Solvent liquefaction of waste materials

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Solvent liquefaction of waste materials

by

Joel Braden

A thesis submitted to the graduate faculty
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Major: Mechanical Engineering

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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2018

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ABSTRACT

Thermochemical processing of biomass into liquid chemicals or fuels is a potential way of offsetting excess carbon released from petroleum derived fuel, however thermochemical processing is hindered by the high cost of biomass feedstock. Using municipal solid waste (MSW) as a feedstock can help because it is very cheap and contains significant amounts of organic materials, however the low upfront cost comes with other processing burdens. In particular, polyvinyl chloride (PVC) is a plastic commonly found in MSW that can contribute to equipment wear, environmental harm, and product contamination through release of hydrogen chloride (HCl) when heated. This work looks at using this release of HCl from PVC as an asset instead of a hindrance during thermochemical processing MSW.

The first project co-converted cellulose and PVC in the polar aprotic solvent tetrahydrofuran (THF), with the hypothesis that the HCl released could catalyze conversion of cellulose. It was found that the addition of 2.5 wt% PVC caused an increase from 7% to 36% of levoglucosan at 310 °C. Testing was also done at different temperatures to determine its effect. Raising the temperature from 285 °C to 335 °C increased levoglucosan production from 29% to 38%.

The second project used a mixture of cardboard (CB), PVC, and polyethylene (PE) as feedstock materials because these materials are commonly found in MSW. The goal was to first apply solvent liquefaction, as was done in the first project, but then perform pyrolysis on the residue to further obtain useful chemicals. The hypothesis was that CB and PVC would degrade in the solvent, but PE would not due to its thermally stable nature. Results showed that the addition of PVC decreased the time to peak oil yield from 120 minutes to 60 minutes during solvent liquefaction. When all three feedstock materials were used, the highest oil yield was obtained at 69%, at 45 minutes of reaction time. The most abundant chemical in the liquid was tetrahydrofurfural alcohol, obtained in the CB case at 2.5%. When the residue from the CB+PVC+PE
case was pyrolyzed, significant amounts of aliphatic hydrocarbons were obtained from the cracking of the residual PE. Additionally, no chlorinated organic compounds were detected in the residue pyrolysis.
CHAPTER 1. INTRODUCTION: OVERVIEW OF BIOFUELS

Excessive consumption of fossil fuels has prompted a need for renewable energy that can close the carbon cycle and reduce societies output of greenhouse gases. This need is especially great in the transportation sector where vehicles, airplanes, and ships are heavily reliant on liquid fuel energy carriers. Almost all forms of transportation use some sort of liquid fuel for power because of its high energy density and well developed infrastructure. Alternative energy sources based on batteries can derive their power from cleaner grid based sources, however there are still major drawbacks to battery power, and some modes of transportation such as airplanes will be reliant on liquid fuel for the foreseeable future.

Biofuel is the term used for fuel that is produced from recent biological sources like plants and trees, as opposed to petroleum fuel, which is extracted from geological reservoirs in the form of crude oil that is then refined into fuel. Biofuels offer multiple advantages over petroleum including domestic production, energy security, rural economic benefit, and reduction in greenhouse gas emissions [1]. The Renewable Fuel Standard (RFS) is a federal program that requires renewable fuels (biofuels) to be blended with petroleum fuel to offset greenhouse gas emissions. Conventional starch based corn ethanol is the current dominant biofuel, but its production requirement is capped at 15 billion gallons [2]. The three other fuel categories are biomass-based diesel, cellulosic ethanol, and other advanced fuels.

Making biofuels from lignocellulosic organic matter is desirable because lignocellulose is inedible, thus it avoids competition with food. However, in practice, it is difficult due to its natural recalcitrance. Lignocellulose is composed of cellulose, hemicellulose, and lignin. Cellulose and hemicellulose are long chains of sugar molecules and are the backbone of plant cell walls. Lignin is an amorphous solid composed of crosslinked phenolic polymers that surrounds and binds cellulose and hemicellulose together. There are many different ways to make fuel from lignocellulose. The first major pathway is the biochemical route, which involves using enzymes and mild processing
conditions to break down the lignocellulose into its individual monomers, which can then be fermented or processed into fuel or chemicals. The second path is thermochemical conversion, which uses a combination of heat, pressure, and chemicals instead of enzymes to achieve the same ends.

Thermochemical processing of biomass is generally broken up into five categories: pyrolysis, gasification, combustion, liquefaction, and hydrolysis. Pyrolysis involves rapid heating in an inert environment to breakdown the biomass into vapors and aerosols, which are then condensed into a crude oil like substance known as bio-oil that can be further refined into fuel. Gasification goes one step further than pyrolysis by using very high temperatures to break the biomass all the way down to syngas (a mixture of hydrogen and carbon monoxide, among other things) which can then be chemically combined into a large variety of fuels or chemicals. Combustion is burning biomass to extract the heat for energy production. Liquefaction and hydrolysis are similar technologies that use heat and pressure in a liquid medium to break down the biomass into usable chemicals.

Cellulosic biofuels are generally more expensive than their petroleum and conventional biofuel counterparts due to the lower energy density feedstocks and greater number of handling steps that must be taken to obtain usable fuel. Techno economic analyses of thermochemical routes to cellulosic biofuels consistently show that feedstock cost is one of the most important factors affecting fuel price [3]. Therefore it is important to consider the lower cost feedstock options first as a means to develop the technology. There is no cheaper feedstock than municipal solid waste, which can often be had for free or negative cost (via tipping fees). There is wide variability in the composition and definition of MSW, but it generally includes household, commercial, and industrial waste destined for landfill; yard trimmings; and wood waste from construction and demolition sites [4, 5].
CHAPTER 2. LITERATURE REVIEW

Direct liquefaction of biomass is an attractive thermochemical conversion route because of its unique ability to handle high water content feedstocks and generally higher quality product than bio-oil from fast pyrolysis. Products can be tailored to by selecting from a large variety of solvents, operating conditions, and catalysts. Pyrolysis has advantages in that capital costs are lower compared to liquefaction processes, but the oil it produces is an unspecific mixture of a large number of highly oxidized compounds that needs heavy refinement for use as a transportation fuel. Gasification is flexible like liquefaction, however high operating temperatures and syngas cleanup has proven it to be cost prohibitive. Additionally, both gasification and pyrolysis require drying of the biomass for proper reactor operation and yield.

Solvent liquefaction can be split up into different categories due to significant differences in reaction mechanics and intended products. Hydrothermal liquefaction (HTL) is a subset that deals specifically with a water reaction medium. The product is usually a bio-oil similar to that of pyrolysis, but with a lower oxygen content. The other category is solvent liquefaction that uses organic solvent as a medium. Organic solvents offer a wider range of operating conditions and product distribution can be more selective. For example, sugar monomers can be produced in high yields for use as commodity chemicals or as an alternative to enzymatic hydrolysis. Many common organic solvents have also been studied using various amounts of acid catalyst and/or water as a co-solvent with mostly positive results.

Feedstock selection for conversion processes is a major economic concern for large scale operations. Lower cost feedstocks will improve economics by reducing operating costs. Municipal solid waste (MSW) is a prime candidate for conversion due to its high organic content and low cost. However, while all feedstocks require some level of pre-processing, particular attention is given for halogens in MSW, due to its problematic behavior on equipment and the environment. Methods have been developed to minimize its effects.
**Solvent Effects on Biomass Processing**

There are two major types of solvent reaction systems: those using primarily water as the medium, and those using primarily organic solvent as the medium. Organic solvents can be further broken up into non-polar (e.g., hexane and other hydrocarbons), polar protic (e.g., methanol and other alcohols, acetic acid), polar aprotic (e.g., THF, acetone, dimethyl sulfoxide), and ionic liquids[6]. Each of these solvent systems have advantages and disadvantages depending on the intended reaction. For example, aqueous reactions are advantageous in that water is non-toxic, environmentally friendly, and very affordable, however selectivities of valuable chemicals such as sugars and furans is much lower than in organic based processes [6]. Polar aprotic solvents, which are the focus of this work, are characterized by their lack of acidic hydrogen atoms. In general, they can hydrogen bond, and have high dielectric constants and strong dipole moments. These properties make polar aprotic solvents particularly useful for biomass conversion because they can produce valuable products in high yields [7].

Biomass conversion reactions in organic solvents also differ in their objective or desired product. Some pre-treatment methods such as organosolv (which was adapted from the paper making industry), use low temperature (185-210°C) alcohol to remove lignin from lignocelluloses. It is primarily employed prior to enzymatic hydrolysis to increase enzyme activity and therefore ethanol yield [8]. Liquefaction is a different regime where biomass is converted into whole bio-oil with emphasis on producing fuels and chemicals directly. Final products and therefore conversion method will largely be determined by feedstock availability, process constraints, and economics.

