN][PF₆], [BMIN][PF₆], and [BMIN][BF₄] were selected to study the effect of the length of the alkyl chain on the cation on Henry's constant. Henry's Law constants for the imidazolium-based RTILs at 30°C (Table 4) decreased as the length of the alkyl group increased. The values were very low, especially for α -pinene, indicating a preference for the liquid phase and suggesting that this class of RTILs would probably work well as an absorbent.

However, we obtained very limited data for the imidazolium-based RTILs because the anions appeared to be unstable under the experimental conditions. The presence of water may have contributed to the instability. After heating to 90°C under a vacuum (to remove the solutes) we observed a strong pungent odor and deterioration of glassware making us suspect the formation of hydrofluoric acid. Given these problems, we decided the imidazolium-based RTILs we selected were not suitable as absorbents for pollutants from the humid exhaust at wood products facilities and work with this class of RTILs was abandoned. All further work was done with phosphonium-based RTILs.

Table 4. Henry's Law constants obtained by the impinger technique for the imidazolium-based and the vial technique for phosphonium-based ionic liquids. Values are a ratio of the mole fraction in the gas to mol fraction in the liquid phase for methanol or α -pinene in dry ionic liquid.

Ionic Liquid	Methanol			α -pinene		
	30°C	60°C	90°C	30°C	60°C	90°C
BMIM-PF ₆	0.62	-	-	0.002	-	-
HMIM-PF ₆	0.01	-	-	0.001	-	-
OMIM-PF ₆	0.007	-	-	0.0004	-	-
TTPP	0.001	0.008	0.036	0.004	0.020	0.067
THPSO ₄	0.007	0.019	0.081	0.005	0.020	0.041
TPD	0.017	0.052	0.191	0.006	0.021	0.084
TBPD	0.020	0.061	0.193	0.006	0.029	0.071
THPD	0.020	0.046	0.211	0.008	0.031	0.087
TTPC	0.022	0.053	0.238	0.009	0.026	0.118
HDPC	0.024	0.070	0.236	0.013	0.038	0.128
TBPT	0.026	0.086	0.417	0.036	0.092	0.110

Henry's Law Constant for Phosphonium-based RTILs: Henry's Law constants for the phosphonium-based RTILs at 30, 60 and 90°C are shown in Table 4. These average values are each based on three or more replicates. The standard error averaged 9%, though was greater than 25% in four cases. The constants are a strong function of temperature.

Based on the analysis of covariance, which allows data taken at the three temperatures to be combined, TTPP had a statistically lower value for Henry's Law constant for methanol than the other phosphonium-based RTILs. It also had a low value for α -pinene, although this was not statistically unique. This indicates a preference for the liquid phase and suggests that TTPP may be best for an absorption application from a partitioning standpoint. However, TTPP has a high viscosity and may demonstrate poor kinetics. TBPT had a statistically higher value for Henry's Law constant for methanol than for the other phosphonium-based RTILs and a high value for α -pinene. Thus, it may be the poorest candidate for an absorption process. Each of these, TTPP and TBPT, has a unique anion compared to the other RTILs, bis 2,4,4 trimethylpentyl phosphinate for TTPP and tosylate for TBPT. This may contribute to the differences. The differences in Henry's Law constants among the other RTILs were not statistically significant. This might be expected because there are some similarities in the chemical structures. Five of the RTILs share either the dodecylbenzenesulfonate or dicyanamide anion. The larger cation on

THPD compared to TBPD did not affect solubility as was seen with the imidazolium-based RTILs.

Plots of $\ln(H)$ versus the inverse of temperature (Figure 9) reinforce the differences discussed above. In addition, a slope of greater magnitude indicates a greater dependence of Henry's Law constant on temperature. Thus, if a desorber was operated at a higher temperature in combination with an absorber operated at a lower temperature, TTPP, with a large slope, might be a good choice for methanol while TBPT might be a poor choice for α -pinene.

Figure 10 shows the effect of the presence of other compounds on the Henry's law constant at 60°C. The values are plotted from an equation for each data set similar to those represented in Figure 9. The analysis of covariance indicated that presence of α -pinene and water had no statistically significant effect ($\alpha=0.05$) on the Henry's Law constants for methanol except for TTPC (Figure 10, top). This 60% increase cannot be attributed to either the presence of water or α -pinene because vials with TTPC and methanol combined with either water or α -pinene, did not exhibit this behavior (data not shown). We did eight three-solute tests and twelve two-solutes tests. To have one of the 20 tests show significance at the $\alpha=0.05$ level does not allow a general conclusion that the effect of water and α -pinene on the Henry's Law Constants for methanol may affect the operation of an absorber.

The effect of other solutes on the Henry's Law constants for α -pinene was less clear. Significant differences were noted for TTPP, TTPC, and THPD; however, the differences were generally less than 15% except for TBPT with a 30% increase (Figure 2). The presence of methanol alone (data not shown) had no effect, probably due to the much lower concentration. The presence of water alone had no effect on the Henry's Law constant for α -pinene (data not shown). Thus, we conclude that the co-solutes did not affect the Henry's Law constant for α -pinene to an extent that would affect the operation of an absorber.

Compared to published values for the Henry's Law constants in other liquids, the values for methanol are low. For example at 30°C, methanol in Paratherm has a Henry's Law constant of 0.8 at 30°C (Poddar and Sirkar 1996) and in silicone oil of 4.7, whereas the highest value for methanol in any of the RTILs is 0.026. Values are not available for α -pinene to which the data can be compared. Averaged over all the phosphonium-based RTILs, the values for α -pinene were 95% of the values for methanol at 60°C and 62% at 90°C.

Henry's Law constant indicates how well a gas stream could be cleaned in an absorber. 100% of the contaminants could, in theory, be cleaned from a gas stream with uncontaminated RTIL. The maximum achievable control technology (MACT) regulations (Federal Register, 2003) for plywood and panel facilities in the wood products industry require a 90% reduction in methanol emissions (or less than 1 ppmv) or a 90% reduction in total VOC emissions (or less than 20 ppmv).

A facility with uncontrolled methanol emissions of 60 ppmv would need to clean to less than 6 ppmv. For Henry's Law constant of 0.06, 6 ppmv in the gas stream would be in equilibrium with $1 \times 10^{-4} \text{ mol}_{\text{solute}}/\text{mol}_{\text{liquid}}$ and an RTIL would need to be cleaned to less than this value to be recycled. For methanol in an RTIL with a formula weight of 400, this is 8 ppmw in the liquid phase, a level easily obtained by cleaning at 90°C and 8 kPa for 60 minutes on a rotary evaporator.

The α -pinene was more difficult to remove from the liquid. With a Henry's Law constant of 0.03, 20 ppmv of α -pinene in the gas stream would be in equilibrium with $6.7 \times 10^{-4} \text{ mol}_{\text{solute}}/\text{mol}_{\text{liquid}}$. For an RTIL with a formula weight of 400, this is 225 ppmw, a level obtained by cleaning at 120°C and 4 kPa for 60 minutes in a rotary evaporator. Considerably more effort is required to remove the α -pinene and recycle the RTIL.

Table 5. A and B, the constants in equation 2, for methanol or α -pinene in the phosphonium-based ionic liquids shown.

Ionic Liquid	Methanol		α -pinene	
	A	B/1000	A	B/1000
TTPP	-6.19	13.76	-5.07	11.27
THPSO ₄	-4.56	9.84	-4.68	10.26
TPD	-4.38	10.30	-4.34	9.52
TBPD	-4.19	9.84	-4.45	9.70
THPD	-4.23	9.80	-4.04	8.09
TTPC	-4.24	9.92	-4.63	10.41
HDPC	-4.14	9.86	-4.17	10.26
TBPT	-4.96	12.60	-2.24	4.11

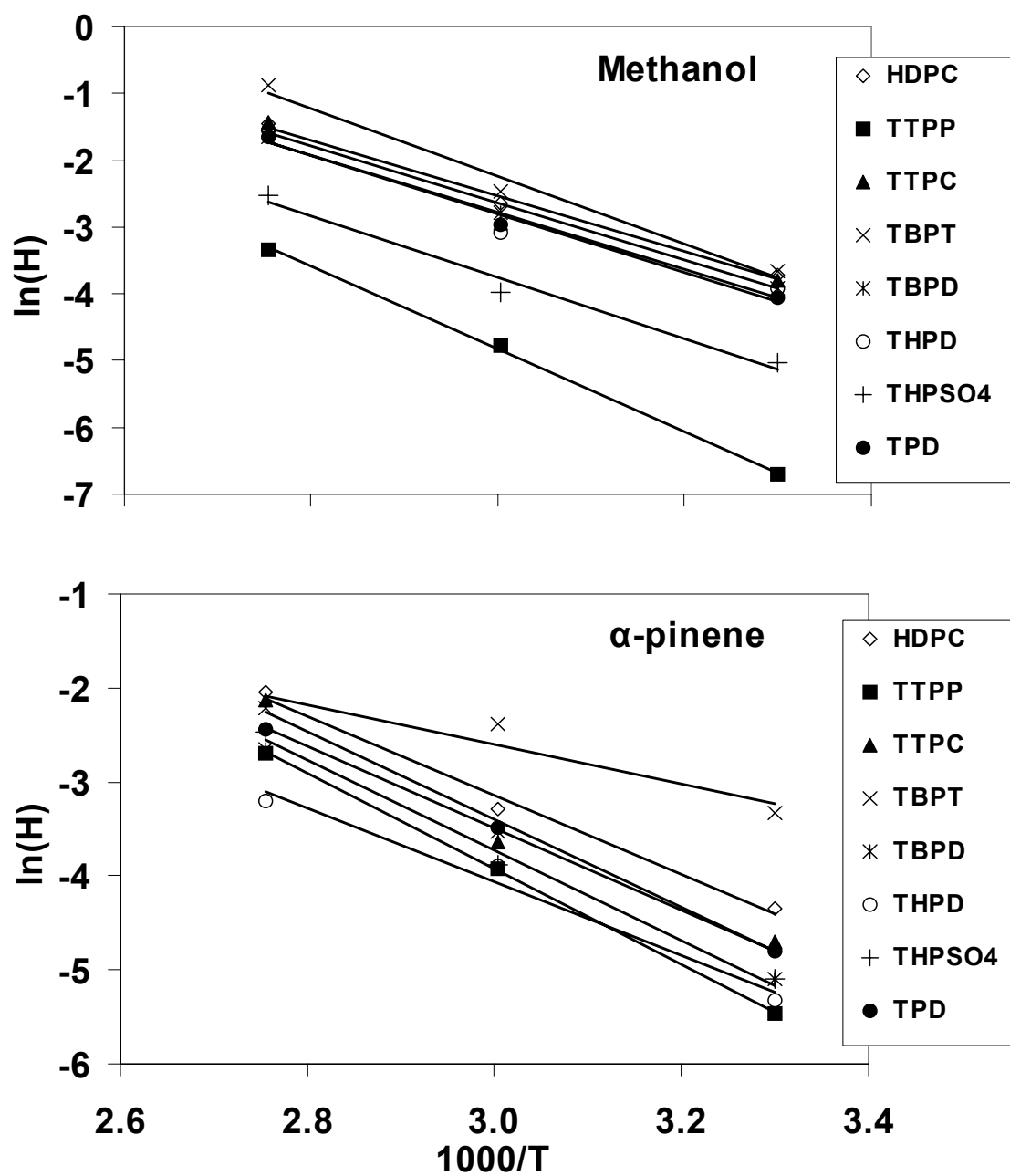


Figure 9. Plots of $\ln(H)$ versus $1000/T$ for methanol (top) and α -pinene (bottom) in the phosphonium-based ionic liquids.

