JOURNAL of THE TURKISH CHEMICAL SOCIETY
SECTION: B
CHEMICAL ENGINEERING
TURKISH CHEMICAL SOCIETY

Acid-Catalyzed Atmospheric Organosolv Treatment By Using γ-Valerolactone and Ethylene Glycol For The Delignification of Hazelnut Shell and Precipitation of Lignin

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Abstract: Lignin-based biorefineries are gaining importance day by day to obtain many value-added products from lignin. One of the most important processes that allow the recovery of both cellulose and lignin in those biorefineries is organosolv pretreatment. In this study, organosolv pretreatment was applied to the hazelnut shell at 130 °C for 60 min with ethylene glycol and γ-valerolactone solvents in the presence of a catalyst (either phosphoric acid or acetic acid). The success of solvent-catalyst systems was assessed by delignification efficiency and lignin recovery. Lignins obtained by precipitation were also analyzed by FTIR, TGA, DSC and Py-GC/MS. Highest delignification efficiency (33.9%) was detected for ethylene glycol-phosphoric acid solvent-catalyst pair. It was observed that acetic acid was not an effective catalyst compared to phosphoric acid. The delignification efficiency of γ-valerolactone was low (< 26 %) under atmospheric conditions, and in the presence of acetic acid, lignin was not precipitated from GVL system.

Keywords: Organosolv treatment, Delignification, Ethylene glycol, γ-valerolactone, Lignin recovery.

Submitted: August 26, 2023. **Accepted:** September 19, 2023.

Cite this: Al, K., & BAŞAKÇILARDAN KABAKCI, S. (2023). Acid-Catalyzed Atmospheric Organosolv Treatment By Using γ-Valerolactone and Ethylene Glycol For The Delignification of Hazelnut Shell and Precipitation of Lignin. Journal of the Turkish Chemical Society, Section B: Chemical Engineering, 6(2), 73–84. https://doi.org/10.58692/jotcsb.1350438.

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1. INTRODUCTION

Among the renewable energy sources, biomass is the main source that allows the production of both power, fuel, and functional materials. Preferring lignocellulosic (including agricultural wastes and residues, food wastes, forestry residues, etc.) among biomass resources can also be a solution to critical problems such as resource scarcity, sustainable energy, waste management, and energy security. Lignocellulosic biomass is also the most accessible feedstock to produce biofuels, bio-based chemicals, and value-added materials (Velvizhi et al., 2022). According to recent research, around 181.5 billion tons of lignocellulosic biomass is annually produced worldwide (Ashokkumar et al., 2022). Lignocellulosic biomass mainly consists of three polymeric structures, cellulose (40-60%), hemicellulose (20-40%), and lignin (10-25%) (Deng et al., 2023). Cellulose, the major component of plant cell wall, consists of a linear polysaccharide in which repeating glucose units are linked by β-1,4-glycosidic bonds (Bhatia et al., 2020). β-1,4-glycosidic bonds are known for being resistant to enzymatic hydrolysis. Hemicellulose is a branched heteropolymer that consist of pentoses (mainly arabinose and xylose) and hexoses (glucose, mannose, and galactose) (Sun et al., 2022a). Lignin is an amorphous polyphenolic macromolecule found in the cell wall of plants, consisting of three main phenylpropane units: coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol (Ferreira et al., 2020; Ponnusamy et al., 2018). Common linkages between phenylpropane units includes β-O-4, α-O-4, β-1, β-5, β-β, 5-5, 4-O-5 and α-O-γ, where the ether β-O-4 linkage is the most abundant and the carbon-carbon bond β-β is the second (Liu, 2013; Jędrzejczak et al., 2021). Due to the irregular structure and high degree of polymerization of lignin, it is highly resistant to chemical and biological degradation (Cao et al., 2019; Lim et al., 2021).