Shuai and Luterbacher [6] published an extensive review of the role of organic solvents in biomass conversion. They found that decomposition is changed primarily by changing reaction behavior. This includes things like lowering activation energy, suppressing secondary reactions, and altering solubility. Product solubility has a large effect on conversion and can change with solvent parameters such as polarity, molecule size, molecule surface area, polarizability, and
hydrogen bond strength. Additionally, each fraction of biomass (cellulose, hemicellulose, and lignin) has different solubility parameters, making for complex reaction mechanisms with whole biomass. Chemical reaction thermodynamics also has a large influence on decomposition. Solvents can change activation energies between species and between species and catalyst. Activation energies can be reduced for desirable products and increased for undesirable products, leading to higher selectivities.

**Cellulose Conversion in Solvents**

Cellulose conversion using organic solvents is useful to study because it is a simpler reaction mechanism than conversion with whole biomass. It provides a clearer signal into what is happening during conversion. Additionally, cellulose is the most abundant biopolymer in most biomass feedstocks, so its products should be a good indication of what might be expected with biomass. Pretreatment methods to remove lignin and hemicellulose from lignocellulose can be remarkably efficient, leaving nearly clean cellulose for use as a possible conversion feedstock if high conversion and selectivities can be achieved, and the products produced are high enough value.

Researchers from the University of Wisconsin Madison have published several studies [9-11] using cellulose as the feedstock with reactions in organic solvent systems. They use tetrahydrofuran to convert cellulose to levoglucosenone and hydroxymethylfurfural (HMF) [10, 11]. They found that anhydrous conditions favor the production of levoglucosenone, a valuable sugar that can be used as a platform molecule for high value pharmaceuticals. When water was added to the reaction, products shifted to glucose at shorter reaction times and HMF at longer reaction times. Formation of anhydrosugars was strongly inhibited by the addition of water.

**MSW as Feedstock**

In the year 2014, the United States generated approximately 258 million tons of MSW [12]. Figure 2-1 shows the composition of this waste. Six of the nine categories (83.4% of the total) are organic containing and could potentially be converted using thermochemical processes.
There are several methods currently used in the United States to manage MSW, including landfilling, composting, recycling, and combusting with energy recovery [12]. Figure 2-2 shows each of these as a percentage of the total MSW generated in 2014 [12].

Recycling is the removal and reuse of waste materials that have completed their intended goal. The most commonly recycled products include paper, glass, steel cans, aluminum cans, and...
certain types of plastic [13]. From an energy standpoint, recycling is less energy intensive than producing from virgin sources, especially for aluminum [14]. Paper recycling is less conclusive. Some studies have shown it to reduce the life-cycle energy use and CO$_2$ emissions compared to paper from virgin pulp [14, 15]. Composting uses microbes to decompose organic matter for use as fertilizer or soil amendment. Combustion with energy recovery involves sorting through trash to separate the easily recycled materials, then burning the rest to make electricity. Landfilling is burying trash underground at a site specifically designed for it.

MSW is, undoubtedly, a dirty feedstock source for making fuels. Its composition can be widely varying from region to region, and even day to day. However on average, over 80% of its composition is organic in nature [12], which has potential to be converted to fuels via thermochemical routes. Brown published a review [3] of techno-economic studies of different thermochemical pathways to liquid biofuels. The review consistently names feedstock cost as one of the most sensitive variables affecting the minimum fuel selling price of biofuels. Biomass based conversion analyses typically assume a moderate price for the biomass feedstock. This is based on the cost to produce, collect, and deliver the biomass, and is usually in the range of $60-$100/ton. However MSW disposal sites like landfills charge a tipping fee to cover the cost of disposal and allow for reasonable profits. Tipping fees can range from $24 per ton to $70 per ton [5]. Therefore tipping fees essentially make for negative cost MSW feedstocks. This reduces the operating cost of a plant by a large margin and is highly favorable to the overall economics, although initial capital costs of MSW based plants are higher than those using biomass due to the extended initial cleanup efforts.

Researchers at Pacific Northwest National Laboratory conducted an extensive two volume study on the feasibility of synthesizing liquid fuels from MSW via thermochemical gasification [5, 16]. Part one focused on MSW as a feedstock and gasification technologies. They note that the high ash and water content of MSW (20 and 30% respectively) has a negative effect on its performance.
as a feedstock. They proposed to convert the MSW into refuse derived fuel (RDF) to decrease its water content and increase its higher heating value. RDF is also easier for feed systems to handle due to its pelletized nature. Part two of their report was the techno-economic analysis of a process to produce mixed alcohols from syngas with a side by side comparison to a similar biomass case. The analysis showed a minimum fuel selling price (MFSP) of $1.85 per gallon for the MSW and $3.05 for the biomass. This assumed no tipping fee for the MSW; increasing the tipping fee to $30 per ton reduced the MFSP by $0.50 per gallon. Their conclusion was that this was a feasible proposal using current gasification technologies.

**PVC Recycling Strategies**

PVC is one of the six main fractions of plastic resins found in MSW. It is a popular thermoplastic due to its extreme versatility and low cost. The structure of PVC is a linear chain of single bonded carbon atoms with every other carbon bonded to a chlorine atom. The chlorine atom makes the polymer strongly polar and limits its level of crystallinity, which allows for high mechanical stiffness and maintenance of these properties when plasticized [17, 18]. However, PVC is unique from the other resins in that it is thermally unstable at comparatively low temperatures, despite the numerous stabilizers and additives designed to prevent decomposition. PVC decomposes by an initial release of hydrogen chloride when heated or exposed to light, followed by release of hydrocarbons from the cracking of the vinyl carbon backbone [19].

PVC recycling is not much different from recycling of other plastic wastes, however as previously mentioned, extra steps must be taken to ensure proper handling of its chloride content. This fact alone makes the economics of PVC recycling difficult. In general, plastic recycling is a mature technology and has been reviewed several times in recent years [20-22]. PVC recycling in particular is problematic due to its chloride content, which can cause numerous environmental problems if care is not taken in its handling [23]. A variety of creative methods of recycling PVC have been invented [19, 24] and summarized below.
Mechanical Recycling

Mechanical recycling is the traditional form of recycling that was popularized in the 1970s. It involves recovery of relatively clean, single resin plastics that are ground then recast into, ideally, the same or similar product that they were initially. However in order for this to take place, a high degree of separation of PVC from other polymers is necessary. Pre-consumer PVC is the easiest to mechanically recycle as it is generated at the manufacturing site and can easily be recovered there. Unfortunately, most PVC waste is from post-consumer, durable goods such as plumbing piping or window framing that are not as clean and take several decades to enter the waste stream.

Mechanical recycling of PVC is difficult due to its susceptibility to thermal and environmental degradation. PVC from durable goods such as vinyl flooring is often degraded and discolored, indicating significant chemical changes have taken place. This process is exacerbated in mechanical recycling, which can include several remelting steps, all of which will change the morphological structures of the polymer resulting in altered mechanical and physical properties of the recycled material [24, 25]. Wenguang et al. [25] studied the mechanical and processing properties of recycled PVC blends. They found that, indeed, the thermal stability of recycled PVC was significantly reduced and additional stabilizers needed to be added to retard thermal degradation. Interestingly, they found that adding recycled PVC bottles to virgin PVC substantially improved its impact strength and elongation at break, likely due to the higher amounts of additives in PVC bottles.

Chemical Recycling

Chemical or tertiary recycling refers to the recovery of the chemical structure of plastic wastes for use as feedstock for new chemicals or polymers. It involves reducing the material into smaller molecules or monomers, often through thermolysis routes, but also through purely chemical means [20, 24]. Recycling through chemical routes is advantageous in that it avoids the high cost of separation necessary for mechanical recycling. Some products contain multiple plastic
resins that are inseparable by any reasonable mechanical means. These types of mixed wastes are ideal for chemical recycling. Thermolysis routes are essentially the same as what is used in biofuels processing (i.e. pyrolysis, gasification) but the liquid product it produces has a much higher heating value and lower oxygen content than typical bio-oil produced from woody feedstock.

Chemical recycling of PVC is unique from the other major polymers in that PVCs release of hydrogen chloride at as low as 100 °C must be taken into account to prevent major contamination, corrosion, or environmental harm [19, 24, 26]. Many researchers [27-30] have studied the effects of a stepwise pyrolysis mechanism of PVC alone and PVC containing plastic wastes. In stepwise pyrolysis, the reactor is first heated to an initial temperature (usually 250-330° C) to facilitate the characteristic dehydrochlorination step of PVC. HCl gas can then be collected separately from the organic decomposition fraction, which occurs after the low temperature step at typical pyrolysis temperatures. In most cases this staged pyrolysis is very effective at separating HCl and therefore avoiding the complications of significant amounts of chlorinated organic compounds. Lopez et al. [29] carried out a detailed study on the effects of the step temperature and time as well as the use of calcium carbonate as an adsorber of HCl. They found an increase gas yield and decrease liquid yield when stepwise pyrolysis was used, with solids remaining approximately the same. There was evidence this gas yield increase could not be entirely attributed to HCl; they suggested partial thermal cracking occurred in the low temperature step, which promoted gas production at the higher step. Chlorine content of their liquid products obtained from conventional one-step pyrolysis was 0.5 wt. %, with their best case stepwise pyrolysis being 0.2%; a more than 50% reduction in chlorinated compounds using stepwise pyrolysis. Chlorine in the solids was also decreased by 66%, while chlorine in the gases remained largely unchanged.