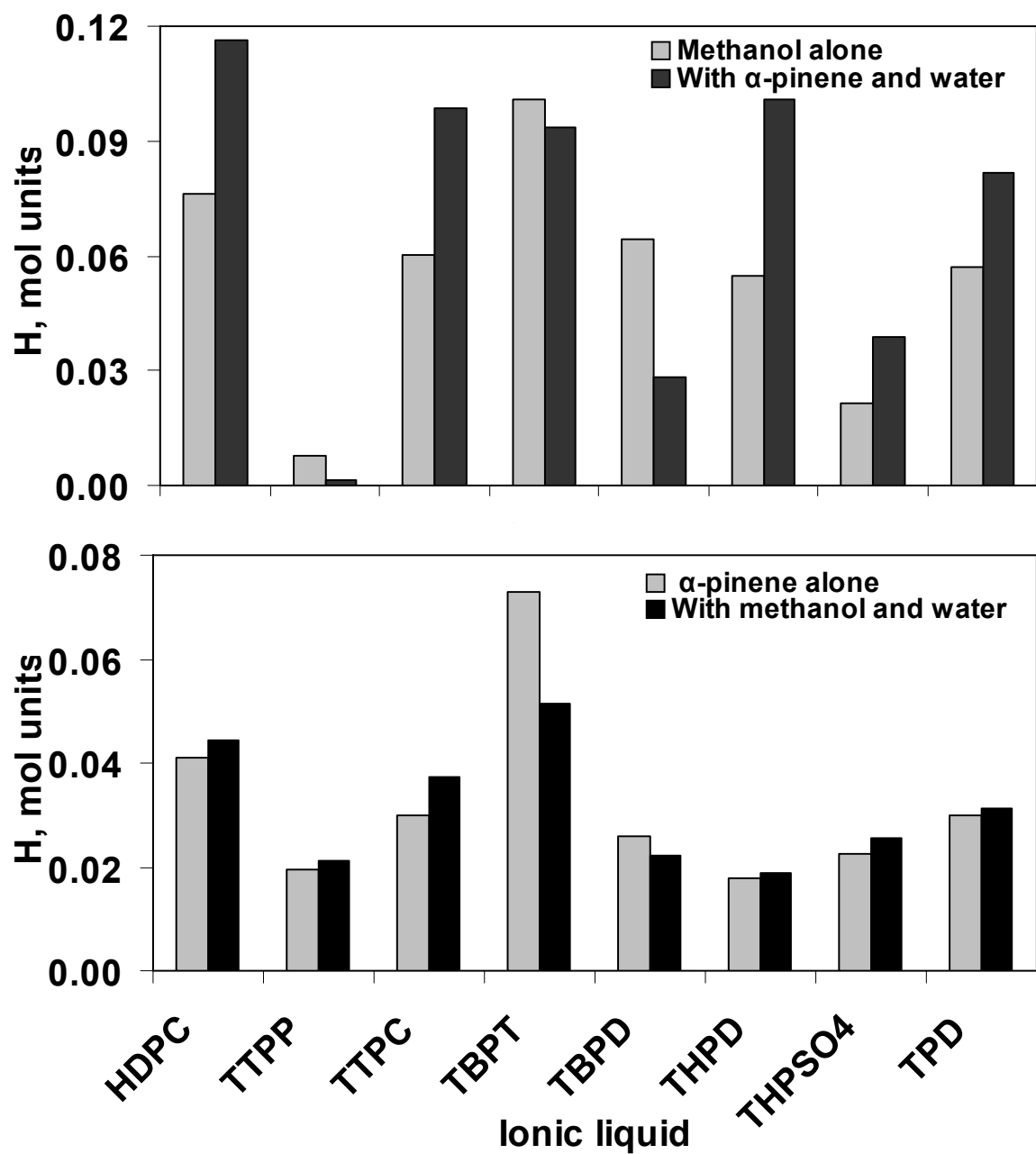


Figure 10. Plots showing the effect of other solutes on Henry's Law constant for methanol (top) and α -pinene (bottom). Values are derived from values shown in Table 5 and similar regressions for the combinations.

Cleaning RTILs in a Rotary Evaporator: To better understand the requirements for desorption, we conducted an experiment with the contaminated IL. Small amounts of IL were placed in a rotary evaporator and cleaned at various temperatures, pressures, and times. The results are shown in Figure 11.

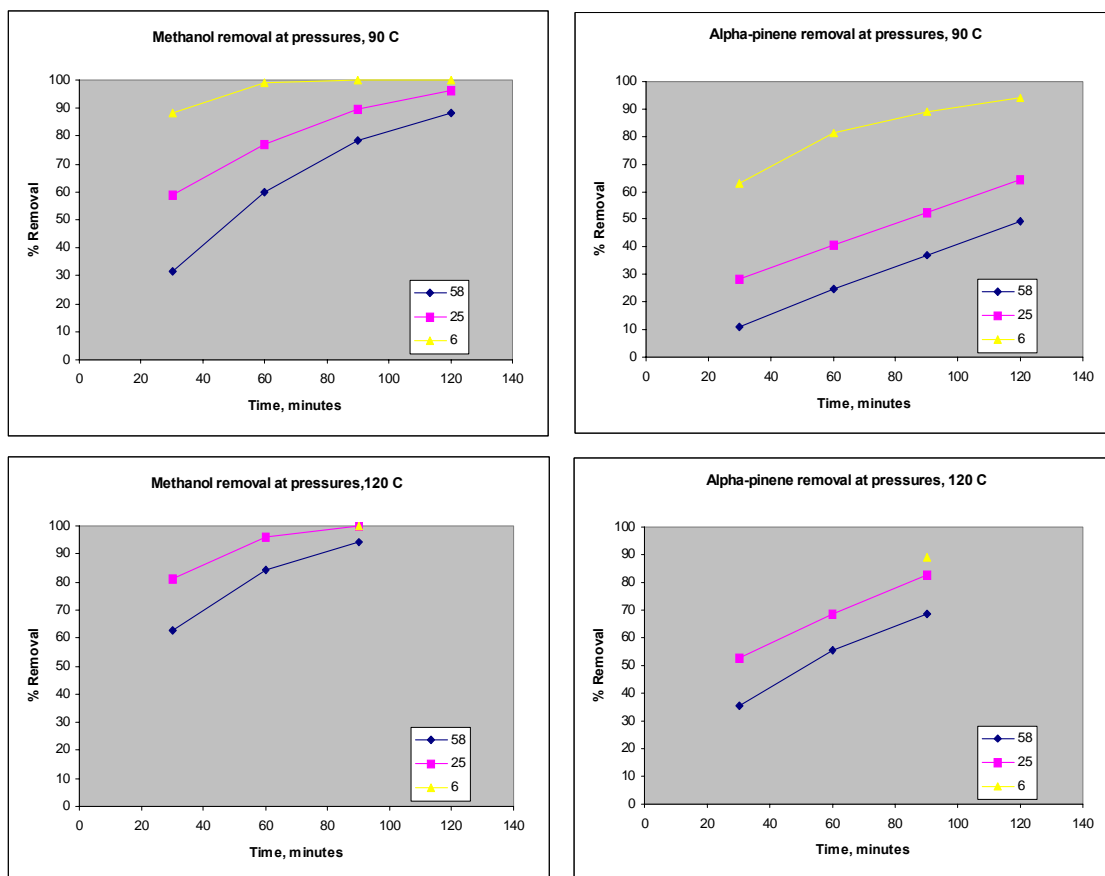


Figure 11a. Removal of contaminants from RTIL in a rotary evaporator

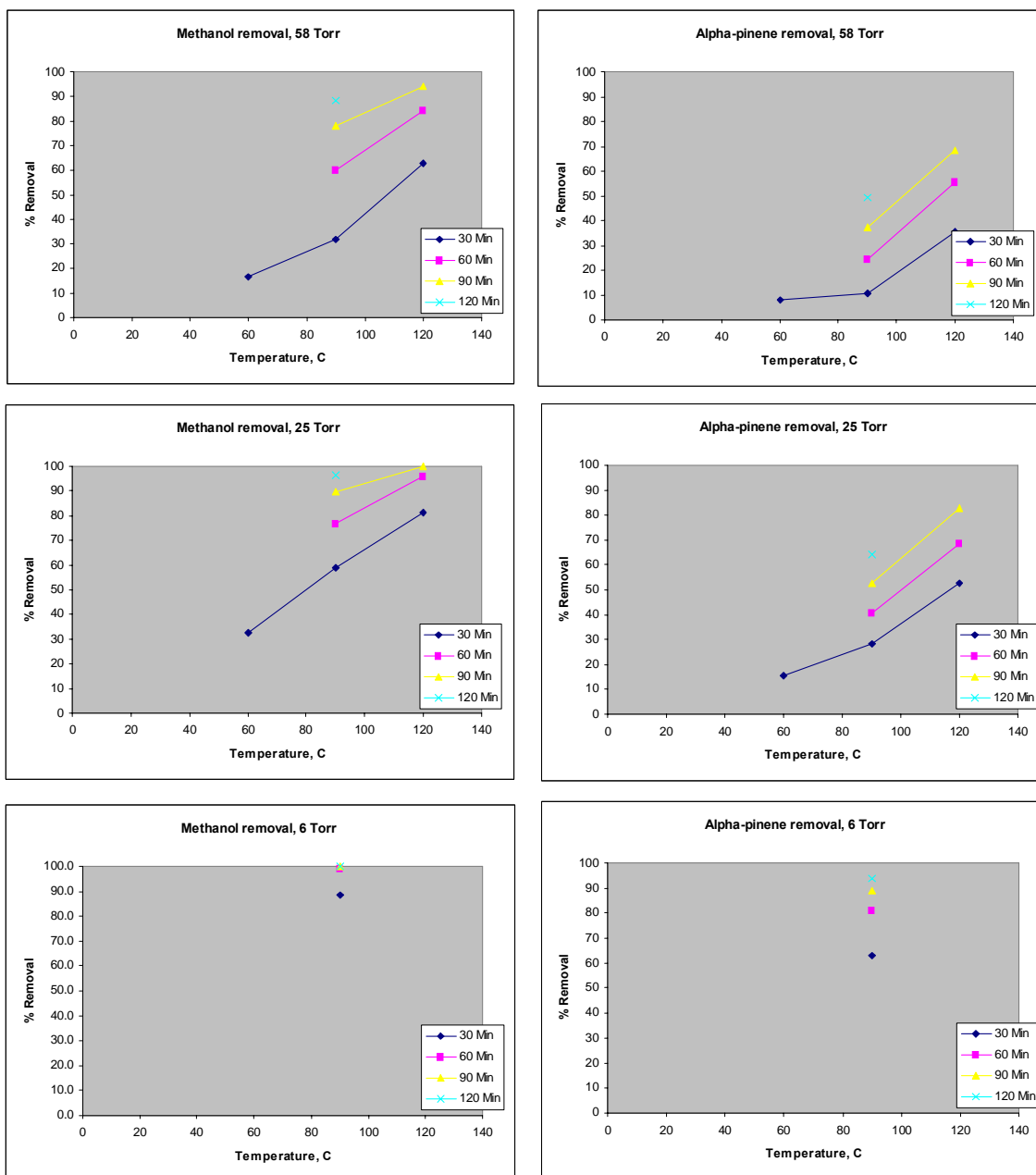


Figure 11b. Removal of contaminants from RTIL in a rotary evaporator

The results obtained in the rotary evaporator confirm the difficulties - 30 minutes at 60°C will not clean methanol or α -pinene from the ionic liquid so that it can be reused. For methanol, 90°C and high vacuum (6 Torr) or 120°C and 25 Torr will be required. For α -pinene, we might not be able to clean the ionic liquid at any of the conditions tested; although, it appears that 120 minutes at 90 to 120°C would remove it. However, it is probably not practical to operate a column this tall. Also, the hydrodynamics maybe better in the rotary evaporator so that more time is required in the column than would be indicated by the charts.