Pretreatment processes, which are required for breaking down the complex structure of lignocellulose, enable the valorization of each cellulose, hemicellulose, and lignin fractions. There are several pretreatment options including physical pretreatment processes (milling, crushing, shredding, microwave pretreatment, ultrasound treatment), chemical pretreatment processes (acidic hydrolysis, alkaline hydrolysis, treatment with ionic liquids and deep eutectic solvents, organosolv treatment), physico-chemical pretreatment processes (steam explosion, hydrothermal treatment, ammonia fiber explosion, supercritical fluid treatment) and biological pretreatment (Dharmaraja et al., 2022; Zhang et al., 2023; Zhou and Tian, 2022). The selection of the pretreatment process depends on the type of biomass, the end-products desired and cost (Haldar and Purkait, 2021).

Since a wide range of products can be obtained from lignin, processes in which lignin can be recovered have been preferred in recent years (Cao et al., 2019; Yao et al., 2022). Among the pretreatment methods, the organosolv treatment enables to recover high quality lignin from lignocellulosic biomass. At the same time, very little degradation of the cellulose occurs as a result of the process and very low amount of ash is produced (Zhang et al., 2021; Pin et al., 2020). The organosolv method is carried out in pressurized systems or atmospheric conditions at temperatures of 100-250 °C with different types of solvents in the presence or absence of catalysts (Vaidya et al., 2022; Rabelo et al., 2022). The yield of delignification and lignin recovery depends on parameters such as solvent type and concentration, solvent/biomass ratio, catalyst type, concentration, temperature, retention time and lignin precipitation conditions (Sidiras et al., 2022; Ferreira et al., 2020). A wide range of solvents are used in organosolv treatment including ethanol (Alio et al., 2021; Tchuidiang et al., 2021; Schmatz et al., 2022), methanol (Weerasai et al., 2021; Pan et al., 2022a), butanol (Teramura et al., 2018), acetone (Salapa et al., 2018) γ-valerolactone (Giannoni et al., 2021; Raj et al., 2021; Momayez et al., 2022) , ethylene glycol (Wei et al., 2021; Ling et al., 2022; Chin et al., 2021), glycerol (Wei Kit Chin et al., 2020; Chotirotsukon et al., 2019; Pascal et al., 2019), tetrahydrofuran (THF) (Liang et al., 2022; Zhao et al., 2022; Kalogiannis et al., 2020). Catalysts are used for promoting the cleavage of the lignin bonds and the selectivity of the solvent (Jiang et al., 2018). The most preferred catalysts are H_2SO_4, NaOH, HCl, oxalic acid, $AlCl_3$, ammonia (Jiang et al., 2018; Ferreira and Taherzadeh, 2020; Rabelo et al., 2023).

Most of the studies focused on delignification of lignocellulosic biomass in pressurized systems. The cost of high-pressure systems and the risk of high pressure limit the use of low boiling point solvents. High-boiling point solvents (such as glycerol, ethylene glycol, γ-valerolactone, etc.) can be used in milder conditions, without requiring pressurized reactors. However, precipitation and recovery of lignin from high boiling solvents have been rarely studied.

This study aims to delignify hazelnut shell and recover lignin by using ethylene glycol (EG) and γ-valerolactone (GVL) as solvents, and phosphoric acid (PA) and acetic acid (AA) as catalysts. While the catalysts FA and AA, which were selected in this study, have not been used with the selected solvents up to now, EG and GVL were preferred as the solvents for the reasons listed below (Sui et al., 2021; Raj et al., 2021; Sun et al., 2022; Meng et al., 2023):

- Organosolv studies with EG and GVL are very few.
- Both EG and GVL are suitable for working under atmospheric conditions since they have high boiling points of 198 °C and GVL 205 °C, respectively.
- Both EG and GVL have high lignin solubility.
-Both EG and GVL are green solvents.

Since the solvent-catalyst pairs (EG-FA, EG-AA, GVL-FA, GVL-AA) used in this study have not been tested before, the results will make an important contribution to organosolv studies and biorefining methods.