**Energy Recovery**

Energy recovery, combustion, or incineration are considered forms of recycling due to the fact that the energy content of the material is “reused”. Combustion is an effective technology to
utilize when the economics of other recovery methods is not feasible [20], such as when the feedstock is heavily contaminated or mixed with other types of waste. Combustion of plastic wastes, especially chloride containing PVC, has been linked with several environmental hazards including increased NOx and SOx emissions, and production of smoke, heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzofurans (PCDFs), and polychlorinated dibenzodioxins (PCDDs) [20].

Controlled combustion of pure plastic waste is not as commonly studied as co-firing or chemical recycling methods [31], likely due to those methods being more sensible when pure streams are available. However, Valavanidis et al. [32] studied plastic burning, including PVC, from an open-combustion perspective. Such scenarios are common in third world countries or in accidental conditions like house fires. They found that PVC, compared to the other common plastics, contained the highest concentrations of metals such as lead, nickel, chromium, aluminum, and copper in the particulate soot emissions. It also contained the highest concentrations of lead, chromium, nickel, and zinc in the bottom ash. Numerous carcinogenic PAHs were detected in the soot and solid ash with PVC forming the highest levels compared to the other plastics.

Formation of PCDFs and PCDDs during combustion of chloride containing wastes has been a well-known hazard since municipal waste combustion started back in the mid-1970s [33]. Yasuhara et al. has reported several times on the role of PVC in the formation of dioxins during combustion [34-36]. They found significant correlation between the amount of chloride in the waste and dioxin formation, particularly PCDD. Low temperature, high carbon monoxide conditions were especially effective at forming PCDDs and PCDFs, indicating how important it is to control combustion conditions in municipal combustors.
CHAPTER 3. PRODUCTION OF VALUE-ADDED CHEMICALS FROM THE MIXTURE OF CELLULOSE AND POLYVINYLCHLORIDE IN POLAR APROTIC SOLVENT

A paper submitted to Waste Management for publication

Abstract

Polyvinylchloride (PVC) is the major halogen source in municipal solid waste (MSW) and its recycling is problematic. PVC can not only cause various environmental problems by releasing halogens, but also negatively impact other MSW compositions during waste to energy conversion. For instance, co-pyrolysis of biomass with PVC increases solid residue and promotes the formation of carbon monoxide (CO) and carbon dioxide (CO$_2$) from cellulose. Herein, we report an approach to dehydrochlorinate PVC while simultaneously enhancing the production of valuable chemicals from cellulose. Specifically, cellulose and PVC were co-converted in tetrahydrofuran (THF). It was found that co-conversion of cellulose with PVC significantly increased liquid yield from cellulose and shortened the conversion time compared to converting cellulose alone. Levoglucosan was the major product from cellulose and its highest yield of 38 wt% was achieved with 2.5 wt% of PVC at 335 ℃ after only 8 minutes of reaction. We have shown that the in-situ generated HCl derived from PVC decomposition serves as acid catalyst to enhance glycosidic bond cleavage in cellulose. Moreover, using a THF/water co-solvent could further enhance the conversion rate and increased liquid yield to a maximum of 92 wt%. Pyrolysis of the solid residue did not release chlorinated organics, suggesting that PVC was fully dechlorinated in THF. The present study may be applied to convert PVC-containing, cellulose rich MSW for higher valued products in an environmentally friendly approach.

Introduction

Municipal solid wastes (MSW) are end-life materials consisting of both organic and synthetic polymers, generated from industrial, commercial, and residential sectors [4]. In 2012 alone, over 1.3 billion tons of MSW was produced worldwide and its number continues to increase [37]. Although waste recycling has been actively promoted for years, the majority of MSW still ends
up in landfills [12]. Waste landfilling presents both environmental and economic challenges. Improper waste disposal could cause groundwater and air pollution, and increase greenhouse gas emission [38]. Transporting bulky wastes to remote landfilling sites also creates an economic burden. Alternatively, Waste-to-Energy (WTE) strategies, such as combustion, gasification, and pyrolysis not only reduce the landfilled MSW, but also promote energy recirculation for sustainability. However, WTE is still under development and facing various challenges, which include poor product quality, pollutant formation, and reactor operability [20-22]. These difficulties are mostly attributed to the heterogeneity of MSW compositions [39]. For instance, halogens present in MSW can cause serious environmental issues during waste conversion [32]. Polyvinyl chloride (PVC) is known as the major halogen source in MSW and it is widely used in packaging, piping, wrappings, bottles, and containers. Compared to other major plastic wastes, PVC can easily decompose at low temperatures to release hydrogen chloride (HCl) and other chlorinated organics [24, 40]. Evaporated HCl may promote clogging and corrosion in reactors, and act as a chlorine source for dioxin formation if combusted [34, 41]. In addition, chlorinated organics can cause serious environmental hazards.

Since traditional recycling of PVC from a complex mixture of MSW is difficult [19], dechlorination of PVC containing wastes has been studied. It has been shown that co-pyrolyzing PVC and organic waste materials could reduce HCl emission compared to pyrolyzing PVC alone [42, 43]. However, the remaining Cl atoms end up in the solid residue or liquid product as organic chlorides. The chloride contaminated tar, pyrolysis-oil, and char can cause significant problems in their handling and subsequent applications. During catalytic gasification, the presence of PVC not only reduced tar cracking efficiency, but also accelerated catalyst poisoning [44]. Recently, hydrothermal treatment has been proposed to be an effective method to dehydrochlorinate PVC [40]. Since HCl is solubilized in water, Shen et al. [45] suggested that the solid residue produced from hydrothermal co-conversion of PVC and lignin has potential application as a clean solid fuel.
However, their study also showed that hydrothermal dehydrochlorination is less effective if PVC was co-converted with other organic components, such as cellulose or xylan. PVC not only causes environmental concern due to halogen release, but also has negatively effects on decomposition of other MSW compositions when co-converted. Zhou et al. [42] found that pyrolysis of biomass with PVC increased char yield and the formation of CO and CO₂. It was also reported that PVC-derived intermediates increase char yield during co-pyrolysis of PVC and other plastic wastes [40].

In the present study, a solvent-based co-conversion of cellulose and PVC was investigated. While the focus of the previously mentioned research dealt with PVC containing wastes for dechlorination, the present study aims to take the advantage of PVC dechlorination to enhance cellulose conversion to valuable chemicals. Cellulose is one of the major MSW fractions because nearly 60% of MSW is cellulose-rich organic wastes, such as paper products, yard trimmings, food wastes, and textiles. Cellulose is also known as the most important biorefinery feedstock for biofuels and chemicals [10, 46-48]. For example, glucose or levoglucosan (LG) can be fermented into ethanol and other advanced biofuels. Furfural and 5-hydroxymethylfurfural (HMF) are useful building block chemicals for further upgrading [46, 49]. In this study, cellulose and PVC were co-converted in the polar aprotic solvent tetrahydrofuran (THF). Unlike water or alcohols, polar aprotic solvents do not donate hydrogen. In recent studies, various polar-aprotic solvents have shown promise in their ability to solubilize cellulose or cellulosic biomass with high efficiencies [7, 10, 47, 50]. For example, Luterbacher et al. [50] produced a high yield of soluble carbohydrates from corn stover using γ-valerolactone as the solvent. Cao et al. [10] produced high yields of levoglucosenone (LGO) by converting cellulose in THF. Cai et al. [47] produced furfural, HMF and levulinic acid by converting pine wood in a mixture of THF and water. Bai et al. [51] converted switchgrass in 1,4-dioxane to produce C₅ and C₆ sugar monomers. More recently, Ghosh et al. [7] converted cellulose in seven different types of polar aprotic solvents at supercritical states and obtained 72-98% yield of soluble products.
While cellulose and PVC were co-converted in THF in this study, the main goal was to test a hypothesis that HCl generated from PVC dechlorination in-situ could act as acid catalyst to promote cellulose conversion. If this hypothesis is correct, there is a potential to positively utilize PVC to obtain valuable chemicals from cellulosic wastes among MSW. Among the common polar aprotic solvents, THF was chosen for this proof-of-concept study due to its easy accessibility, low boiling point and biomass-derivable nature [52].

