

Volume Reduction of Expanded Polystyrene with Limonene

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Abstract: Expanded polystyrene (EPS) is widely used in packaging but it has significant environmental challenges due to its non-biodegradable nature and the inefficiency of conventional recycling methods, such as chemical, mechanical and thermal recycling, which are often costly and environmentally unfriendly. Unlike many plastics, EPS can dissolve in certain organic solvents, but these solvents typically have negative environmental impacts. This study has explored an eco-friendly alternative by utilizing agricultural waste, citrus fruit peels from oranges, mosambi and rough lemons, which are typically discarded. These peels contain a naturally occurring secondary metabolite called limonene, capable of reducing volume of EPS and dissolving it into a semi-solid form. This semi-solid material can then be further processed to recover polystyrene products or the monomer styrene through pyrolysis for reuse. This method not only reduces the volume of EPS waste but also provides a sustainable recycling pathway using natural, biodegradable solvents, thereby regulating environmental pollution.

Keywords: limonene, polystyrene, citrus fruit, styrene

I. INTRODUCTION

The word *plastic* originates from the Greek term *plastikos*, meaning “able to be molded into different shapes” [1]. Plastic is a non-biodegradable material that does not break down easily. According to the Association of Plastic Manufacturers in Europe (APME), the most commonly used plastics are classified into two categories: thermoplastics such as polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyethylene terephthalate etc and thermosets, which include polyurethane, polyester, vinyl ester, silicon, and melamine resin. Thermoplastics are used more widely than thermosets because they can be recycled [2].

Polystyrene (PS) accounts for at least 6% of the world’s plastic production [3]. It is typically manufactured in three forms: extruded polystyrene, expanded polystyrene foam, and extruded polystyrene foam, each serving various applications [4]. Over the past two decades, the production of expanded polystyrene (commonly known as thermocol) has risen sharply due to its versatility in products like disposable trays, cups, packaging materials, containers, and insulation boards for floors, walls, and roofs. Consequently, the accumulation of thermocol waste in the environment has become a significant concern. Improper disposal or burning of thermocol releases harmful chemicals into the environment [20].

Thermocol, the commercial name for expanded polystyrene (EPS), is typically white and made from pre-expanded polystyrene beads. Its lightweight, rigidity, and moldability contribute to its widespread use [17]. In 2016, global production of polystyrene and EPS reached approximately 14.7 million metric tons (MMT) and 6.6 MMT per year, respectively [5]. Since EPS takes around 500 years to degrade completely [19], it is crucial to minimize its production and promote recycling and reuse.

Common organic solvents used to dissolve EPS include acetone, methanol, chloroform, and toluene [6]. Although effective, these solvents are highly toxic, polluting, and pose environmental hazards. To address these issues, we explored more environment friendly alternatives such as limonene. Limonene is a naturally occurring compound found abundantly in the oils extracted from citrus fruit peels, including mosambi (*Citrus limetta*), rough lemons (*Citrus jambhiri*), limes (*Citrus aurantiifolia*), grapefruits (*Citrus paradisi*) and oranges (*Citrus sinensis*). Chemically, limonene is a monoterpene characterized as cyclohex-1-ene with a methyl group at position 1 and a prop-1-en-2-yl group at position 4, making it a



cycloalkene and a p-methadiene [7]. Current study specifically concentrates on orange, mosambi and rough lemon, as their potential applications in the volume reduction of EPS.

II. MATERIALS AND METHODS

Collection and peeling of citrus fruits

Citrus fruits like mosambi, orange, rough lemon, etc. were collected from nearby source and cleaned it. After sample collection the rind of citrus fruits were removed by peeling using kitchen peeler [9].

Extraction of limonene

A steam distillation procedure was performed at 25g mass of citrus peel fruits. The sample was mixed with 100 ml of distilled water. The steam distillation was performed until the medium volume boiled down to a half of its initial volume. Once the distillation procedures were finished, a hydrophobic layer could be visible in each of the tested samples. It was taken out of the tubes with a syringe [10].

Functional group detection test

KMnO₄ test: Added 1% alkaline potassium permanganate solution drop wise to the extracted citrus oil and shaken it, observed for pink colour disappearance which indicates unsaturation.

Bromine water test: Added dilute bromine water solution to the citrus oil extracted. Observed for change in the colour of the Bromine water from red-brown to pale yellow which indicates unsaturation.

FTIR test: The functional groups of peels of citrus fruit extracts were identified by FTIR (Fourier Transform Infrared Radiation). The steps were carried out as per protocol given in the manual. Styrene obtained after pyrolysis of EPS was also analysed through FTIR spectroscopy [11].