2. EXPERIMENTAL SECTION

2.1. Materials

In the present study, the hazelnut shell was preferred as lignocellulosic biomass because of the reason that 70% of worldwide hazelnut production is supplied by Türkiye, resulting a considerable amount of agricultural waste (FAO, 2023). Hazelnut shell (HS) samples were supplied from Of district, Trabzon. All samples were dried (105 °C for 24 h) before analyses. After grinding, samples were sieved by using RESTCH AS 200 vibrating sieve to have a uniform particle size (250 μm). Chemicals including GVL (BioRenewable, ≥99.9%, Sigma-Aldrich ReagentPlus®), EG (Extra pure, TK.010101.05001, Tekkim), PA (Merck), AA (100%, Merck) and H_2SO_4 (95-97%, 07208, Sigma-Aldrich) were of analytical grade and used without further purification.

2.2. Organosolv Pretreatment

10 g of dry HS, 160 mL of solvent (either EG or GVL), 40 mL of deionized water, 10 mL catalyst (either AA or FA) were mixed (EG-AA, EG-FA, GVL-AA, GVL-FA) in a two-necked glass reactor equipped with a reflux condenser and a thermocouple. The mixture was continuously stirred under reflux at 130 °C for 60 min. At the end of the treatment, cellulose-rich pulp was separated from the liquor, and washed with hot water (water at 55 °C) and then dried in an oven at 100 °C for 24 h. To precipitate the lignin, filtrate was diluted with deionized water to 1 L (at 55 °C) and the pH was decreased to 2-2.5 by using 0.1 M H_2SO_4. After precipitation, lignin was separated, washed with deionized water, and then dried. All

organosolv treatments were repeated in triplicate. The lignins and cellulose rich pulps were named as: EGAAL (solvent: ethylene glycol, catalyst: acetic acid, product: lignin), EGAAP (solvent: ethylene glycol, catalyst: acetic acid, product: cellulose rich pulp), EGFAL (solvent: ethylene glycol, catalyst: phosphoric acid, product: lignin), EGFAP (solvent: ethylene glycol, catalyst: acetic acid, product: cellulose rich pulp), GVLAAL (solvent: γ-valerolactone, catalyst: acetic acid, product: lignin), GVLAAP (solvent: γ-valerolactone, catalyst: acetic acid, product: cellulose rich pulp), GVLFAL (solvent: γ-valerolactone, catalyst: phosphoric acid, product: cellulose lignin), GVLFAP (solvent: γ-valerolactone, catalyst: phosphoric acid, product: cellulose rich pulp).

The efficiency of each organosolv solvent-catalyst system was assessed in terms of delignification efficiency and lignin recovery:
Delignification efficiency (%) = ((lignin in the sample (g lignin)- lignin in the pulp (g lignin)) / lignin in the sample (g lignin)) x100
Lignin recovery (%) = (lignin precipitate (g lignin) / lignin in the sample (g lignin)) x100

2.3. Analyses

The thermal behavior of each pulp and lignin sample was done in Ege University Applications and Research Center for Testing and Analysis (EGE-MATAL) by using a simultaneous thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC) (TA Instruments SDT Q600). The analyses were conducted in the temperature range of 25 °C-800 °C at a heating rate of 15 °C/min, under N_2 atmosphere (100 mL/min).

The C, H, and N analyses were carried out in an elemental analyzer (LECO CHN628). Acid-insoluble lignin content of each sample was determined by using gravimetric method as described in NREL/TP-510-42618 (Sluiter et al., 2012). Extractive content was identified according to ASTM E1690–08 Standard Test Method for Determination of Ethanol Extractives in Biomass (American Society for Testing and Materials, 2016).

Fourier Transform Infrared (FTIR) spectra of EGAAL, EGFAL and GVLFAL were obtained using a spectrometer (Perkin Elmer Spectrum 100) coupled with a universal attenuated total reflectance (ATR) sampling device with a diamond crystal. The spectra were recorded with a resolution of 4 cm^{-1}, in the range between 650 and 4000 cm^{-1}.