**Materials and Method**

**Materials**

Cellulose from Sigma-Aldrich with an average particle size of 50 µm was used. Stabilized HPLC grade THF with 0.025% butylated hydroxytoluene was purchased from Fisher Chemical. Fine ground PVC was obtained from the Shanghai Yangli Mechanical and Electrical Technology Co., Ltd.

Analytical standards were used for quantification of LG, HMF, furfural, glucose, cellobiose, and cellobiosan. LG (99.9%) and cellobiosan (98.7%) were purchased from Carbosynth Ltd. HMF (99%), furfural (99%), and cellobiose (99.2%) were purchased from Sigma-Aldrich. Glucose (99%) was purchased from Fisher Scientific.

**Method**

The solvent conversion experiments were conducted in 316-stainless-steel Swagelok reactors consisting of two 3/8 inch plugs and a 3/8 inch port connector. The total volume of the reactor was 2 ml. For each experiment, 20 mg of cellulose and 0.25, 0.5 or 0.75 mg of PVC (corresponding to 1.25, 2.5, and 3.75 wt% of cellulose) were added to the reactors along with 1.2 ml of solvent. In the case of PVC conversion alone, 10 mg of PVC was loaded and reacted at 310 °C. The solvent was either THF or a 90/10 (v/v) mixture of THF and deionized water. The sealed reactors were then shaken for 15 minutes to enhance the mixing of the solids in the solvent. An industrial fluidized sand bed was used to supply heat for the reaction. Once the bed reached the preset temperatures, the reactors were dropped into the fluidized sand for heating. After the
desired reaction time was reached, the reactor was quickly taken out of the bed and immediately quenched in a room temperature water bath. The reaction times were counted from when the reactors entered the fluidized bed until they were dropped in the water. Reactions were run in triplicate and presented as averages.

The liquid/solid suspension inside the cooled reactor was first extracted with a syringe. The solid residue was then separated from the liquid using a 0.45 μm glass filter. The solid residue was dried at room temperature overnight before it was weighted. To determine the amount of gas products, the reactor was weighted both before and after the reactor cap was loosened to release the trapped gases.

Yield of liquid product was calculated on a cellulose basis using the following equation:

\[
\text{Liquid product yield wt\%} = \left(1 - \frac{\text{residue wt}}{\text{cellulose wt}}\right) \times 100
\]

**Product Characterization**

An Agilent 7890B Gas Chromatograph (GC) equipped with Mass Spectrometer (MS) and Flame Ionization Detector (FID) with two ZB-1701 (60 m × 250 μm × 0.25 μm) capillary columns was used to analyze the liquid products. Initially the GC oven temperature was held at 40 °C for 3 minutes, and then heated to 280 °C at a ramp of 4 °C/min. Finally, the oven was held at this temperature for additional 4 min. In the GC, helium was the carrier gas with the column flow rate of 1 ml/min, and the split ratio of 20:1 at the GC inlet. The composition of the liquid products was identified with MS and quantified by FID. The compounds were quantified based on calibration curves of the authentic chemicals. For each compound, a five-point calibration was performed to achieve the regression coefficient higher than 0.99.

The liquid products were also analyzed using a Dionex 3000 Ultimate series high performance liquid chromatography (HPLC) system equipped with a RI detector. A Thermo Scientific HyperREZ carbohydrate column was used for monomer quantification with water as the eluent. The flow rate of water was 3 ml/min, and the column temperature was 85 °C. The system
was calibrated for LG, glucose, cellobiosan, and cellobiose. Gel Filtration Chromatography (GFC) was performed with the same system using two Agilent PL aquagel-OH 20 columns kept at 25 °C with the water eluent flown at .8 ml/min. GFC calibration was done with polysaccharide standards.

FTIR analysis of solid residue was conducted using a Thermo Scientific Nicolet iS10 (Thermo Fisher Scientific Inc., Waltham, MA) equipped with a Smart iTIR accessory. The wave numbers of the FTIR analysis ranged from 750 cm⁻¹ to 4000 cm⁻¹. The sample was scanned 32 times at a resolution of 4 cm⁻¹ and interval of 1 cm⁻¹.

The solid residue was pyrolyzed in a Tandem micro-pyrolyzer system (Rx-3050 TR, Frontier Laboratory, Japan). The micropyrolyzer consists of two reactor ovens sequentially connected. The details of the reactor setup can be found elsewhere [53]. A stainless sample cup containing 500 µg of the solid residue was dropped into the top oven maintained at 500 °C. The downstream oven temperature was maintained at 350 °C to prevent vapor condensation. Helium was used as the carrier gas and the pyrolysis vapors were swept into the GC/MS-FID described above for instant product analysis. The flow rate of helium at the front inlet of the GC was 156 ml/min, and the split ratio was 50:1. Cellulose was also pyrolyzed in the same pyrolyzer for comparison.

Ion Chromatography (IC) was conducted to determine the amount of free chloride ions in the liquid product. Analysis was conducted on a Thermo Scientific IC instrument equipped with an IonPac AS12A analytical column and Dionex ERS 500 suppressor. The eluent was 2.7 mM Na₂CO₃/0.3 mM NaHCO₃, flown at 1 ml/min.

**Results and Discussion**

**Effect of PVC**

Figure 3-1 shows the yields of liquid product and solid residue when cellulose was converted in THF at 310 °C with varying amounts of PVC. Since gas yields in this work were negligible, the liquid yields were determined by subtracting the solid residue yields from 100%.
With cellulose alone in THF, the liquid yields were much lower whereas the liquid yields increased dramatically when cellulose was co-converted with PVC, despite PVC being only 1.25 ~ 3.75 wt% of cellulose.

![Graph of residue yield vs. reaction time for different PVC contents](image)

**Figure 3-1.** Yields of (a) solid residue and (b) liquid product with varying amounts of PVC as a function of reaction time (THF, 310 °C).

Increasing the PVC content also accelerated the conversion rate, especially at the early stage of the reaction. At the 8 minute reaction time, yields of solid residue were 40%, 34% and 22% for the 1.25%, 2.5% and 3.75% of PVC cases, respectively, compared to 61% for the non-PVC case. The maximum liquid yield from cellulose was 89.7%, achieved with 2.5% PVC after 20 minutes of reaction time. The optimum liquid yields obtained with the 1.25% and 3.75% PVC cases were similar. In comparison, the maximum liquid yield from cellulose was only 44% at 24 minutes when PVC was absent.

**Major Liquid Products**

Four major species were found in the liquid product: LG, HMF, furfural, and 1.6-anhydro-β-D-glucofuranose (AGF, an isomer of LG). Time resolved yields of LG, HMF, and furfural are shown in Figure 3-2.
Yields of cellulose-derived monomers with varying amounts of PVC as a function of reaction time in THF at 310 °C; (a) no PVC; (b) 1.25% PVC; (c) 2.5% PVC; (d) 3.75% PVC.

The yield of the anhydro monosaccharides (both LG and AGF, but mainly LG) increased significantly by co-converting cellulose with PVC. The maximum yield of the monosaccharides was 40.7% obtained with 2.5% PVC after 16 minutes, compared to 7.3% from the non-PVC case. The increase of the sugar is clear evidence that the presence of PVC promotes glycosidic bond cleavage and therefore cellulose depolymerization. Dehydration reactions were also enhanced by PVC, since the yields of HMF and furfural also increased. In Figure 3-2, the yield of monosaccharides reached a peak then declined, while HMF and furfural yields were relatively steady with the increasing reaction time. The furans can repolymerize to form humins, but LG degradation also produces furans to counter balance the repolymerization loss.

Cellulose depolymerization products could include both anhydro-monosaccharides and oligosaccharides. Since only LG and AGF are GC/MS detectable, the soluble saccharides were also investigated using the GFC and the chromatogram is shown in Figure 3-3. In the figure, the peaks
centered at retention times of 24 min and 27 min stand for celllobiosan (the dimer of LG) and LG, respectively, and the elevated baseline that appears at lower retention times represents the oligosaccharides with higher degrees of polymerization (DP). As shown, the oligosaccharides increased up to the reaction time of 4 minutes. When the reaction time further increased to 6 minutes, the oligosaccharides with higher degrees of polymerization (DP) decreased accompanied by the increases in celllobiosan and LG peaks. This suggests that the high DP oligosaccharides were depolymerized to low DP saccharides as the conversion progressed. On the other hand, the LG peak was observed at 2 minutes, where high DP saccharides were barely detected, and then increased with reaction time. This suggests that LG could be directly produced from cellulose through an alternative pathway, such as end chain unzipping of the glycosidic bonds.

Figure 3-3  GFC analysis of liquid products (reaction condition: cellulose with 2.5% PVC, THF, 310 °C).