Volume reduction of polystyrene

The type of EPS used in this study was foam sheet. EPS was placed in a beaker and its volume was reduced with the help of essential oil limonene extracted from the peels of citrus fruits [8].

Recovery of Limonene

The produced mixture of limonene and EPS was then treated with the methanol as it separates the EPS from limonene. The mixture of limonene and methanol separated from jelly like EPS was steam distilled. As considering their boiling points methanol boils very earlier than the limonene i.e. at 64.7°C, so they can be easily separated and limonene can be recovered and can be reused.

Depolymerisation of polystyrene

The volume reduced EPS was heated inside the flask with a Bunsen burner (roaring flame). The depolymerisation started within a minute. A cloudy gas of styrene travelled through the condenser down to the round bottom flask where it stayed at the bottom and condensed. As styrene cooled down, a white- yellow oily liquid with a strong and unpleasant smell was formed [12].

III. RESULTS AND DISCUSSION

Extraction of limonene

The essential oil content from peels of orange, rough lemon and mosambi are presented in Table 1. The maximum yield obtained in case of mosambi i.e. 13.44% followed by orange and rough lemon at 96°C for 30 min. The direct extraction by heating would result in decomposition whereas steam distillation does not destroy the chemicals involved. Increase in temperature and heating time resulted in increase in limonene yield[10]. Optimized hydrodistillation of *Citrus sinensis* peels produced 3–4% essential-oil, whereas un-optimized hydrodistillation yielded slightly lower oil [33]. Reports suggest that species such as pomelo (*Citrus maxima*) yields far less oil only 0.96–1.09% [34]. Reviews on lemon, bitter orange, and sweet-lime indicated highly variable yields (approximately 0.5–1.3% oil and wide-ranging limonene



content), and industrial waste-peel processes often yield very little oil (e.g., **0.52%** on a dry basis), though limonene remains the dominant constituent [35].

The percentage yield was calculated by following formula [21].

$$\% \text{ Yield} = \frac{\text{Oil obtained (gm)}}{\text{Sample weight (gm)}} \times 100$$

Table1: Percent yield of extracted limonene from different peels of citrus fruits

Fruit Name	Mass of peels used (g)	Limonene Yield (g)	Yield percentage
Orange	25	1.176	4.704 %
Rough Lemon	25	1.26	5.04%
Mosambi	25	3.36	13.44%

Functional group detection

When KMnO_4 test was performed, disappearance of pink color had shown presence of unsaturation present in limonene and styrene. Similarly in bromine water test, color changed from red-brown to pale yellow confirmed presence of unsaturation in limonene and styrene [23]. FTIR analysis was carried out to confirm functional groups present in the limonene (from different natural sources), the resulting spectra showed satisfactory matches with standard reference spectra, indicating successful isolation and identification of the target compounds.

The FTIR spectra of citrus samples show characteristic limonene functional groups. Among them, Mosambi exhibits the closest match to standard limonene, with nearly identical C–H and C=C stretching bands, indicating high limonene content. Orange also showed strong similarity with minor peak shifts, while Rough lemon displays noticeable deviations, suggesting the presence of other compounds and comparatively lower limonene dominance.

Table 2: FTIR analysis of limonene

Bond Stretching	Standard limonene	Orange	Rough lemon	Mosambi
C-H (alkene)	3082 cm^{-1}	3090 cm^{-1}	2950 cm^{-1}	3082 cm^{-1}
C-H (alkane)	2965 cm^{-1}	2950 cm^{-1}	2850 cm^{-1}	2964 cm^{-1}
C=C	1644 cm^{-1}	1640 cm^{-1}	1645 cm^{-1}	1644 cm^{-1}
C-C (alkane)	1435 cm^{-1}	1500 cm^{-1}	1500 cm^{-1}	1436 cm^{-1}