Given these results, it's likely that we can clean methanol from IL105 and get the desorber to achieve a >90% methanol reduction in the exhaust gas. For α -pinene, we may not get enough removal in the desorber to achieve a 90% reduction of α -pinene in the exhaust gas. If these compounds are representative of what might be expected from the exhaust, then there may be a problem cleaning the higher molecular weight compounds from the RTIL.

Phase 2, Capturing VOCs in a Bench-scale Column

Tetradecyl(trihexyl)phosphonium dicyanamide was selected as the RTIL absorbent for this phase of the project. In phase one it was determined that it has good absorption properties for methanol and α -pinene, is thermally stable, and is relatively easy to synthesize. It has a density of 0.89 g/mL at 20°C and a molecular weight of 549.9 g/mol.

The viscosity of the RTIL was measured using a Brookfield DV-2 viscometer with a LV-1 spindle. The RTIL was first dried by heating to 137°C, then allowed to cool overnight. It was then heated from 20°C to 120°C while the viscosity was measured. The RTIL was again allowed to cool overnight, 3% by weight water was added, and viscosity measurements were made from 20°C to 80°C after which the water content was 2.7%.

The viscosity of the dry RTIL varied from 525 mPa•s at 20°C to 26 mPa•s at 80°C, and 14 mPa•s at 107°C. When the RTIL contained 3% water, the viscosity was lower, 380 mPa•s at 30°C and 22 mPa•s at 80°C. This is important in the operation of equipment. The RTIL absorbs water in the absorber and it operates at the lower viscosity, at least in the lower portion. In the desorber the water flashes from the RTIL before it reaches the packing so the entire desorber operates at the higher viscosity.

Absorption system description

An absorption-desorption system was constructed using 25-mm inside diameter by 1-m-long glass columns which were electrically heated and insulated (Figures 12 and 13). Stainless steel packing (Aceglass 6624-04) was added to each column to a depth of 50 cm.

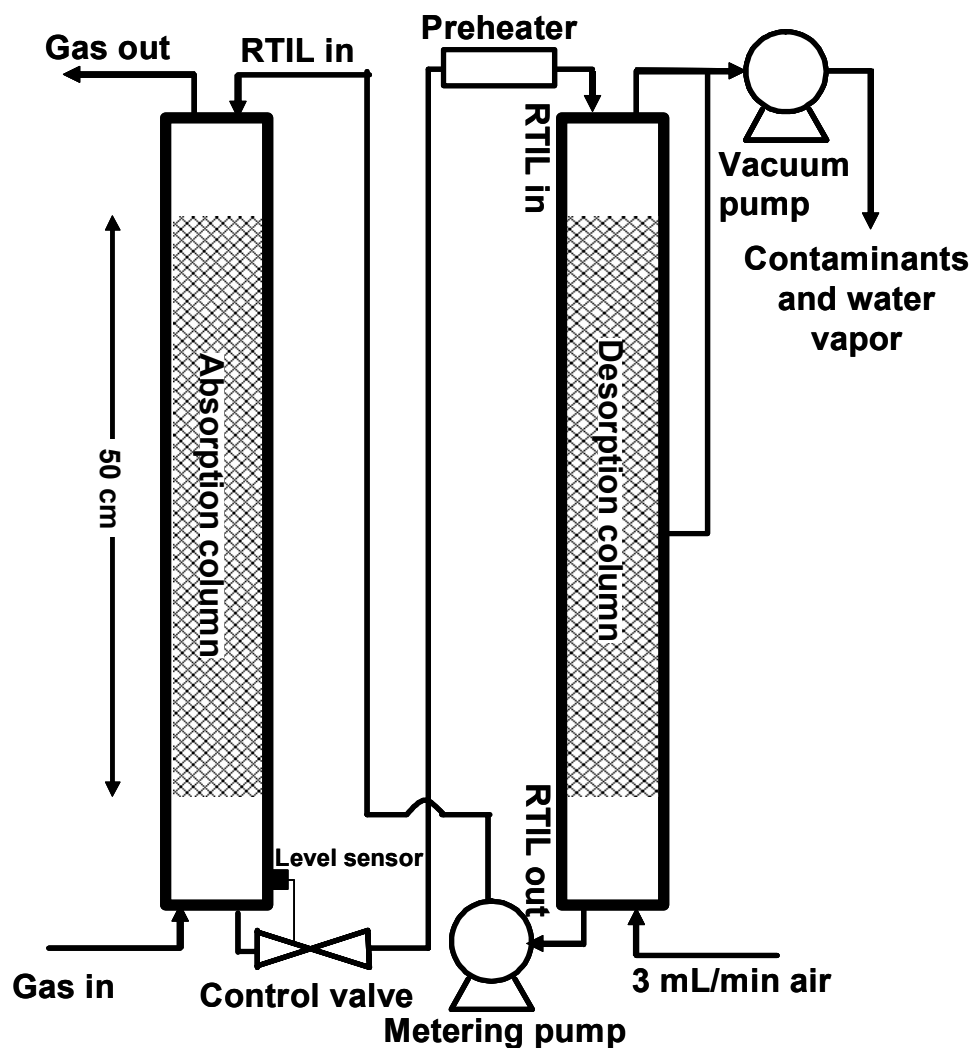


Figure 12. Absorption and desorption columns. Column heaters and insulation are not shown.



Figure 13. Lower part of columns without insulation with pump.

A metering pump circulated RTIL from the desorber to the top of the absorber where it dripped onto the packing and flowed through it at 4 mL/min. Gas at a temperature of 60°C containing contaminants entered the bottom of the absorption column, passed through the packing, countercurrent to the RTIL, at 400 to 500 mL/min. The absorption column was heated to 60°C to better simulate what might happen in a large industrial column. Without heat, the small-diameter column would have readily cooled to ambient temperature even if the gas entering the column was hot. The absorption column was operated at approximately atmospheric pressure. A control valve on the outlet line maintained the RTIL in the bottom of the absorber at a level below the packing.

The desorber was heated to 120°C and operated at subambient pressure, approximately 1 kPa. The combination of vacuum and high temperature caused the contaminants to transfer from the liquid to the gas phase. Ports to a vacuum pump were located at the top of the column and approximately half way up the packing. The low pressure in the desorption column drew RTIL from the bottom of the absorption column, through the control valve and a preheater. In the desorber, the RTIL dripped onto the packing and flowed through it. The metering pump removed the RTIL from the bottom of the absorber for reuse. A small amount of ambient air, 3 mL/min, was allowed to enter the bottom of the desorber through a critical orifice.

Testing the absorption system

Testing of the device occurred in three stages. First, we used gas containing methanol, α -pinene, and/or water generated in the laboratory. Second, we used gas from a laboratory lumber kiln. The kiln provided a convenient source of actual wood dryer exhaust that was close to other lab equipment. Finally, the device was taken to a commercial facility and gas was sampled from the exhaust of veneer dryers.

Tests on laboratory-generated gas (procedures): The laboratory-generated gas contained methanol at 25 to 60 ppmv and α -pinene at 150 to 170 ppmv as surrogates for the VOCs in dryer and press exhaust. The balance was air. Methanol was added from a permeation tube (VICI Metronics, Poughkeepsie, NY), the temperature of which was controlled in a GC-oven.

A second air stream was saturated with α -pinene at a controlled temperature of 40 to 80°C. A third air stream was saturated with water at a controlled temperature. These streams were mixed and diluted to obtain the desired concentrations in the gas stream. Concentrations were verified based on the weights of methanol and α -pinene evaporated. Transfer lines were heated to 60°C to prevent condensation.

A 0.2 mL sample of the gas entering and leaving the absorption column was sampled using a 1 mL gas tight syringe. The syringe was stored at 33 kPa and 60°C to remove contamination. The GC responses to the methanol and α -pinene were converted to concentrations using response factors obtained by injecting 1 μ L of dichloromethane containing 4, 40, or 400 mg/L of methanol and α -pinene. Solution injections were made daily to check for drift in the response factors. The GC was operated with a 60 m long, 0.53 mm inside diameter, type 624 fused silica capillary column. The carrier gas was helium at 40 cm/sec. The oven temperature ramped from 45°C to 200°C over 10 minutes. The injection port was held at 200°C and contained a 2 mm inside diameter glass liner. The FID was held at 250°C and used hydrogen at 47 mL/min, air at 400 mL/min, and makeup helium at 25 mL/min.

Samples of the ionic liquid were taken before and after the absorber and analyzed using headspace analysis. Headspace analysis was used because the RTIL does not evaporate when directly injected into the GC injection port, even at 200°C. A 0.5 mL liquid sample was placed in a 4 mL vial. After 8 hours of equilibration at 60°C a 0.2 mL sample of the vial headspace gas was injected into the GC as described above. The liquid phase concentrations were determined from the gas phase concentrations based on the Henry's Law constants for the respective compounds in the RTIL (Wang et al, 2007).

Two tests are reported. The gas entering the absorber was dry and contained 24.7 ppmv methanol and 150.9 ppmv α -pinene in the first. In the second, the gas contained 20% water vapor by volume, 59.4 ppmv methanol, and 169.5 ppmv α -pinene. The tests lasted nine days and three days respectively. Sampling occurred at 12- and 24-hour intervals during tests, respectively.

Tests on laboratory-generated gas (results): We initially tried to operate the desorber at 60 to 90°C and a pressure of 4 kPa. This was not adequate to remove α -pinene from the RTIL (Figure 14). The efficiency of the desorber decreased over several days of operation because the RTIL entering it contained an increasing amount of α -pinene indicating that

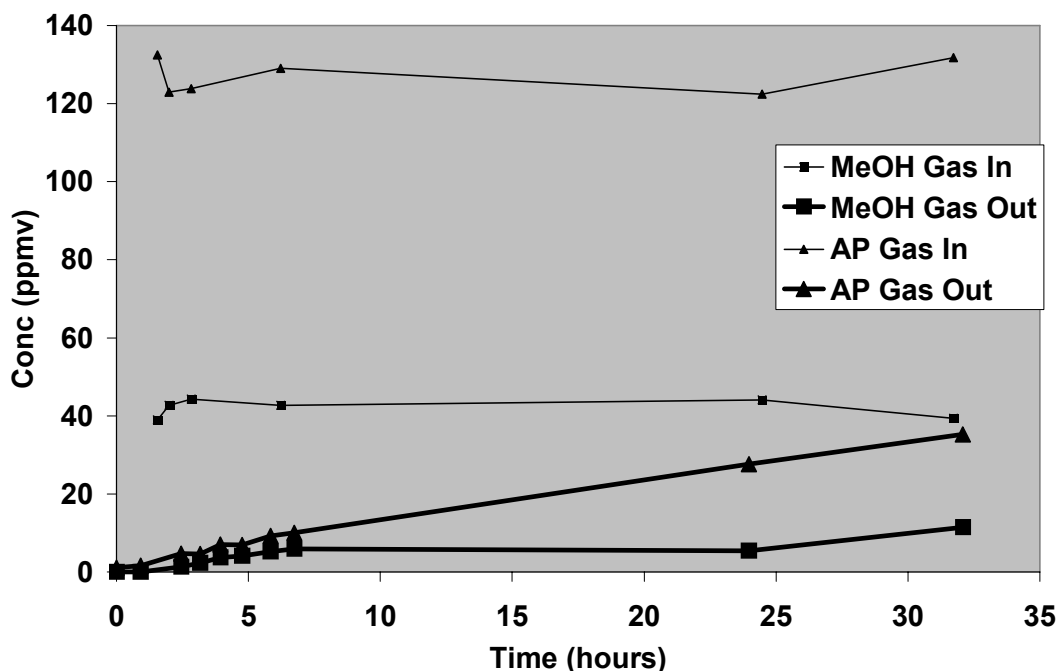


Figure 14. Lab gas attenuation with desorber at 60 to 90°C and a pressure of 4 kPa.

the desorber was not removing contaminants from the ionic liquid. We therefore increased the temperature and reduced the pressure to those described in the procedure, 120°C and 1 kPa.