It was shown that the addition of PVC had a strong effect on cellulose conversion by enhancing depolymerization and dehydration reactions. Previous studies have shown that acid
catalyst has a similar effect in polar aprotic solvent systems such as the current study [10, 48], however no acid was added in the current study. A plausible explanation is that the cellulose decomposition was catalyzed by the acid produced from PVC in-situ, since PVC is well known to release hydrogen chloride at temperatures as low as 100 °C [19]. It was reported that pyrolytic decomposition of PVC includes two stages. At the initial stage, PVC releases HCl as the main product through dehydrochlorination. Polyene can also be produced at this stage. At the later stage, polyene further degrades to produce liquid and char. Thus, it is likely that PVC derived HCl acted as the acid catalyst to promote cellulose conversion. Nevertheless, it should be noted that there is a distinct difference between using PVC derived HCl to catalytically convert cellulose and converting cellulose in a solvent premixed with acid catalyst. In the latter case, a constant amount of acid is in the solvent throughout the entire conversion process. In the present system, acid is generated in-situ by decomposing PVC. Therefore, the acid concentration in the solvent is expected to be a function of reaction time and temperature. The timing of PVC decomposition compared to cellulose conversion is also critical. In order to catalyze cellulose conversion, PVC has to be decomposed before or simultaneous to cellulose decomposition. To confirm HCl formation, the Cl ions in the liquid product were measured using IC, and corresponding molar concentrations of HCl in the solvent are plotted in Figure 3-4.

HCl was detected as early as 1 min of reaction time, suggesting PVC decomposition initiates rapidly. The HCl concentration continually increased to reach a maximum of 1.4 mM at the reaction time of 10 minutes. Afterward, HCl concentration decreased with increasing reaction time.
Figure 3-4  HCl concentration in solvent and liquid mixture as a function of reaction time (reaction condition: cellulose with 2.5% PVC, THF, 310 °C).

The decrease of HCl was related to the formation of 4-chlorobutanol that was also detected among the liquid product. This compound is the result of a secondary reaction, produced when HCl reacts with THF at elevated temperatures. This secondary reaction of HCl could be prevented by employing a more stable polar aprotic solvent.

It was shown that the HCl from PVC greatly promoted cellulose depolymerization despite its low concentration in the solvent. This strong catalytic activity is attributed to the use of polar aprotic solvent. Polar aprotic solvent can promote depolymerization of polysaccharides by lowering the activation energy for glycosidic bond cleavage, while the exquisite solvation capability can dissolve depolymerized products [6, 7]. Solvent conversion is also greatly affected by acid catalyst. It has been shown that the same amount of acid could have several orders of magnitude stronger catalytic effect in polar aprotic solvents compared to in water or other protic solvents. Mellmer et al. [54] indicated that polar aprotic solvent could affect the stability of the acidic proton relative to protonated transition states, leading to accelerated reaction rates for acid-catalyzed conversion. As a result, even a very small amount of acid can effectively catalyze the reactions.
**Effect of Reaction Temperature**

The effect of reaction temperature on co-conversion of cellulose and PVC was investigated by conducting reactions at 285-335 °C. The PVC amount was fixed at 2.5% as it was the optimum concentration that produced the highest LG yield at 310 °C. As shown in Figure 3-5, increasing reaction temperatures not only accelerated the conversion rate to shorten the reaction time, but also increased the liquid yield.

![Figure 3-5](image_url)

**Figure 3-5** Effect of reaction temperature on (a) residue yield and (b) liquid yield (reaction condition: cellulose with 2.5% PVC, THF).

The yields of cellulose-derived monomers are compared in Figure 3-6 for varied reaction temperatures. Increased yields of LG were obtained at shorter reaction times with higher reaction temperatures. Maximum yield of LG at 335 °C was 38.4%, compared to 36.4% at 310 °C and 29.9% at 285 °C. Additionally, the maximum yield at 335 °C was reached in only 8 minutes, versus 16 minutes and 34 minutes for 310 °C and 285 °C respectively. Furfural yields increased with temperature in a similar way to LG, however HMF yields were more stable in their respective maximum yields between temperature conditions. During co-conversion, reaction temperature affects decomposition of cellulose and PVC differently. For cellulose, higher temperatures promote glycosidic bond cleavage that enhances depolymerization. Higher temperature also allows PVC to...
decompose more rapidly. As a result, HCl concentration in the solvent is expected to increase faster with higher reaction temperature so that cellulose is more readily converted at earlier reaction times. At lower temperatures, both PVC and cellulose decompose slower, making for lower HCl concentrations and giving more time for secondary reactions to limit yields.

Figure 3-6  Yields of cellulose-derived monomers with varied reaction temperature in THF with 2.5% PVC; (a) 285 °C; (b) 335 °C; the yields at 310 °C is previously given in Figure 3-2 (c).

**Effect of Water as a Co-Solvent**

The effect of using water as a co-solvent with THF was also investigated. Previous studies reported that adding water can enhance acid catalyzed conversion of cellulose in polar aprotic solvent [50]. Investigating water effect has a potential significance in converting cellulose and PVC containing wastes since water is almost certainly present as moisture in real world wastes.

Cellulose and 2.5% PVC were converted in a 90/10 (v/v) THF/water at 310 °C, and the product distribution was compared with the above work done at the same conditions but without water.

As shown in Figure 3-7, cellulose conversion was significantly faster with the mixture of THF/water compared to THF alone. Not only does the water addition complete conversion in a shorter time, the yield of liquid product also increased. Within 6 minutes of reaction time, liquid yield was already at 92%, compared to only 66% at 8 minutes of reaction time without water addition.
Figure 3-7 Effect of water as co-solvent on (a) the yield of solid residue and (b) liquid yield (reaction condition: cellulose with 2.5% PVC, 310 °C).

The yields of cellulose-derived monomers with increasing reaction time are plotted in Figure 3-8. Glucose was found among the products, indicating water induced hydrolysis reactions. However LG yield decreased, implying that there is a competition between depolymerization of cellulose into LG and hydrolysis of LG to glucose. The results also showed that the yields of HMF and furfural increase noticeably with the co-solvents. Acid can also catalyze dehydration of glucose to produce HMF and furfural.

Figure 3-8 Yields of cellulose-derived monomers when using 90/10 (v/v) THF/water as the solvent (reaction condition: 2.5% PVC, 310 °C).
The effect of water on the soluble carbohydrates was also studied. The GFC chromatogram given in Figure 3-9 shows that the liquid product obtained with the THF/water co-solvents contains significantly more oligosaccharides than the liquid produced with THF alone, although the monomeric saccharides were more selectively produced in the THF only case. It could be that the oligosaccharides have better solubility in water than THF. Thus, the oligosaccharides with higher DPs could be solubilized and better recovered as liquid products with THF/water co-solvents. With THF alone, these high DP oligosaccharides may remain undissolved until they are further depolymerized into lower DP oligosaccharides with higher solubility.

In Figure 3-9, the peaks for cellobiose are at 23 minutes, then 23.5 minutes for glucose, 24 minutes for cellobiosan, and 27 minutes for LG. All these peaks increased from 2 to 4 minutes, implying hydrolysis and depolymerization occur simultaneously with water as co-solvent. At 6 minutes, the intensities of these peaks all decreased, and a new peak at 19 to 21 minutes of
retention time appears. This new peak could be attributed to secondary degradation or polymerization.

Water can affect acid catalyzed cellulose conversion in polar aprotic solvent, and it may also affect PVC decomposition and accompanying HCl release. To investigate this possibility, PVC alone was converted in THF and THF/water solvents.

![Graph showing conversion of PVC alone in THF or 90/10 (v/v) THF at 310 °C.](image)

Figure 3-10 Conversion of PVC alone in THF or 90/10 (v/v) THF at 310 °C.

In Figure 3-10 it can be seen that the addition of water increases the rate of PVC decomposition. Mass loss at the 8 minute mark is 15% higher for the 90% THF case, but then levels off, whereas the pure THF case has slightly higher conversion but at a later time. It is noteworthy to mention that PVC has some degree of solubility in THF, but none in water. Thus, using THF/water co-solvents should not increase the solubility of PVC. Accordingly, the lower solid mass in THF/water compared to in THF alone is likely due to an enhanced reaction rate of PVC in the co-solvents. Therefore, it can be expected that HCl was released faster in the co-solvents, which also contributed to the higher conversion rate and liquid yield of cellulose.
Char Characterization

The functional groups in the solid residue produced from cellulose and PVC co-conversion in THF was investigated using FTIR. Figure 3-11 shows the FTIR of the 8 and 16 minute reaction times residue compared to unreacted cellulose. The peaks for OH (3330 cm\(^{-1}\)) and C-OH stretching (1000-1100 cm\(^{-1}\)) decreased in the solid residue compared to cellulose. This is due to the glycosidic ring cleavage. Peaks for C-C stretching (1600 cm\(^{-1}\)) and C-O stretching (1700 cm\(^{-1}\)) increased with time, which is a result of cellulose dehydration [55]. The alkyl halide C-Cl peak normally occurs between 600-800 cm\(^{-1}\) was not found in the FTIR of the residues.