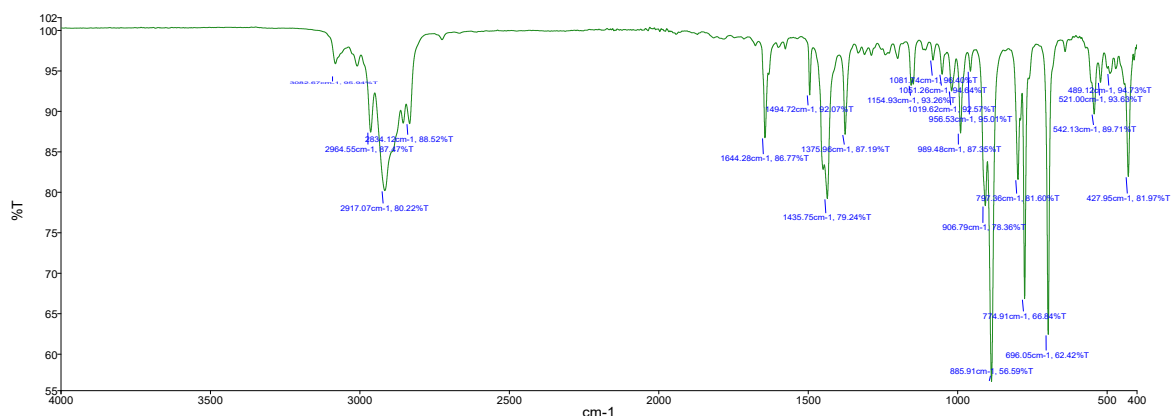


Fig1: Standard limonene FTIR



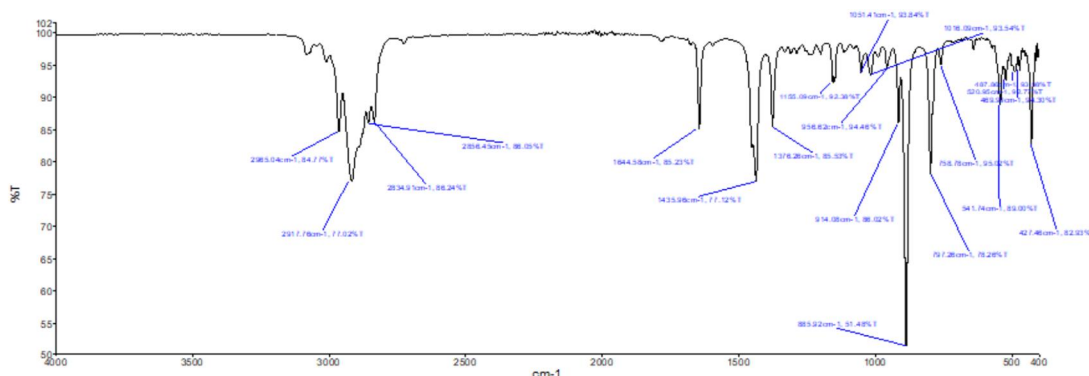


Fig2: Limonene FTIR from orange

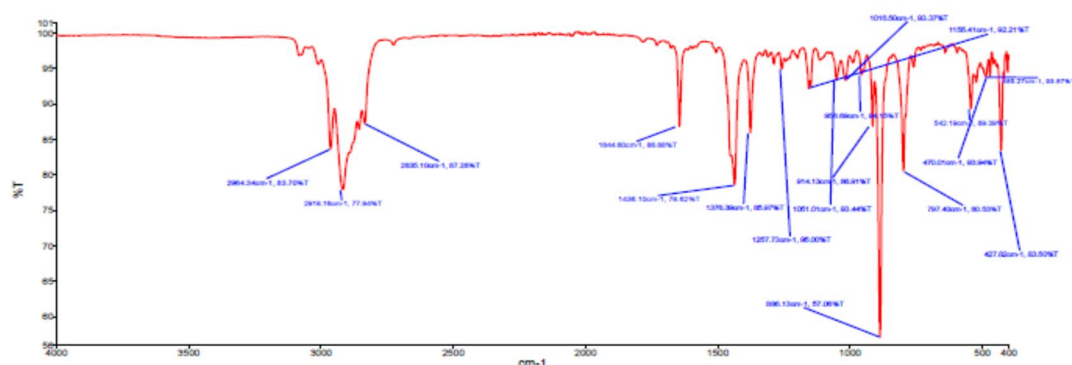


Fig3: Limonene FTIR from rough lemon

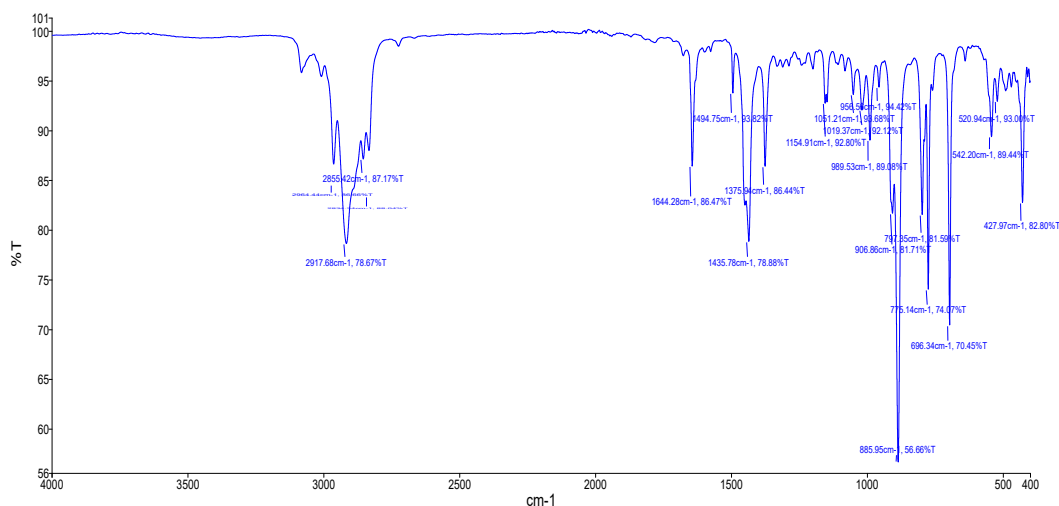


Fig4: Limonene FTIR from Mosambi

Volume Reduction of EPS

The type of EPS used in this study was foam sheet. EPS was placed in a petri plate and the volume of EPS was reduced with the help of essential oil limonene present in the peels of citrus fruit [8]. The treatment reduced the EPS volume from 129.2 cm³ to 1.5 cm³, corresponding to a 98.83% reduction.



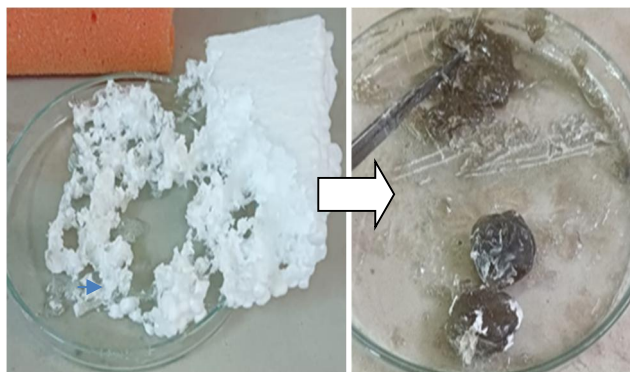


Fig5: Volume Reduction of Polystyrene

Hardjono highlighted disintegrating polystyrene based on the essential oil-D-Limonene, ethanol and water, in proportions of 1:0:0; 1:0:3; 1:1:2; 1:2:1 and analyzed the time it took to disintegrate various forms of EPS (food packaging, electronic packaging, foam boards and cup noodles). He demonstrated that the most suitable ratio for disintegration was 1:1:2, with a higher percentage of destruction of 9.37% for electronic packaging [8].

Solvents such as gasoline, toluene, xylene, chloroform and tetrachloroethane (CCl_4) used to dissolve expanded polystyrene. The results had shown that it took a day to form a homogeneous mixture with gasoline [37]. Whereas, biobased vegetable oil limonene act as an antioxidant that prevents chains from scission caused by radicals, this approach reduces the volume of EPS foam by a factor of 20 and is recyclable [12]. D-limonene can dissolve up to 55% of EPS at 323.15 K and 47.1% at room temperature [40].