Initially, when the ionic liquid was clean, the ability of IL105 to remove methanol and α -pinene from air in the absorption column was outstanding. Figure 13 demonstrates that the removal efficiency during the first few hours of operation was nearly 100% for methanol and approximately 98% for α -pinene. This removal efficiency would easily meet the MACT requirements. As the column was operated for a longer time, the removal efficiency decreased because the concentrations of methanol and α -pinene in the ionic liquid were increasing.

To improve desorption, we added an airflow of 3 mL/min into the desorber at the bottom. At a given level of vacuum, this small airflow resulted in a decreased partial pressure of the contaminants in the desorber which, in turn, lowers the concentration of contaminants in the liquid phase in equilibrium with the gas. The temperature was increased in the desorber and the pressure was decreased. After the modifications, the absorber removed 92 to 95% of the methanol and nearly 100% of the α -pinene from the contaminated gas

(Figure 15 and Table 6).

The values in Table 6 are averages of two measurements for test one and four measurements for test two. The high absorption of α -pinene was expected because of the difficulties in removing it from the RTIL. Similarly, the methanol was relatively easy to clean from the RTIL and was more difficult to remove from the air. Moisture in the gas in the second test, 20% by volume, had no noticeable effect on the absorption. This is consistent with the work in Phase one in which the Henry's Law constant was not significantly different when the RTIL contained 2% water compared to dry.

Table 6. Concentrations of methanol and α -pinene in the gas entering and leaving the absorber for lab gas. Test 1 is with dry gas and in test 2 the gas contains 20% water by volume. Removal is the reduction in concentration as a percentage.

	Test 1			Test 2		
	Concentration		Removal %	Concentration		Removal %
	Enter ppmv	Exit ppmv		Enter ppmv	Exit ppmw	
Methanol	24.7	1.7	92.9	59.4	3.0	94.9
α -pinene	150.9	0.2	99.9	169.5	0.3	99.8

After approximately 20 days of operation, the ionic liquid had changed from a pale yellow to a dark brown color. Infrared and NMR analysis on the brown ionic liquid indicated that the ionic liquid was stable and that the brown color comes from the breakdown of the α -pinene upon heating (data not shown). We concluded that the most likely cause of the brown color is a small amount of verenol and a larger amount of verbenone. This did not appear to affect the absorption characteristics of the ionic liquid.

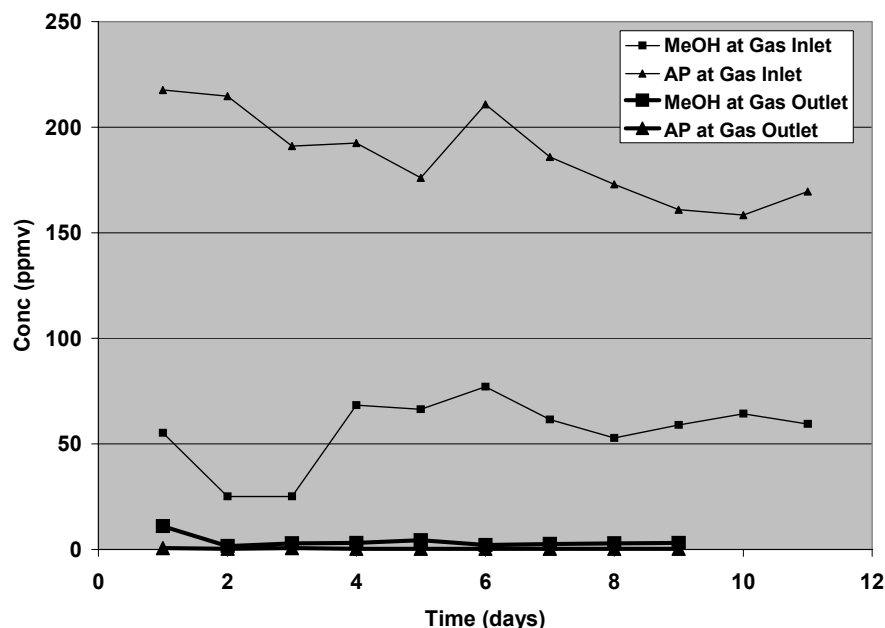


Figure 15. Lab gas attenuation with desorber at 120°C and a pressure of 1 kPa.

Tests on lumber kiln gas (procedure): The absorption and desorption columns were unchanged from the description above. A heated box containing a pump, filter, and flow meter was constructed to move an exhaust sample from the kiln through the columns. The sampling methods were changed so that the performance of the absorber was measured using a total hydrocarbon analyzer and two chilled impinger trains. Valves in the heated box allowed gas from before or after the absorption column to be sampled. All transfer lines were heated to 120°C. The equipment as installed on the lab kiln is shown in Figure 16.

A total hydrocarbon analyzer (THA) (JUM, 3-200) was used to detect the concentration of organic compounds before and after the column. The detector was calibrated to propane in air each time the gas was sampled. The THA sample flow rate was 2.5 L/min which exceeded the column flow rate of 500 mL/min. The balance of air to the detector was supplied using ambient air that had passed through a charcoal filter. This was approximately a 6:1 dilution ratio. To maintain the same system pressure and not recalibrate the analyzer, the same dilution ratio was used for samples taken prior to the

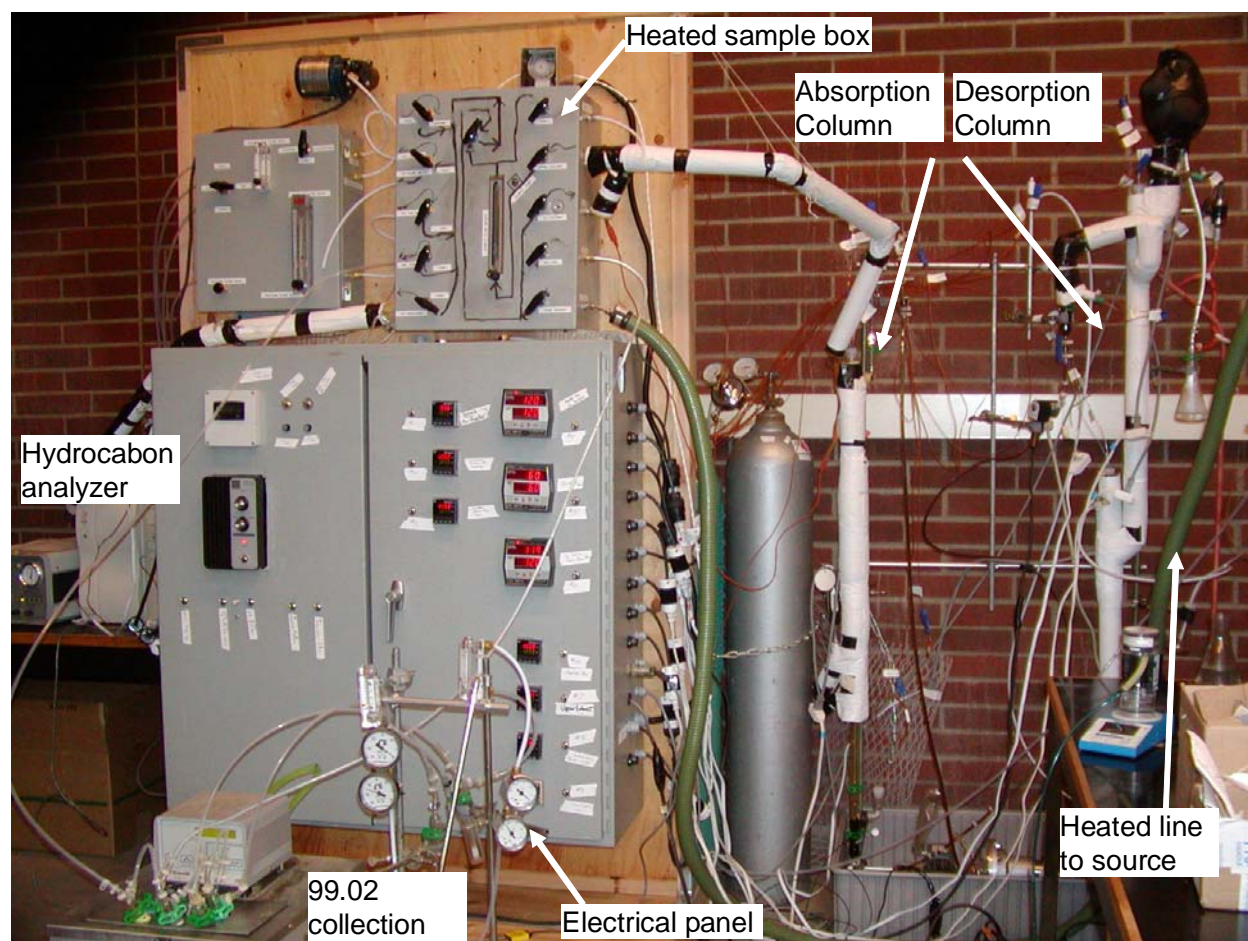


Figure 16. Columns and associated control and sampling equipment set up to sample from lab kiln.

column. To provide paired measurements, the gas stream leaving the column was measured, then flow to the column was stopped for approximately 30 seconds and the gas stream was sampled prior to the column.

Two impinger trains were operated to sample for methanol and formaldehyde according to NCASI method 98.01 (NCASI, 1998). Simultaneous operation on pre- and post-column gas provided paired measurements. The flow rate through each train was 110 to 250 mL/min. The impinger aqueous samples were stored in 100 mL bottles and refrigerated prior to analysis. Gas chromatography and visible spectrophotometry were used according to the NCASI method to determine the concentrations of methanol and formaldehyde, respectively. The instrument detection limits were 0.26 and 0.10 ppmw in the condensate, respectively. The method detection limits were 0.11 ppmv for methanol and 0.05 ppmv for formaldehyde in the gas phase.

Sampling occurred during two kiln charges over 2- and 3-day periods. The kiln was operated at a 78°C dry-bulb temperature and a 68°C wet-bulb temperature. The kiln contained western hemlock for the first charge and a mixture of hemlock and white spruce for the second. The type of wood and operating conditions were not the subject of study. The kiln was used to provide a source of emissions containing a broader array of compounds than the lab-generated source.

Tests on lumber kiln gas (results): The concentrations and removal efficiencies for the absorption column on kiln exhaust are shown in Table 7. The total hydrocarbon, a relative measure of all the organic compounds in the gas, was reduced by approximately 80%. This is lower than expected based on the relatively high methanol and α -pinene reductions on the lab-generated gas. Methanol and formaldehyde removal efficiencies were variable with the average removals near 90%. Again, this is somewhat lower than for the lab-generated gas. The source gas contained 39% water by volume which was almost twice as high as for test two with lab generated gas. The ionic liquid at the bottom of the absorption column contained approximately 4% water by weight during these tests. The water content of the gas did not appear detrimental to the operation of the device. However, water in the RTIL might interact, or hydrate with the ionic liquid and reduce the absorption of other polar compounds. This level of water, 4% by weight, is approximately 60% on a molar basis.

Table 7. Concentrations in the gas entering and leaving the absorber for kiln exhaust. Removal is the reduction in concentration as a percentage.

Test	Sample	THC			Methanol			Formaldehyde		
		Concentration		Removal %	Concentration		Removal %	Concentration		Removal %
		Enter ppmv	Exit ppmv		Enter ppmv	Exit ppmv		Enter ppmv	Exit ppmv	
1	1	36.9	6.8	81.7	51.0	6.7	86.9	0.67	0.11	83.7
	2	27.4	5.0	81.8	86.9	15.0	82.7	0.67	0.05	92.8
	3	23.5	3.6	84.5	64.3	1.88	97.1	0.82	0.05	94.5
	Average			82.6			88.9			90.3
2	1	44.9	8.3	81.5	28.0	0.7	97.7	0.39	0.09	76.6
	2	48.2	9.7	79.7	27.9	0.6	97.9	0.21	0.01	95.7
	3	38.7	10.2	73.5	25.9	0.0	100	0.18	0.01	93.7
	Average			78.2			98.5			88.7

Tests on veneer dryer gas (procedure):

A 3-day field test was conducted at a commercial site where the combined exhaust from two veneer dryers was fed to a regenerative catalytic oxidizer (Figure 17).