![FTIR spectrums of solid residues produced with cellulose and 2.5% PVC in THF at 335 °C compared to pure cellulose.](image)

To further understand the composition of the solid residue, it was pyrolyzed in a micropyrolyzer and the composition of volatile products was analyzed. The solid residue produced at 335 °C at 16 minutes reaction time was pyrolyzed, since that case had the maximum LG yield in the liquid product. The pyrolysis products of the solid residue were similar to pyrolysis of pure cellulose. LG, HMF, furfural and levoglucosenone were found among the pyrolysis vapors. The result suggests that the residue after cellulose depolymerization and dehydration in the liquid
medium still retains some of original cellulose structure. Also, no chlorinated organic compounds were detected among the vapors. Chlorinated organics are commonly found when PVC is pyrolyzed [40], so this is a good indication that the original PVC was fully dechlorinated during the solvolysis reaction and thus precluded organochlorides from forming when pyrolyzed.

**Conclusion**

In this work, we enhanced the production of valuable chemicals from cellulose by co-converting cellulose and PVC in THF. Although PVC content was only 1.25-3.75 wt% of cellulose, its presence significantly increased the yield of liquid product compared to cellulose conversion without PVC. PVC decomposed in THF at the early stage of reaction to release HCl, which then acted as acid catalyst to enhance cellulose depolymerization and accelerate conversion. Liquid products were mainly anhydro-saccharides and the highest LG yield was 40%, achieved with a 2.5 wt% of PVC at 335 °C and 8 minutes of reaction time. The study also showed that using THF/water co-solvents can further accelerate the conversion and reduce the amount of solid residue. Moreover, pyrolysis of the solid residue did not generate chlorinated organics, implying the absence of cross interactions between cellulose and PVC. Overall, this preliminary study presents a potentially attractive route for producing value-added products from halogen containing cellulose rich wastes. Instead of being evaporated during pyrolysis or gasification of PVC, HCl can be dissolved in the solvent to reduce pollutant release. Also, the secondary reaction of HCl could be avoided by choosing HCl non-reacting polar-aprotic solvents. In future studies, the concept will also be applied to convert representative MSW.
CHAPTER 4. TWO STEP CONVERSION OF MSW USING SOLVENT LIQUEFACTION AND PYROLYSIS

Introduction

Development of advanced biofuels will potentially help to reduce dependence on foreign oil and reduce greenhouse gas emissions. Domestic production of energy can provide jobs and sustain our economy from within and lessen our reliance on foreign governments. Biofuels can be produced from almost any type of organic matter, including that found in our trash. Waste disposal by landfilling is a practice as old as civilization itself. If we were able to update this outdated way of disposal it would be possible to increase biofuels production, reduce wasted resources, and improve our land use management.

Waste to energy (WTE) technologies such as combustion, gasification, and pyrolysis attempt to use municipal solid waste (MSW) normally destined for landfill to produce useful energy or chemicals. However several issues arise when these technologies are applied to inherently dirty feedstocks such as MSW. Halogens contained in MSW tend to promote char formation, corrode reactors, and generate numerous genotoxic compounds such as polychlorinated dibenzo-p-dioxins (PCDDs) and other chlorinated aromatic compounds [20-22, 56, 57]. Polyvinyl chloride (PVC) is one of the major plastic resins found in MSW and it is the main source of halogen in MSW [56].

PVC is well known to decompose at temperatures as low as 100 °C [19, 24, 40]. It starts by releasing hydrogen chloride (HCl), then transitions to producing aromatics and other hydrocarbons as the temperature increases. Due to its highly toxic and corrosive nature, this release of HCl must be taken into consideration when WTE technologies are used, and many studies have been conducted to determine a suitable method for dechlorination. For example, several researchers [27, 28, 30, 58] have proposed a so called stepwise pyrolysis scheme, where pyrolysis temperatures are initially held around 350 °C to drive off HCl, then are increased once the majority of chloride is removed. One study [30] found this method to be 99.5% efficient at chlorine removal at 1 minute of
reaction time. These are notable results, however the first stage still consists of HCl gas, which is highly corrosive and must be collected and neutralized using ancillary equipment.

Other researchers [41, 45] used hydrothermal routes to convert chloride containing MSW into solid fuel meant for use as a coal substitute. They achieved chlorine removal efficiencies as high as 90% by co-converting PVC and lignin. However, the efficiency decreased when PVC was co-converted with cellulose. Moreover, heating water can be a thermodynamically expensive technique, and the targeted products from their process were low-value solid fuels for combustion.

We previously suggested a new approach to convert PVC containing wastes in polar aprotic solvent. Our previous work showed that the HCl released from PVC conversion could, in-situ, act as an acid catalyst to promote conversion of cellulose to sugars and other valuable chemicals. We found that the addition of small amounts of PVC increased the conversion rate despite low HCl concentrations. With only 2.5 wt% of PVC, levoglucosan yield increased by more than 5 times. Moreover, the solid residue remaining after the solvent treatment did not contain chloride. This treats the HCl inherent in PVC waste as an asset instead of a liability.

The present study expands on our previous work by using a surrogate MSW. MSW consists of both organic and plastic synthetic materials, and we propose a two-step conversion strategy. Firstly, PVC containing MSW is converted using polar aprotic solvent. It is hypothesized that PVC would decompose during the first stage to release HCl, therefore promoting the conversion of organic waste to useful chemicals. It is also hypothesized that major plastic wastes (non-PVC plastics) do not decompose during solvent treatment due to their higher thermal stability. Thus, the solid residue remaining after the solvent liquefaction can be chloride free, high energy density plastics. At the second step, this solid residue can be pyrolyzed to produce cleaner and higher quality fuels. Compared to a single stage pyrolysis, the proposed two stage conversion has potential to produce higher quality products. To test the above hypotheses, a mixture of cardboard (CB), PVC, and polyethylene (PE) was converted in a tetrahydrofuran/water mixture. The liquid products
were analyzed for the yield and chemical composition. The solid residue was then pyrolyzed to produce hydrocarbon fuel range chemicals. CB is one of the major organic wastes in MSW stream and PE is the most abundant waste plastic [59].

**Materials and Method**

**Materials**

Clean CB was recovered from a recycling bin and reduced to a fluffy powder using a knife mill. Tetrahydrofuran (THF) with 0.025% butylated hydroxytoluene was purchased from Fisher Scientific. Fine ground PVC and PE were purchased from Shanghai Yangli Mechanical and Electrical Technology Co. Ltd.

**Method**

Solvent liquefaction reactions were conducted in a 300 mL autoclave stirred tank reactor made from 316 stainless steel. For each experiment, approximately 7 g of CB was weighed and added to the reactor, along with 150 mL of 90/10 (v/v) THF and water co-solvent. PVC and PE were the variables being tested and were added accordingly. A 1 wt% (CB basis) addition of PVC (70mg) and 15 wt% (CB basis) addition of PE (1050mg) were used to maintain similar ratios to what is found in real MSW. Once all fractions were added to the reactor, it was bolted to the apparatus and charged with ~100 psi of nitrogen. Reactions were carried out at 250 °C which required about 50 minutes of heating to reach. Time zero was once the vessel reached 250 °C. Samples were taken at various times through a dip tube which was immersed in the reaction solvent. Upon completion of the reaction time, the heat was turned off, the heater removed, and cooling water circulated through a spiral immersion chiller in the reaction liquid. Cooling took approximately 1 hour. Three different cases were examined and hereafter referred to as CB (for CB only), CB+PVC (for CB and PVC mixed together), and CB+PVC+PE (for CB, PVC, and PE mixed).

Remaining solids were filtered and weighed to determine the amount of initial CB that dissolved into liquid. Liquid yield was calculated based on the initial mass of CB.
An Agilent 7890B Gas Chromatograph (GC) equipped with Mass Spectrometer (MS) and Flame Ionization Detector (FID) with two ZB-1701 (60 m × 250 μm × 0.25 μm) capillary columns was used to analyze the liquid products. Initially the GC oven temperature was held at 40 °C for 3 minutes, and then heated to 280 °C at a ramp of 4 °C/min. Finally, the oven was held at this temperature for additional 4 min. In the GC, helium was the carrier gas with the column flow rate of 1 ml/min, and the split ratio of 20:1 at the GC inlet. The composition of the liquid products was identified with MS and quantified by FID. The compounds were quantified based on calibration curves of the authentic chemicals. For each compound, a five-point calibration was performed to achieve the regression coefficient higher than 0.96.