Recovery of limonene from volume reduced EPS

Limonene was successfully recovered from limonene-polystyrene mixture, by the addition of methanol which separated the polystyrene in jelly like form. After the removal of that jelly like EPS, the mixture of methanol and limonene was again treated with steam distillation. As considering their boiling points methanol boils very earlier than the limonene i.e. at 64.7°C [36], so they can be easily separated and limonene can be recovered and can be reused. From 4ml limonene used 2ml can be recovered by steam distillation.



Fig6:Limonene recovered

Depolymerization of EPS

The yield of white-yellow oily liquid (Styrene) with a strong and unpleasant smell formed after pyrolysis of 4 g of volume reduced expanded polystyrene was found to be 2ml.



FTIR analysis of styrene after Depolymerization

The IR spectra of standard styrene and pyrolyzed styrene had shown nearly identical absorption bands, indicating minimal structural change after pyrolysis. The C-H (alkene) stretching peak appears at 2963 cm^{-1} in both samples, confirming the presence of the vinyl group. The C-H (alkane) stretch shows a slight shift from 2917 cm^{-1} to 2922 cm^{-1} , likely due to minor changes in the chemical environment caused by thermal treatment. The C=C stretching band at 1644 cm^{-1} remains unchanged, indicating that the carbon-carbon double bond is preserved. Overall, the results suggest that pyrolysis does not significantly alter the functional groups of styrene.