Figure 17a. Sample port with heated line to equipment. RTO is to the right. Equipment is behind large duct.



Figure 17b. Equipment (covered) and analyzer (right).

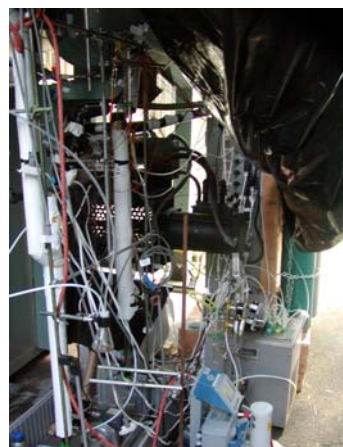


Figure 17c. Columns (left), vacuum pump (bottom), chiller (lower right).

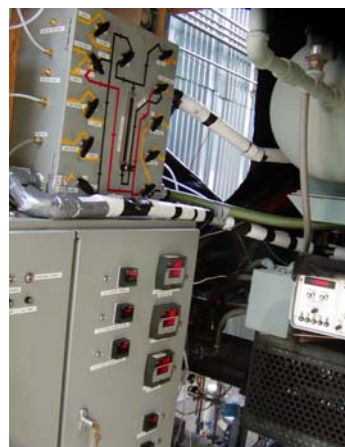


Figure 17d. Gas flow control equipment (upper), electrical control (lower), and analyzer (right).

The absorber and sampling equipment were not changed except that the 500 mL/min sample was drawn from a duct prior to the pollution control device instead of a kiln. The device was set up and allowed to operate overnight. Sample collection began on the second day; however, the dryers were operating at reduced volume giving very low levels of contaminants in the exhaust gas. On the second afternoon, both dryers began re-drying hemlock and on the third morning both dryers began drying green Douglas-fir heartwood. The sampling and analytical procedures were the same as described for the kiln gas.

Tests on veneer dryer gas (results): The concentrations and removal efficiencies for the absorption column on veneer dryer exhaust are shown in Tables 3 and 4. The total hydrocarbon was reduced by approximately 73%. It was suggested that the lower removal was because this was a direct-fired dryer the gas may contain gases from the combustion unit that may be difficult to absorb. Again, as the inlet concentration increased, the removal efficiency tended to increase. While absorber efficiency should not be a function of concentration if all flows are constant, the desorber might become the limiting part of the system. At a given total pressure, the partial pressure of the contaminants can only be brought to a certain level. In turn, the contaminate level in the RTIL cannot be lower than its equilibrium concentration based on Henry's Law.

Table 8. Total hydrocarbon concentrations in the gas entering and leaving the absorber for veneer dryer exhaust. Removal is the reduction in concentration as a percentage.

Day	Time	Concentration		Removal %
		Enter ppmv	Exit ppmv	
1	14:22	81.5	14.4	82.3
	19:08	71.6	8.1	88.7
	19:21	45.9	18.8	59.1
2	8:30	76.3	13.2	82.7
	15:49	30.0	11.6	61.2
3	9:11	38.1	14.0	63.3
Average				72.9

Table 9. Methanol and formaldehyde concentrations in the gas entering and leaving the absorber for veneer dryer exhaust. A concentration of zero indicates no detection on the chromatograph. Removal is the reduction in concentration as a percentage.

Day	Time	Methanol			Formaldehyde		
		Concentration		Removal %	Concentration		Removal %
		Enter ppmv	Exit ppmv		Enter ppmv	Exit ppmv	
1	15:17	3.9	0.0	100	4.0	0.31	92.1
	19:40	7.5	0.0	100	12.8	0.11	99.1
2	9:10	4.3	0.0	100	7.7	0.21	97.3
	15:30	5.4	0.0	100	11.9	0.17	98.5
3	9:01	5.8	0.0	100	9.9	0.5	94.9
Average				100			96.4

The methanol concentration in the dryer exhaust was lower and the formaldehyde concentration was higher than in kiln exhaust. The combustion unit probably contributed to the high formaldehyde concentration. Reductions in excess of 95% were obtained for both compounds. The zero values for methanol mean that the gas was cleaned to less than the method detection limit of 0.11 ppmv. If we used one-half of the method detection limit for the exit concentration (as required in some environmental testing), the methanol removal would have been 98.9%. The moisture content of the gas from the veneer dryer was lower than that from the kiln, low enough that we did not accumulate water in the impingers during the NCASI 98.01 method. Although the NCASI method is only validated methanol, formaldehyde and phenol, we were also able to observe reductions of ethanol (100%), acetone (83 to 100%), and acetaldehyde (36 to 100%) based their concentrations in the impinger catch,

The concentration reduction required in the EPA rule for maximum achievable control technology (MACT) (Federal Register, 2005) for wood processing is 90% for total hydrocarbon, methanol, or formaldehyde. Alternatively, outlet concentrations of less than 20 ppmv for total hydrocarbon or 1 ppmv (if > 10 ppmv uncontrolled) for methanol or formaldehyde are acceptable. The absorption column with RTIL met the MACT for percent reduction of methanol and formaldehyde and the concentration rule for total hydrocarbon.

The concentration of methanol in the RTIL at the end of testing was 0.1 ppmw entering and 1.6 ppmw leaving the absorber. A mass balance between the two phases indicates that

the calculated mass of methanol entering the liquid phase was 22% less than that leaving the gas phase. While this is not as good as hoped, we consider it acceptable given the number and complexity of the measurements. Applying the methods described in Treybal (1980) for the concentration and flow data shows the number of theoretical stages in the column to be 3.1. Thus, the height of a theoretical plate for the absorber as tested is 16 cm. The assumptions in this estimate are a linear equilibrium curve and dilute concentrations.

In all, we used the RTIL for approximately 40 days of testing in this phase of the project with the temperature of the ionic liquid cycling from 60°C to 120°C. Other than darkening, which we attributed to some breakdown of the contaminants, the RTIL at the end of testing had similar characteristics to clean RTIL. The Henry's Law constant for the used ionic liquid was within the range of data described in Wang et al. (2006) for clean ionic liquid indicating that the absorption properties are similar.

Phase 3, Longer-Term Testing in Prototype

An absorption-desorption system was constructed using 85-mm inside diameter stainless steel pipe. Four 46-cm long sections were joined together to make by two columns approximately 2-m in length. These were electrically heated and insulated. Stainless steel packing (Aceglass 6624-04) was added to each column section to a depth of 38 cm. Schematically, Figure 12 shows the system. Figures 18 and 19 show the system in the lab and in operation at a commercial facility.

Absorber description

A metering pump circulated recycled RTIL from the bottom of the desorber to the top of the absorber where it dripped onto the packing and flowed through it at a rate of 24 to 32 mL/min. Dryer or press exhaust gas entered the bottom of the absorption column, passed through the packing, countercurrent to the RTIL, at 4 to 8



Figure 18. Columns with and without insulation. Heaters (two of four) are shown on right column.

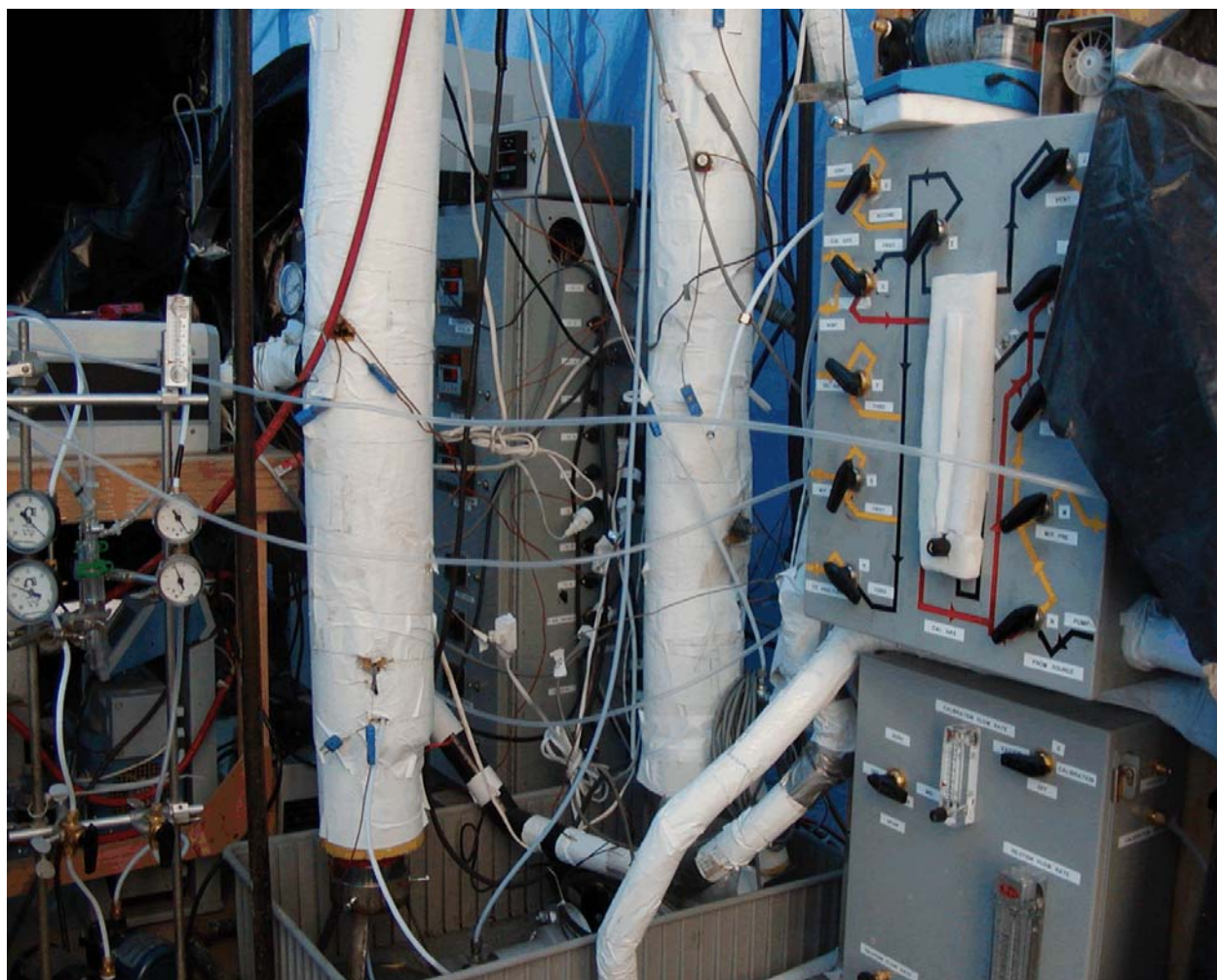


Figure 19. Equipment at commercial facility.

L/min. The line from the dryer or press to the column was maintained at a temperature of 120°C . The gas could be removed after any of the four column sections allowing different packing heights to be simulated. The absorption column was heated to 60°C for most sampling periods to better simulate what might happen in a larger industrial column. Without heat, the column would have readily cooled. Cooling would improve absorption, but not realistically simulate a larger column. The absorption column was operated at approximately atmospheric pressure. A control valve on the outlet line maintained the RTIL in the bottom of the absorber at a level below the packing.

Desorber description

The desorber was heated to 120°C for most of the sampling periods and operated at subambient pressure, approximately 1 kPa. The combination of vacuum and high temperature caused the contaminants to transfer from the liquid to the gas phase. Ports to a vacuum pump were located at the top of the column and approximately half way up the packing. The low pressure in the desorption column drew RTIL from the bottom of the absorption column, through the control valve and a preheater. The control valve opened in response to the liquid level at the bottom of the absorber. In the desorber, the RTIL dripped onto the packing and flowed through it. The metering pump removed the RTIL from the bottom of the absorber for reuse. A small amount of ambient air, 5 mL/min, was allowed to enter the bottom of the desorber through a critical orifice.