A gel permeation chromatography (GPC) analysis was also performed on the liquid products to determine the presence of non-volatile compounds. A Dionex Ultimate 3000 HPLC system with diode array detector was used with THF as the mobile phase. Polystyrene standards were used to calibrate the system for molecular weight distribution. Two Agilent PLgel 3 μm x 100 Å, 300 mm x 7.5 mm columns and one Mesopore 300 mm x 7.5 mm column were used with THF flowing at 1 ml/minute.

FTIR analysis of solid residue was conducted using a Thermo Scientific Nicolet iS10 (Thermo Fisher Scientific Inc., Waltham, MA) equipped with a Smart iTR accessory. The wave numbers of the FTIR analysis ranged from 750 cm⁻¹ to 4000 cm⁻¹. The sample was scanned 32 times at a resolution of 4 cm⁻¹ and interval of 1 cm⁻¹.

The solid residue was pyrolyzed in a Tandem micro-pyrolyzer system (Rx-3050 TR, Frontier Laboratory, Japan). The micropyrolyzer consists of two reactor ovens sequentially connected. The details of the reactor setup can be found elsewhere [53]. A stainless sample cup containing 250 μg of the solid residue was dropped into the top oven maintained at 500 °C. The downstream oven temperature was maintained at 350 °C to prevent vapor condensation. Helium was used as the carrier gas and the pyrolysis vapors were swept into the GC/MS-FID described
above for product analysis. The flow rate of helium at the front inlet of the GC was 156 ml/min, and the split ratio was 50:1.

Ultimate analysis of solid residue recovered from the autoclave reactor was conducted using an Elementar elemental analyzer (vario MICRO cube). Samples of 5 mg were combusted at 900 °C and the products were quantified using a TCD. Weight percentages of C, H, N, and S were then calculated based on the amounts of these combustion products, with oxygen calculated as the difference.

Thermogravimetric analysis (TGA) was performed on the residue using a Mettler Toledo TGA/DSC Star System. Samples of 20 mg were heated in a nitrogen atmosphere from 25-105 °C at 10 °C/minute, then held at 105 °C for 40 minutes. The temperature was then increased to 900 °C at 10°C/minute and held there for 20 minutes. Air was introduced for 30 minutes to combust the remaining char at 900 °C.

Results and Discussion

Liquid Product

The liquid yields of the three different cases is shown in Figure 4-1. For CB alone, the liquid yield peaks at 66.6% at 2 hours. For CB+PVC, peak liquid is 66.2% at 1 hour of reaction time, with only a slight decrease after 2 hours of reaction. CB+PVC+PE had the highest liquid yield at 68.7% at 45 minutes. The CB+PVC reached the high liquid yield significantly faster than the CB case. The CB+PVC and CB+PVC+PE cases had similar results, however CB+PVC+PE had higher yield at the 45 minute mark.
Figure 4-1 Yields of (a) solid residue and (b) liquid product from CB, CB + PVC, and CB + PVC + PE. Reactions were done at 250 °C with 7 g of CB, 70 mg PVC, and 1050 mg PE.

For all cases, the peak liquid yield is approximately 64 to 68%. Both cases with PVC had significant increases in reaction rate. PE addition seemed to increase the liquid yield over PVC.

Composition of the liquid product

A list of all products identified by GC/MS is shown in Table 4-1. It can be seen there are a large number of furans, light oxygenates, and lignin monomers from the degradation of CB, as CB contains both carbohydrates and lignin. No short chain alkenes were detected, which would be expected if PE were decomposing. Benzene is present in the CB+PVC and CB+PVC+PE cases, which can be produced from PVC or CB during pyrolysis [29].
Table 4-1 A list of the GC/MS detectable compounds found in the liquid product.

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>compound</th>
<th>FID retention time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>furan</td>
<td>6.12</td>
</tr>
<tr>
<td>2</td>
<td>2-methyl-furan</td>
<td>7.50</td>
</tr>
<tr>
<td>3</td>
<td>benzene</td>
<td>9.00</td>
</tr>
<tr>
<td>4</td>
<td>2,5-Dimethylfuran</td>
<td>9.85</td>
</tr>
<tr>
<td>5</td>
<td>acetic acid</td>
<td>10.90</td>
</tr>
<tr>
<td>6</td>
<td>1-hydroxy-2-propanone</td>
<td>11.95</td>
</tr>
<tr>
<td>7</td>
<td>toluene</td>
<td>12.20</td>
</tr>
<tr>
<td>8</td>
<td>3-hydroxy-2-butanone</td>
<td>13.35</td>
</tr>
<tr>
<td>9</td>
<td>propanoic acid</td>
<td>14.50</td>
</tr>
<tr>
<td>10</td>
<td>1-hydroxy-2-butanone</td>
<td>15.74</td>
</tr>
<tr>
<td>11</td>
<td>3-pentanol</td>
<td>16.68</td>
</tr>
<tr>
<td>12</td>
<td>2-hydroxy-3-pentanone</td>
<td>17.05</td>
</tr>
<tr>
<td>13</td>
<td>furfural</td>
<td>18.24</td>
</tr>
<tr>
<td>14</td>
<td>tetrahydrofurfural alcohol</td>
<td>19.20</td>
</tr>
<tr>
<td>15</td>
<td>furfuryl alcohol</td>
<td>19.98</td>
</tr>
<tr>
<td>16</td>
<td>2-Methyl-2-cyclopentenone</td>
<td>20.52</td>
</tr>
<tr>
<td>17</td>
<td>4-chloro-1-butanol</td>
<td>23.26</td>
</tr>
<tr>
<td>18</td>
<td>5-methyl-furfural</td>
<td>23.65</td>
</tr>
<tr>
<td>19</td>
<td>butyrolactone</td>
<td>24.42</td>
</tr>
<tr>
<td>20</td>
<td>o-Guaiacol</td>
<td>28.25</td>
</tr>
<tr>
<td>21</td>
<td>Butanoic acid, 2-furanylmethyl ester</td>
<td>31.48</td>
</tr>
<tr>
<td>22</td>
<td>levulinic acid</td>
<td>31.59</td>
</tr>
<tr>
<td>23</td>
<td>eugenol</td>
<td>37.32</td>
</tr>
<tr>
<td>24</td>
<td>5-HMF</td>
<td>37.80</td>
</tr>
<tr>
<td>25</td>
<td>Syringol</td>
<td>38.22</td>
</tr>
<tr>
<td>26</td>
<td>isoeugenol</td>
<td>40.65</td>
</tr>
<tr>
<td>27</td>
<td>vanilin</td>
<td>41.42</td>
</tr>
<tr>
<td>28</td>
<td>1,6-Anhydro-2,3-dideoxy-β-D-erythro-hexopyranose</td>
<td>44.15</td>
</tr>
<tr>
<td>29</td>
<td>1,6-Anhydro-2,3-dideoxy-β-D-threo-hexopyranose</td>
<td>44.30</td>
</tr>
<tr>
<td>30</td>
<td>Levoglucosan</td>
<td>47.85</td>
</tr>
<tr>
<td>31</td>
<td>Methoxyeugenol</td>
<td>48.40</td>
</tr>
</tbody>
</table>
Figure 4-2 shows FID chromatograms of the liquid from each condition. Although the product distributions are similar with the three feedstock conditions, there is a notable increase in peak sizes of the cases with plastic added.

Figure 4-2 GC/FID chromatograms of the liquid products at 45 minutes of reaction time with selected products labeled.
Yields of six selected major compounds in the liquid product were quantified using GC/FID and are shown in Figure 4-3. For four of the six compounds, the CB+PVC and CB+PVC+PE cases had increased yield over the CB case, despite the overall liquid yield being almost equal at the two hour mark, indicating PVC or PVC+PE addition produced valuable chemicals in higher concentrations. Only one species, tetrahydrofurfural alcohol, had higher yield without plastic addition.

The differences between the CB+PVC and CB+PVC+PE cases are less dramatic. For each compound quantified they follow the same trend and result in similar yields. However, furfural yields are initially higher at the first three data points, indicating PE may have an effect in the primary decomposition of cellulose or hemicellulose to furfural. Furfural is thought to be produced from hexoses through the selective cleavage of the C-C bond [60].