Table 3: FTIR analysis of styrene

Bond Stretching	Standard styrene	Pyrolyzed styrene
C-H (alkene)	2963 cm^{-1}	2963 cm^{-1}
C-H (alkane)	2917 cm^{-1}	2922 cm^{-1}
C-C (alkane)	1644 cm^{-1}	1644 cm^{-1}

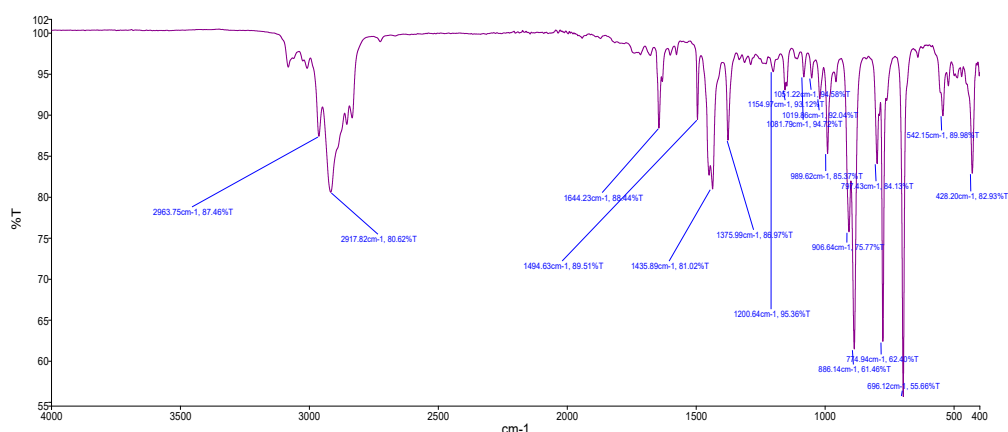


Fig7: Standard styrene FT-IR

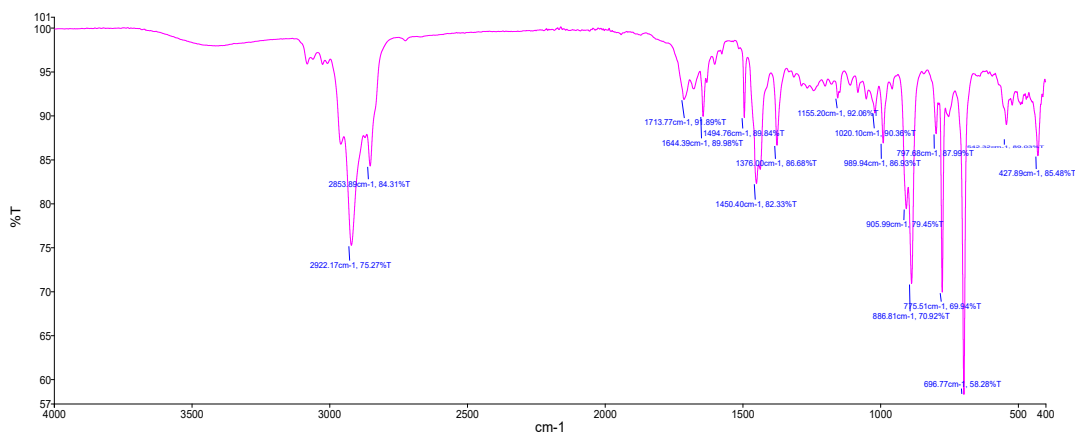


Fig 8: Styrene obtained after pyrolysis FT-IR

It was found that in case of thermal pyrolysis of polystyrene yield of liquid product increased with increasing temperature and maximum yield was obtained at 550°C . After 550°C yield of liquid product starts decreasing with increasing temperature [4]. But on other side it was reported that polystyrene pyrolytic oil has the highest yield of 82.5 wt. % at 550°C [38]. In microwave-assisted pyrolysis the process achieves very high liquid yields (up to 94.3 wt%), with the liquid product being clear and of low viscosity under optimal conditions [39].



IV. CONCLUSION

The proper disposal and reuse of waste thermocol (EPS) is a critical environmental challenge due to its lightweight nature, buoyancy, and persistence in the environment. The use of limonene for volume reduction of EPS presents an effective and eco-friendly solution, significantly minimizing its bulk and facilitating easier handling and processing. Since limonene is derived from citrus fruit peels, this approach also promotes the utilization of organic waste, creating additional economic opportunities for the fruit and vegetable processing industries through limonene production. Furthermore, the subsequent pyrolysis of volume-reduced EPS to recover styrene enables material recycling and reduces dependence on newly produced polystyrene. Overall, this integrated approach not only mitigates plastic pollution but also supports sustainable waste management, resource recovery, and circular economy practices, benefiting both the environment and society.

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