The system was charged with approximately four liters of tetradecy(trihexyl)phosphonium dicyanamide. In phase one it was determined that this RTIL has good absorption properties for methanol and α -pinene, is thermally stable, and is relatively easy to synthesize. In Phase two it was successfully used in the small column. It has a density of 0.89 g/mL at 20°C and a molecular weight of 549.9 g/mol. The viscosity of the dry RTIL varied from 525 mPa•s at 20°C to 26 mPa•s at 80°C, and 14 mPa•s at 107°C. When the RTIL contained 3% water, the viscosity was lower, 380 mPa•s at 30°C and 22 mPa•s at 80°C.

Sampling for total hydrocarbon

A control box was constructed to direct the gas flows (upper right in Figure 19). Gas could be sent to a total hydrocarbon analyzer (JUM 3-200) before passing through the absorption column or gas could be sent to the total hydrocarbon analyzer from after the column. The ratio of these two values indicated the percent reduction in total hydrocarbon due to the column. When sampling, the post-column reading was first taken, then a pre-column reading was taken. This was done because the pre-column reading affected the airflow through the column for the sampling period. Sampling required approximately 10 seconds. Due to the cyclic nature of the exhaust at the particleboard facility, we sampled the absorber exhaust for approximately 12 minutes, then sampled the gas entering the absorber for approximately 12 minutes. The values recorded over two (approximately) 5-minute press cycles were averaged and used to determine the reduction in total hydrocarbon due to the column. The analyzer was calibrated with propane in air.

Sampling for HAPs

Gas was also sampled from before and after the column for analysis by NCASI 105 (chilled impinger method with BHA for methanol, formaldehyde, acetaldehyde, propionaldehyde, acrolein, and phenol). Each sampling train had its own pump so this did not affect the column flow. Pre- and post-column sampling was done simultaneously over two- to three-hour period.

Sampling method: The sampling Method was NCASI Method 105. The impingers were in a glycol solution maintained at -1 C. Prior to each sampling interval, the impingers were laboratory-washed and 10 to 15 mL of BHA solution were added to each impinger. The fourth impinger was not used. The system was then assembled and a vacuum check was performed with the valves at each end closed. Less than 1" Hg of pressure change over 2 minutes was acceptable. This was met. The flow rate through the system was then measured by taking four flow readings by attaching the probe tip to a Gilibrator flow meter. This was approximately 500 mL/min. The probe tip was then inserted into the kiln and the sampling interval begun. The collection interval time varied from 2 to about 3 hours, depending on the condensation rate of water.

At the end of each interval, the flow rate was again measured. The sampling line(s) was rinsed. The fluid in the three impingers was weighed, placed in a vial. The impingers were then rinsed with 10 mL of water followed by 3 to 5 mL of hexane. The rinses were also placed in the vial and it was sealed. Samples were kept refrigerated and in the dark until lab analysis was done. Lab analysis was done within two weeks after sample collection. The local airport altimeter setting and the lab temperature were recorded at the beginning and end of each interval so the flow rates could be adjusted to standard conditions.

Lab analysis for aldehydes: The aldehyde standard was prepared by the volumetric dilution of neat aldehydes into a solution of ortho-benzylhydroxylamine hydrochloride (BHA) and water (30g BHA per liter of water). The BHA solution was vigorously agitated and allowed to sit for 15 minutes to allow for derivatization of the aldehydes into aldoximes. The derivatized aldehyde solution was extracted with three aliquots of hexane and brought to volume to make 1000 mg/L. A standard curve was prepared by volumetric dilution in hexane at a range from 1 to 100 mg/L as aldehydes into autosampler vials with 100 mg/L of nitrobenzene as an internal standard.

The samples were prepared by extraction in a separatory funnel with three aliquots of hexane for a total hexane volume of approximately 25 mL. The volumes of the two phases were calculated from their weights. A 1 mL aliquot of the hexane fraction was transferred to an autosampler vial and spiked with internal standard.

The analytical instrument was a Shimadzu GC model 2010 with a flame thermionic detector (FTD), the Shimadzu equivalent of a nitrogen phosphorous detector (NPD). The column was a 105-meter Restek RTX-5 capillary with a 0.25 mm outside diameter and a stationary phase thickness of .25 μ m. The oven schedule was: 2 minutes at 120°C, 2°C/min ramp to 160°C, 40°C/min ramp to 220°C and 6.5 minutes at 220°C. The column flow was 25 cm/sec, with 3 mL/min septum purge, and a 1:10 split ratio with a glass wool packed split injection liner. The detector make up He was set to 20 mL/min and the H₂ was set to 3 mL/min. The air was set to 140 mL/min, and the source current was set to 2 pA. The He and H₂ gases were grade 5 and the air was grade 0.1. The injector temperature was 200°C and the detector temperature 280°C. An AOC-20i autosampler was used to perform 1 μ L injections using a 10 μ L syringe with a steel plunger.

Lab analysis for alcohols: The methanol standard was prepared by the volumetric dilution of neat methanol into water. The phenol standard was prepared by the gravimetric addition of solid phenol to a known volume of water. The alcohol mixed standard was prepared by volumetric addition of methanol to a gravimetrically prepared phenol standard. The mixed standard was prepared at a concentration of 1000 milligrams per liter (mg/L). A standard curve was prepared by the volumetric dilution of the mixed standard at a range from 5 mg/L to 1000 mg/L into autosampler vials.

Samples were prepared by transferring aliquots of the previously hexane extracted aqueous fractions into autosampler vials. The analytical instrument was a Shimadzu GC model 2010 with a FID detector. The column was a 60-meter Restek Stabilwax capillary with a 0.53 mm outside diameter and a stationary phase thickness of 1.5 μm . The oven schedule was: 3 minutes at 80°C, 10°C/min ramp to 240°C, and 10 minutes at 240°C. The column flow was 30 cm/sec, with 3 mL/min septum purge, and a 1:10 split ratio with a glass wool packed split injection liner. The detector make up He was set to 25 mL/min and the H₂ was set to 50 mL/min. The air was set to 500 mL/min. The He and H₂ gases were grade 5 and the air was grade 0.1. The injector temperature was 175°C and the detector temperature 250°C. An AOC-20i autosampler was used to perform 1 μL injections using a 10 μL syringe with a PTFE plunger.

Tests on veneer dryer exhaust (procedure)

The absorption columns and associated equipment were transported to a facility where Douglas-fir veneer was dried. A sample of dryer exhaust gas was drawn from a sampling port after a knock out box for dust and prior to an RCO (2 Photos). The duct contained the combined exhaust from two dryers. Either green veneer, redry veneer, or both were feed to the dryers at various times. The gas was fed to the bottom of the absorption column through a line that was heated to 120°C (green line in photo). The veneer dryer was relatively high moisture source compared to the press described later. The dryers were operated in the 155 to 170°C range for green veneer and less than 140°C for dry veneer.



Figure 20. Samling port with heated line

The conditions for testing are shown in Table 10. The active packing height in the absorber was 38, 76, 114, and 152 cm with a gas flow rates between 3 and 8 L/min and an RTIL flow rate of 24.5 or 32 mL/min.

Tests on veneer dryer exhaust (results)

Hydrocarbon attenuation: The hydrocarbon attenuation through the absorption column is shown in Table 10. Attenuation was poor, with 36 to 51% of the hydrocarbons being absorbed by the system.

Lines one to four of the table show the effect of packing height. The shortest packing height gave the poorest attenuation while the 114 and 156 cm packing heights gave the greatest attenuation. The reduction values are averages of six to nine readings taken over several days. The standard deviation of the values ranges from 13 to 18%.



Figure 21. Columns and other equipment set up at veneer dryer.

Attenuation was reduced when the gas flow rate was increased to 8.7 L/min.

Table 10. Conditions for absorber and reduction in total hydrocarbon for tests on veneer dryer exhaust.

Elapsed time		Absorber conditions				Total Hydrocarbom		
Start	End	Gas	Liquid	Temp	Sect.	Pre	Post	Reduction
hr	hr	L/min	mL/min	°C	cm	ppm	ppm	%
0	124	3.7	24.4	60	38	67	44	36
124	189	3.3	24.4	60	76	116	72	42
189	284	2.9	24.5	60	114	79	45	49
284	382	2.5	24.5	60	156	87	51	46
382	385	4.5	24.5	60	156	171	80	52
385	550	6.4	32.0	60	156	100	49	51
550	594	8.7	32.0	60	156	46	33	28
594	597	6.1	32.0	60	156	26	15	42
597	645	6.1	32.0	90	156	101	56	44

HAPs Attenuations: The column performed much better on the attenuation of HAPs. The plywood and wood panel MACT (Maximum Achievable Control Technology) standard (also covers lumber) specifies that six HAPs are to be tested and serve as surrogates for all HAPs that might be present in dryer and press exhaust. In the tables below, these HAPs have been divided into alcohols, the more concentrated aldehyde HAPs, and the aldehyde HAPs that are present in low concentration. For the first five entries in the tables values are an average of two pre and post NCASI 105 tests. The values in the tables for the remainder of the entries represent a single set of pre and post samples. For all HAPs, the attenuation by the absorption column was not satisfactory for a packing height of 38 cm, the lowest height tested.

The alcohols showed the poorest absorption of the six HAPs, except for acetaldehyde (Table 11). Over 90% of the methanol was removed from the exhaust gas by the absorber for most sample pairs. The attenuation of phenol was not as good; however, it is present in a much lower concentration which makes it harder to capture. It has the lowest polarity of the HAPs tested (1.45 debyes) which probably makes it less likely to be absorbed, but a high molecular weight which should help it to be absorbed.

Formaldehyde was readily absorbed by the RTIL (Table 11). 100% attenuation was achieved for many of the sample pairs. Acetaldehyde, however, was not absorbed well. Its boiling point is 20.8°C compared to 65°C for methanol and -21°C for formaldehyde. Methanol has a polarity of 1.70 debyes and formaldehyde has a polarity of 2.33 debyes. The polarity of acetaldehyde is 2.69 debyes. A comparison of the boiling points and polarity for these compounds which would lead one to believe that acetaldehyde should be readily captured by the RTIL.

The other two HAPs, acrolein (mw = 56.07g/mol, b.p.=52.5°C. pol=3.12 debyes) and propionaldehyde (mw = 58.08 g/mol, b.p.=48.8°C. pol=2.52 debyes) were present in low concentrations. Acrolein was not detected in many sample pairs, but seemed to be readily absorbed by the RTIL. Propionaldehyde was detected in every sample and was readily absorbed.

Table 11. Conditions for absorber and reduction in HAPs for tests on veneer dryer exhaust.