GPC analysis of the liquid generated from the CB+PVC+PE case was conducted to investigate its molecular weight distribution. GPC columns separate the sample based on molecular size, with larger molecules eluting faster than smaller ones; this allows for determination polymers that are not volatile enough to be detected by GC/MS. In Figure 4-4, the peaks appearing at retention times from 16-23 minutes corresponding to large oligomers and the peaks shown at retention times between 24 and 26.8 minutes correspond to monomers and dimeric products. The intensity of all the peaks increased as the reaction progresses due to the higher concentrations of the compounds in the liquid. The monomer/dimer peaks nearly did not change between 45 minutes reaction and 120 minutes reaction. However, the large oligomer peaks increased significantly with the 120 minutes reaction. This is likely due to repolymerization reactions between the CB products. The extended time inside the closed reactor could promote secondary repolymerization of primary products [61].
Figure 4-3 Yields of six of the major compounds found in the liquid product.
Residue Characterization

The functional groups in the residue were studied using FTIR. In Figure 4-5, the peaks for the OH groups (3330 cm⁻¹) decrease in this order: unreacted CB > CB+PVC ~ CB+PVC+PE, likely due to glycosidic bond cleavage from cellulose depolymerization.
The two large peaks (2800-2900 cm\(^{-1}\)) in the CB+PVC+PE case are from the alkyl C-H stretch, indicating PE remains in the residue. The peaks at \(\sim 1600\) cm\(^{-1}\) corresponding to C=O or C=C stretching all increased significantly over the unreacted CB, indicating cellulose dehydration reactions. Peaks at 1000-1100 cm\(^{-1}\) are from C-OH stretching and they decrease with the addition of plastic, also indicating cellulose dehydration. There are clearly significant differences between the unreacted CB and the residues. However in the previous data it was unclear whether the addition of PE had an effect over the CB+PVC case. In Figure 4-5 it can be seen that the CB+PVC and CB+PVC+PE cases do not overlap, especially in the 1600 cm\(^{-1}\) and 1000-1100 cm\(^{-1}\) ranges, corresponding to an increase in C=C or C=O groups, and a decrease in C-OH groups respectively.

![Figure 4-6](image)

Figure 4-6 Separated residue from the CB+PVC+PE 60 min case. Large PE agglomerates can be seen in the left pile.

Two types of solid residue were recovered in the CB+PVC+PE case. In Figure 4-6, the residue shown in the right side was a homogenous fine powder, whereas the left side residue was agglomerated, probably because of PE remaining in the residue. The two types of the residue were pyrolyzed to determine the effect the pretreatment had on their susceptibility to conversion.
Figure 4-7 shows pyrolysis FID chromatograms of the two types of solid residues produced from co-conversion of CB+PVC+PE (pictured in Figure 4-6), compared to unreacted CB+PVC+PE.

Figure 4-7 Pyrolysis chromatograms of the CB+PVC+PE residue compared to the unreacted feedstocks.
The pyrolysis products of the residue are similar to that of pure PE, consisting of alkanes and alkenes with different carbon numbers. These hydrocarbons are produced from the cleavage of the PE chain. This result indicates that the sold residue mainly consists of unconverted PE since CB and PVC are mostly removed as liquid products. In comparison, direct pyrolysis of unreacted CB+PVC+PE resulted in a much more complex product distribution, consisting of both CB-derived oxygenated products and some PE-derived aliphatic hydrocarbons. Undesirable chlorinated organics were also detected in this case, indicating HCl from PVC can interact with CB. In comparison, no chlorinated organics were detected in either of the residues during pyrolysis.

An elemental balance of the CB+PVC+PE residue compared to the unreacted raw materials was performed and is shown in Table 4-2. Hydrogen and especially carbon show significant increases in the residue. This is likely due to several reasons, the first being the condensation reactions that take place in the CB. This is supported by the reduction in oxygen by nearly half, as well as the reduction in OH functionality groups that was shown in Figure 4-5. The second reason is from the concentration of PE in the residue. The GC/MS of Table 4-1 and GPC analysis shows there is no breakdown of PE in the liquid, but a significant amount of mass of CB is removed. Therefore the ratio of PE to CB is increased in the residue, which increases carbon and hydrogen numbers due to PE only being composed of carbon and hydrogen.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
<th>S %</th>
<th>O %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB+PVC+PE 45 minute residue</td>
<td>68.795</td>
<td>8.158</td>
<td>0.235</td>
<td>0.0135</td>
<td>22.7985</td>
</tr>
<tr>
<td>Unreacted CB+PVC+PE</td>
<td>51.72</td>
<td>6.652</td>
<td>0.195</td>
<td>0.0515</td>
<td>41.3815</td>
</tr>
</tbody>
</table>

These results support the benefits of the two-step reaction scheme proposed here, versus a single step pyrolysis. Lower oxygen and higher carbon content feedstocks provide higher heating values, which in turn reduce operating costs associated with heating pyrolyzers. Additionally, the bio-oil produced is less likely to have oxygenated species.
Figure 4-8 shows the TGA performed on the residue to determine ash content and weight loss behavior compared to the unreacted raw materials.

![Graph showing TGA of the CB+PVC+PE 45 minute residue compared to the unreacted raw products.]

Figure 4-8 TGA of the CB+PVC+PE 45 minute residue compared to the unreacted raw products.

The residue shows significant differences in weight loss behavior compared to the unreacted products. The residue has gradual volatile loss with no definite stages until 430 °C, which corresponds to the temperature of PE decomposition in a TGA [62]. Alternatively, the unreacted CB+PVC+PE has distinct weight loss stages from CB volatile loss at 250 °C, followed by a bump at 430 °C from PE decomposition. PE volatile loss in both samples happens at roughly the same temperature, indicating PE was not significantly chemically altered during solvent liquefaction. Additionally, the amount of volatile loss from PE is much larger in the residue due to the removal of CB products during the solvent liquefaction step, which concentrated the PE in the residue. The ash content in the raw materials was 4.4%, which increased to 6.5% in the residue. This is expected because ash was only present in the CB, however the increase is lower than predicted. During
solvent liquefaction, 68% of the CB is removed, but ash content is only increased by 47%. This discrepancy could be from ash being removed during solvent liquefaction.

**Conclusion**

Mixtures of CB, PVC, and PE (a surrogate for MSW) were first liquefied in polar aprotic solvent to remove chlorine and obtain liquid products from CB. The residue was then pyrolyzed to obtain valuable hydrocarbons from PE. We found that PVC catalyzed CB decomposition during solvent liquefaction due to its release of HCl, and that PE did not interact. When the residue was pyrolyzed, large amounts of hydrocarbons were seen from the decomposition of PE, and no volatile chlorinated organics were detected, indicating solvent liquefaction was effective at removing the chloride. These results outline a potentially useful two step conversion method for MSW for the production of fuel grade chemicals.
CHAPTER 5. CONCLUSION

Biofuels are an important part of the American economy and have the potential to reduce greenhouse gas emissions from internal combustion engines. Current biofuel production practices use corn starch to produce sugar for fermentation into ethanol, or lipids from soybeans for transesterification into bio-diesel. These feedstocks are edible and could be used as cattle feed or exported to foreign countries. This makes for a so-called food versus fuel debate that questions the usefulness of food based biofuels. To combat this, second generation biofuels have been developed that are made from the inedible (lignocellulosic) portion of plants. These new biofuels are advantageous in that they are made from waste products and that they further reduce greenhouse gas emissions over conventional biofuels.

Making lignocellulosic fuels affordable is a critical step in realizing their long term viability, and feedstock cost is generally one of the main drivers in determining if an operation can break even. One of the cheapest feedstocks is municipal solid waste (MSW), otherwise known as garbage. MSW contains significant percentages of cellulosic organic material that can potentially be transformed into fuels by using thermochemical conversion. A major drawback when using MSW for feedstock is the presence of contaminates. Polyvinyl chloride (PVC) is a common plastic found in MSW, and it can cause significant problems during thermochemical conversion due to its release of hydrochloric acid at low temperatures.

Two separate studies were carried out to determine the effect of PVC on the dissolution of feedstocks during the thermochemical conversion strategies solvent liquefaction and pyrolysis. The first study used solvent liquefaction with cellulose as the feedstock and different percentages of PVC. It was determined that the addition of PVC increased the reaction rate and overall yield of liquid products. In particular, the anhydrosugar levoglucosan reached a maximum yield of 38 wt% cellulose basis. This catalytic effect of PVC was attributed to its release of hydrochloric acid, which was found in the solvent after reaction.
The second study used a two-step conversion strategy, employing solvent liquefaction first, followed by pyrolysis. Corrugated cardboard was the feedstock, with PVC and polyethylene (PE) addition to determine their effect. This study was carried out in a much larger reaction vessel and with a lower reaction temperature than the previous study with cellulose. The addition of PVC increased the rate of liquid yield from cardboard during solvent liquefaction, and PE did not interact. The highest liquid yield was found to be 68.7 wt% cardboard basis at 45 minutes of reaction time with both plastics added. Pyrolysis of the residue from solvent liquefaction yielded high amounts of hydrocarbons from the PE.

These two studies outline a new method for obtaining valuable chemicals from MSW, while avoiding the pitfalls that commonly occur when attempting traditional thermochemical conversion on MSW. Chloride released from PVC can be harmful to people, equipment, and the environment, and it has traditionally been dealt with through separation and neutralization. This work aims to use it as an asset, while still ensuring its proper ultimate disposal.
REFERENCES


[38] Kumar A, Sharma M. Estimation of GHG emission and energy recovery potential from MSW landfill sites. Sustainable Energy Technologies and Assessments 2014;5:50-61.