Elapsed time		Absorber conditions				Methanol			Phenol		
Start	End	Gas	Liquid	Temp	Sect.	Pre	Post	Reduction	Pre	Post	Reduction
hr	hr	L/min	mL/min	°C	cm	ppm	ppm	%	ppm	ppm	%
0	124	3.7	24.4	60	38	12.4	4.3	65.3	0.4	0.2	58.3
124	189	3.3	24.4	60	76	6.8	0.6	92.0	0.3	0.1	59.6
189	284	2.9	24.5	60	114	10.1	0.5	95.8	0.3	0.1	64.4
284	382	2.5	24.5	60	156	9.0	1.3	88.5	0.5	0.2	60.7
382	385	4.5	24.5	60	156	19.4	1.3	94.3	0.7	0.2	66.8
385	550	6.4	32.0	60	156	14.2	0.3	97.8	0.6	0.2	70.0
550	594	8.7	32.0	60	156	11.1	0.8	93.0	0.4	0.1	63.8
594	597	6.1	32.0	60	156	14.6	1.8	87.3	0.4	0.2	61.9
597	645	6.1	32.0	90	156	13.2	0.9	93.4	0.8	0.4	51.3

Elapsed time		Absorber conditions				Formaldehyde			Acetaldehyde		
Start	End	Gas	Liquid	Temp	Sect.	Pre	Post	Reduction	Pre	Post	Reduction
hr	hr	L/min	mL/min	°C	cm	ppm	ppm	%	ppm	ppm	%
0	124	3.7	24.4	60	38	13.3	1.9	85.3	5.9	4.1	31.8
124	189	3.3	24.4	60	76	7.9	0.0	100.0	10.6	8.3	21.1
189	284	2.9	24.5	60	114	3.1	0.0	100.0	6.8	5.1	12.5
284	382	2.5	24.5	60	156	9.0	0.0	100.0	7.5	3.1	38.5
382	385	4.5	24.5	60	156	17.7	6.3	58.1	21.6	22.4	3.5
385	550	6.4	32.0	60	156	13.1	0.0	100.0	8.2	5.7	30.2
550	594	8.7	32.0	60	156	12.0	1.5	87.5	5.0	1.9	61.5
594	597	6.1	32.0	60	156	11.3	0.0	100.0	6.5	5.2	19.4
597	645	6.1	32.0	90	156	14.1	0.0	100.0	12.9	10.1	21.6

Elapsed time		Absorber conditions				Acrolein			Propionaldehyde		
Start	End	Gas	Liquid	Temp	Sect.	Pre	Post	Reduction	Pre	Post	Reduction
hr	hr	L/min	mL/min	°C	cm	ppm	ppm	%	ppm	ppm	%
0	124	3.7	24.4	60	38	1.8	0.5	73.6	0.2	0.1	73.3
124	189	3.3	24.4	60	76	0.2	0.0	100.0	0.2	0.0	100.0
189	284	2.9	24.5	60	114	0.3	0.0	100.0	0.1	0.0	50.0
284	382	2.5	24.5	60	156	0.0	0.0		0.1	0.0	
382	385	4.5	24.5	60	156	0.4	0.3	33.1	0.3	0.2	42.8
385	550	6.4	32.0	60	156	0.0	0.0		0.3	0.0	100.0
550	594	8.7	32.0	60	156	0.0	0.0		0.2	0.0	100.0
594	597	6.1	32.0	60	156	0.0	0.0		0.2	0.0	100.0
597	645	6.1	32.0	90	156	2.1	0.0	100.0	0.3	0.0	100.0

Tests on press exhaust (procedure)

The absorption columns and associated equipment were transported to a facility where particleboard was pressed. A sample of press exhaust gas was drawn from an exhaust stack (Figures 22 and 23). The duct temperature was 25 to 30°C. The gas was fed to the bottom of the absorption column through a line that was heated to 60°C. The sample was low in moisture.

The conditions for testing are shown in Table 12. The active packing height in the absorber was either 114 or 152 cm with a gas flow rates between 4 and 7 L/min and an RTIL flow rate ranging from 10 to 35 mL/min.

Tests on press exhaust (results)

Hydrocarbon attenuations: The attenuation of VOCs was improved on the press compared to the dryer. It ranged from 56% to 83% (Table 12). The hydrocarbon entering the absorber varied with the press cycle (pre-column line) while the hydrocarbon concentration leaving the absorber was steady (post-column line) (Figure 24) The post-column steady line in Figure 24 indicates that the performance of the absorber is limited by the ability of the desorber to clean the ionic liquid. Recycled ionic liquid enters the column at the top and is contacted with the gas immediately before the gas leaves the column. The gas and RTIL are in equilibrium at this point (the steady nature of this line indicates this). If the desorber was able to lower the concentration of contaminants in the RTIL to a lower amount, Henry's Law dictates that the gas concentration would be lower.



Figure 22. Sampling point for press exhaust.



Figure 23. Equipment set up at particleboard facility. Sampling line from Figure 22 enters at right.

Table 12. Conditions for absorber tests on press exhaust. Averages shown on right with average total hydrocarbon attenuation.

Elapsed Time	Absorber conditions					Absorber conditions				
	Gas	Liquid	Temp	Packing	%	Gas	Liquid	Temp	Packing	Atten
hrs	L/min	mL/min	°C	cm		L/min	mL/min	°C	cm	%
0	6.34	20.0	60	114	61					
23	5.75	20.0	60	114	52	6.0	20.0	60.0	114	56.2
27	5.71	35.0	60	114	70					
97	6.86	40.7	60	114	66					
97	6.86	40.7	60	114	71					
145	6.62	40.7	60	114						
145	6.62	40.7	60	114	41					
148	6.62	40.7	60	114	76	6.5	39.8	60	114	64.8
217	6.70	10.0	60	114	64	6.7	10.0	60	114	64.4
265	6.66	10.0	60	156	84	6.7	10.0	60	156	83.8
388	6.72	30.0	60	156	70	6.7	30.0	60	156	70.0
456	6.72	30.0	40	156	74	6.7	30.0	40	156	73.5
484	4.64	15.0	60	156	32	4.6	15.0	60	156	31.8
504	4.64	16.0	60	156	-150	4.6	16.0	60	156	-150.4
550	4.20	16.0	60	156	10	4.2	16.0	60	156	9.7

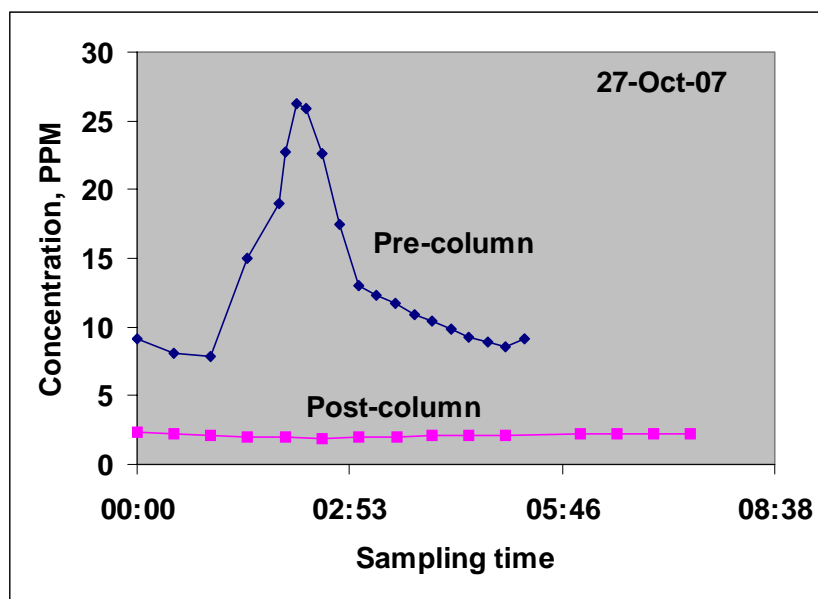


Figure 24. Pre- and post-column total hydrocarbon concentrations for press exhaust.

Towards the end of the trial we experienced some very low or even negative attenuations. We were also having considerable trouble with our hydrocarbon analyzer throughout both trials (we replaced it after the trials). However, on 11-3-07 the desorber temperature was raised from 120°C to 135°C in an attempt to better clean the RTIL. All tests of the absorber after this showed poor hydrocarbon attenuation. At the end of the trial the concentration leaving the column was greater than the concentration entering the column for some parts of the press cycle. The post-column line was still steady with respect to time, but had moved up from 2 to 5 ppm prior to raising the desorber temperature to 8 to 18 ppm (Figure 25). This reflects an inability to clean certain components from the ionic liquid.

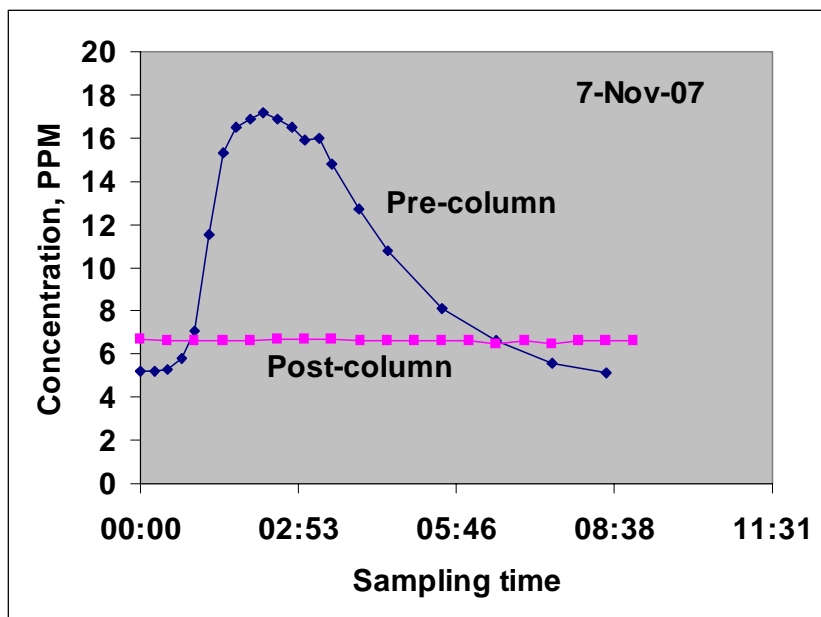


Figure 25. Pre- and post-column total hydrocarbon attenuation for press exhaust toward end of trial.

On two occasions, once at each facility, evacuated cans were used to sample some pre- and post-column gas. We attempted to analyze this with a GC-Mass Spectrophotometer; however, it was borrowed time on the instrument and our options were limited. The owners were having difficulty getting results, even when we ran a sample with only α -pinene. Therefore we were limited to running some of the pre- and post-gas on our GC with an FID.

Tables 13 and 14 show the results for the dryer and press gas, respectively. 100% attenuation for a compound may just mean it was in low enough concentration in the exhaust gas that we were unable to detect it. Compounds that appear in the post-column gas but not the pre-column gas are generally in very low concentrations. They were just not detected in the entering gas. Early peaks (at RT < 10) do not mean much because of the column used. The dryer data is not very consistent, but the press data readily supports the results measured by the total hydrocarbon analyzer. All of the compounds detected elute later than alpha-pinene using the Rtx-5 column, and so are likely to be less volatile than alpha-pinene.

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In the press data (Figure 14), it should be noted that nearly all the large (area > 100,000) peaks show attenuations of 70 to 100% with most near 80%. This is consistent with the analyzer results.

Table 13. GC-FID peaks on gas samples before and after the column at end of dryer trial. * is α -pinene.

10/4/2006 - End of dryer trial					
Pre		Post		Time Diff	% Atten
Time	Area	Time	Area		
		* 21.771	15207.7		
		22.283	1918.5		
23.084	20439.1	23.082	40218.9	-0.002	-96.8
24.627	2364.8	24.631	1196.2	0.004	49.4
24.754	1753.4				100.0
25.182	1437.3				100.0
26.173	8102.1	26.172	7408	-0.001	8.6
26.411	5204.6				100.0
26.576	75535.2	26.575	70508.8	-0.001	6.7
26.75	35985.8	26.75	28668.6	0	20.3
27.641	1837.2	27.651	1394	0.01	24.1
		27.651	1394		
27.772	1137.7				100.0
28.142	2945.7				100.0
28.289	22289	28.288	11591	-0.001	48.0
28.635	11119.5	28.634	1631.6	-0.001	85.3
28.807	16042	28.806	6077.1	-0.001	62.1
28.966	2294.2				100.0
29.017	4152.8				100.0
		29.076	1497		
29.348	14293.7	29.348	4770.8	0	66.6
29.443	1807.4				100.0
29.59	13693.4	29.59	2802.2	0	79.5
29.666	23205.5	29.665	5990.2	-0.001	74.2
30.645	1903.8				100.0
30.828	2320.9				100.0
30.99	2705.3				100.0
31.053	1015.2				100.0
31.134	1577.4				100.0
31.279	1038.6				100.0
31.936	2391.3				100.0
32.11	2095.1				100.0
32.403	5329.3				100.0
32.955	1002.4				100.0
34.384	1029.5				100.0
34.894	1188.4				100.0
35.553	1061.2				100.0

Table 14. GC-FID peaks on gas samples before and after the column at end of press trial. * is α -pinene.

11/10/2006 - end of Press trial					
Pre		Post		Time Diff	% Atten
Time	Area	Time	Area		
		8.939	92105.2		
9.138	487380.6				100.0
21.783	14702				100.0
22.831	9553.4	22.853	8693.5	0.022	9.0
23.087	257647.4	23.084	51674.3	-0.003	79.9
		24.5	1212.5		
24.633	4445.2	24.636	5377.6	0.003	-21.0
24.752	7972.8	24.746	2378.2	-0.006	70.2
25.193	1224.9				100.0
25.706	3090.9				100.0
26.175	71000.3	26.173	12289.7	-0.002	82.7
26.414	43656.9	26.411	7749	-0.003	82.3
26.586	637687.2	26.576	116869	-0.01	81.7
26.756	313280.8	26.751	56656.2	-0.005	81.9
27.076	1914.7				100.0
27.166	3500.9				100.0
27.781	1218.5				100.0
28.143	18363.2	28.141	4123.3	-0.002	77.5
28.293	194600.1	28.289	36277.4	-0.004	81.4
28.636	90761.4	28.634	15331.8	-0.002	83.1
28.81	143781	28.806	27003.2	-0.004	81.2
28.968	23868	28.966	5920.8	-0.002	75.2
29.186	3661.4				100.0
29.35	98667.7	29.348	29296.8	-0.002	70.3
29.447	4626				100.0
29.493	4265				100.0
29.593	107984.3	29.59	23991.7	-0.003	77.8
29.67	174022.7	29.666	38798.7	-0.004	77.7
		29.975	1461.8		
29.857	1211.5				100.0
29.976	6908.8				100.0
30.21	2990.7				100.0
30.446	2704				100.0
30.645	13416.2	30.644	3589.2	-0.001	73.2
30.827	10653.1	30.827	3273.9	0	69.3
30.927	1262.2				100.0
30.99	16701.2	30.989	5549	-0.001	66.8
31.132	6204.8	31.132	1924.5	0	69.0
31.2	3272.3				100.0
31.281	3846.5	31.28	1216.6	-0.001	68.4
		31.845	1186.1		
31.936	10964.1	31.935	4479	-0.001	59.1
32.037	4212.6	32.037	1612.8	0	61.7
32.11	7698.6	32.109	3467.7	-0.001	55.0
32.403	21037.3	32.402	8671.2	-0.001	58.8
32.965	1110.8				100.0
33.188	1530.1				100.0
33.256	1703.9				100.0
		34.288	1487.2	34.288	
34.108	1366.2				100.0
34.387	2236.6				100.0
34.438	1834	34.459	6950.6	0.021	-279.0
34.531	1712.4				100.0
		34.541	6027	34.541	
		34.765	2437.3	34.765	
34.894	1782.8	34.893	1640.5	-0.001	8.0
35.553	1874.8	35.552	1557	-0.001	17.0
36.71	1778.4				100.0
37.591	1405.1				100.0
37.666	2194.1				100.0
37.816	2397				100.0
38.192	2808.7	38.195	1566.9		44.2
39.534	1257.6				100.0

HAP attenuation: As with the veneer exhaust, the HAP attenuation was better than the attenuation of total VOCs. The methanol concentration from the particleboard press was higher than the veneer dryer, but all other HAPs had lower concentrations. Acrolein and phenol were “no detects” for the entire month. Propionaldehyde was detected once at less than 0.05 ppm. Therefore no results are reported for these HAPs. The acetaldehyde concentrations are also low so it is difficult to get a consistent attenuation. The system very effectively captured the formaldehyde and methanol. The 144-cm packing height was more effective at capturing the methanol than 76 cm. Even at the end of the trial, when VOC attenuation was poor, the HAP attenuation was very good.

Table 15. HAP attenuations for press gas.

Elapsed Time	Sample #	Absorber conditions				HAPS								
		Gas	Liquid	Temp	Packing	Methanol			Formaldehyde			Acetaldehyde		
		L/min	mL/min	°C	cm	Pre	Post	% red	Pre	Post	% red	Pre	Post	% red
72	21	6.70	35.0	60	76	20.9	1.9	91.1	4.7	0.0	100.0	0.3	0.3	-15.3
96	22	6.70	35.0	60	76	24.7	1.0	95.9	5.2	0.0	100.0	0.2	0.2	13.3
168	24	6.70	40.7	60	76	16.0	1.2	92.7	6.6	0.0	100.0	0.0	0.0	ND
264	25	6.70	10.0	60	76	16.8	8.6	49.0	8.8	0.0	100.0	0.0	0.0	ND
288	26	6.70	10.0	60	76	11.5	0.0	100.0	0.0	0.0	ND	0.2	0.0	100.0
312	27	6.70	20.8	60	114	12.1	5.3	56.6	6.4	0.0	100.0	0.2	0.3	-5.3
336	28	6.70	20.8	60	114	8.2	0.3	96.5	0.0	0.0	ND	0.2	0.2	9.9
408	30	6.70	30.0	60	114	10.5	0.2	98.3	7.2	0.0	100.0	0.3	0.3	4.7
432	31	6.70	30.0	60	114	11.7	0.0	100.0	4.9	0.0	100.0	0.0	0.0	ND
480	33	6.70	30.3	40	114	8.7	0.0	100.0	5.8	0.0	100.0	0.4	0.4	11.2
504	34	4.60	15.0	40	114	9.7	0.4	95.6	6.8	0.1	99.0	0.4	0.4	-24.2
528	35	4.60	30.0	60	114	10.9	0.0	100.0	3.2	0.0	100.0	0.0	0.0	ND
576	37	4.60	16.0	60	114	9.9	0.0	100.0	6.1	0.0	100.0	0.0	0.5	ND

Ionic liquid after the trials

After approximately 20 days of operation in the small column, the ionic liquid had changed from a pale yellow to a dark brown color. We were concerned about breakdown of the ionic liquid. However, after infrared and nmr analysis on the brown ionic liquid, we concluded that the ionic liquid was stable. The brown comes from the breakdown of the α -pinene upon heating. Among possible choices (from the nmr) that include carveol, myrtonal, terpineol, verbenyl hydroperoxide, and α -pinene epoxide, we concluded that the most likely cause of the brown color is a small amount of verenol and a larger amount of verbenone. These are tightly held to the ionic liquid and probably will not be liberated in the absorber. We cannot remove them in the rotary evaporator. Their effect on the absorption characteristics of the ionic liquid is unknown.

The concern of material building up in the ionic liquid was again addressed with samples of the RTIL taken during the about three weeks into the press trial. Table 13 shows the results of headspace analysis with SPME on the samples. At the beginning of the press trial (also the end of the veneer dryer trial), there were two compounds detected in the headspace. At the end of the trial, there were four and they were different compounds. That they are different compounds (different retention times) is not surprising because the starting samples are essentially samples from the end of the dryer trial. One would expect dryer and press exhaust to have different compositions. Since these initial samples come from before and after the absorber, it is likely that the peaks represent compounds that built up during the veneer dryer trials.

Table 16. Peak on GC-FID for the headspace over RTIL. Methanol would be at a retention time of 6.3 min and α -pinene at 9.3 minutes.

IL Sample 11-03-06 (Toward end of press trial)		
Ret. Time	Area	Approx ppmv
10.6	19800	0.9
12.1	49300	2.2
25.4	4470	0.2
35.4	2500	0.1

Initial IL Absorber (at start of press trial)		
Ret. Time	Area	Approx ppmv
12.7	4040	0.2
18.2	8320	0.4

The four peaks in the 11-03-06 sample are compounds not being removed during the press trial. Whether or not these are an issue depends on their volatility and how they affect the solubility of the contaminants in the RTIL. There is insufficient data to make this determination. Note that it is possible and, quite likely, that there are other compounds in the RTIL that we are not detecting because their volatility is too low. The SPME is done at 60°C and the desorber operates at 120°C. Therefore one would expect the desorber to remove much of what we would detect with the SPME fiber.

Initial IL Desorber (at start of press trial)		
Ret. Time	Area	Approx ppmv
12.7	8160	0.4
18.2	14260	0.6

The lack of a good lab method to detect the contaminants in the RTIL is related to its low volatility. It does not evaporate in the desorber and similarly, if shot into the GC, it does not evaporate in the injection port. It moves into the liner and then it either moves on column or sits in the bottom of the port. Either is undesirable because of the need to clean the port or replace the column. If one had prior knowledge of what the compounds were and knew how they would partition into a solvent, it might be possible to do a liquid-liquid extraction and quantify them. If the prior knowledge existed, however, there would probably be no need to do this. This particular issue was difficult throughout the study.

Accomplishments

Milota, M., P. Mosher, and K. Li. 2007. VOC and HAP removal from dryer exhaust gas by absorption into and ionic liquid. Accepted, Forest Products Journal 7-18-06

Wang, Fujun, M.R. Milota, Paul Mosher, Kaichang Li, and Michelle Yankus. 2007. Henry's Law constants for methanol and α -pinene in ionic liquids. Accepted, Wood and Fiber Science 9/06.

Milota, Michael R. and Paul Mosher. 2006. VOC Capture in ionic liquids. In proceedings of: Quality Drying for the 21st Century. Forest Products Society. Bellingham, WA. November 15-17.

Milota, Michael R. and Kaichang Li. 2004. Preliminary Work on VOC and HAP Recovery Using Ionic Liquids. In:2004 Paper summit, Spring Technical and International Environmental Conference. May 3-6. Atlanta, GA (pp. Electronic proceedings).

Wang, F. 2005. Henry's Law constants for pollutants from the wood industry in room temperature ionic liquids. M.S. Thesis. Oregon State University. Corvallis, OR. 109 pp.

Project objectives were met in that we tested twelve room temperature ionic liquids in two classes, imidazoliums and phosphoniums, for absorption properties and demonstrated their efficacy for commercial use.

Conclusions

Contrary to a reputation for stability, RTILs with the BF_4 or PF_6 anion may break down either at temperatures above 90°C or in the presence of water. We saw evidence of this through inconsistent results, etched glassware, and foul odors.

The phosphonium-based RTILs tested have low values for Henry's Law constants and would likely be good absorbents. They also were stable during the experiments. In light of this, it may be possible to use phosphonium-based RTILs to absorb pollutants from dryer and press exhaust gas and recycle the RTIL through a regenerative process.

Contaminants from kiln and veneer dryer exhaust can be absorbed into an RTIL and the RTIL can be recycled after cleaning with vacuum and heat. The reductions for HAPs are likely to meet the requirements of the MACT rule.

The extended testing in this project, eight weeks on commercial exhaust, was sufficient to establish how well the process works. The removal efficiency over a longer period of time needs to be evaluated.

Recommendations

There may be other ionic liquids that perform better in the absorption system. The best absorbent may not give the overall best performance in the system because of the difficulty in cleaning the ionic liquid. An RTIL that does not retain the compounds as well might be cleaned better in the desorber. This would put cleaner RTIL at the top of the absorber. Since the gas and liquid are coming to equilibrium, this would result in cleaner gas. The main obstacle to commercialization is the ability to clean the ionic liquid.

The long-term stability does not appear to be a problem for tetradecyl(trihexyl)phosphonium dicyanamide. There may be compounds building up in the ionic liquid; however, it was not determined if this was happening or if it would be a problem.

The concept works. Scale up design is needed with an industrial packing. The packing used in the columns in this study was small and would give too much pressure drop in a commercial system. The advantage for the proof-of-concept was a small column.

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