Py-GC/MS analyses were done in Bilecik Şeyh Edebali University Central Research Laboratory (BARUM). Fast pyrolysis analyses were performed in a pyrolyzer (Frontier/PY2020is), which was connected to a GC/MS (Shimadzu/QP 2010 Ultra). Each fast pyrolysis was performed at 600 °C (heating rate: 10 °C/ms) with a dwell time of 15 s. Pyrolysis products were purged with He (1 mL/min) into a GC capillary column (Teknokroma, 30 m*0.25 mm*0.25 µm). The oven temperature of GC was held at 40 °C for 2 min and then programmed to 200 °C with a heating rate of 5 °C/min and held there for 2 min, then further heated to 280 °C with a heating rate of 10 °C/min and held there for 2 min. The MS was operated by electron impact ionization at 70 eV with the mass scan range of m/z 30–600 amu. The ion source temperature and interphase temperature were 230 °C and 280 °C, respectively. Peaks were identified by NIST mass spectral library, which was configured in GC/MS.

3. RESULTS AND DISCUSSION

The elemental composition and proximate analysis of HS is given Table 1. HS is a lignin-rich agricultural residue, which contains considerable amount of carbon.

The delignification efficiencies and lignin recovery rates of EG-FA, EG-AA, GVL-FA and GVL-AA solvent-catalyst pairs are shown in Figure 1. In order to compare the efficacy of solvent-catalyst pairs, all organosolv treatments were carried out at the same temperature and mixing period. The lignin precipitation procedures were also the same for all solvent-catalyst pairs. Accordingly, EG-FA was the solvent-catalyst pair with the highest delignification with 33.9% efficiency. This system was followed by the GVL-FA solvent-catalyst pair with a delignification efficiency of 25.8%. The delignification efficiencies of GVL-AA and EG-AA solvent-catalyst pairs were close to each other (20% and 19%, respectively) and the efficiency was lower compared to other solvent-catalyst pairs (Dong et al., 2022; Pan et al., 2022b; Gaudino et al., 2018; Xu et al., 2023; Li et al., 2019). Millan et al. (2022) delignified *Pinus Radiata* using GVL and EG, where lignin extraction efficiency of EG-%1 H_2SO_4 solvent-catalyst pair and GVL-%1 H_2SO_4 solvent-catalyst pair were 33% and 48 %, respectively.

Based on Figure 1, AA is not an effective catalyst for EG and GVL solvents when it comes to delignification. In the recovery of lignin by precipitation, the highest recovery rate was found in the EG-FA solvent-catalyst pair (40.6%). The lignin recovery rate from the EG-AA solvent-catalyst couple was higher (26%) compared to the GVL solvent systems. In the GVL-FAA system, lignin recovery was less than 20%, while lignin was never recovered from the GVL-AA solvent-catalyst pair. Millan et al. (2022) also showed that the amount of water which was added to precipitate lignin affected the purity and amount of lignin. Yu et al. (2019), who also observed the dependency of lignin recovery to the water amount, found the maximum lignin recovery was 27% (biomass: softwood mixture; solvent: EG; catalyst: 1 wt% H_2SO_4; temperature: 180 °C). Low lignin recovery (< 15%) from GVL containing solvent-catalyst systems was also observed by Wu et al. (2016).

Table 1: Elemental and proximate analysis of HS.

Hazelnut Shell	
Ethanol extractives (%, db*)	14.16
Klason lignin (%, db*)	41.4
Volatile matter content (%, db*)	75.3
Fixed carbon content (%, db*)	21.4
Ash (%, db)	3.3
C (%, db*)	48.98
H (%, db*)	6.31
N (%, db*)	0.64
S (%, db*)	0
O (%)	40.77

* db: dried basis

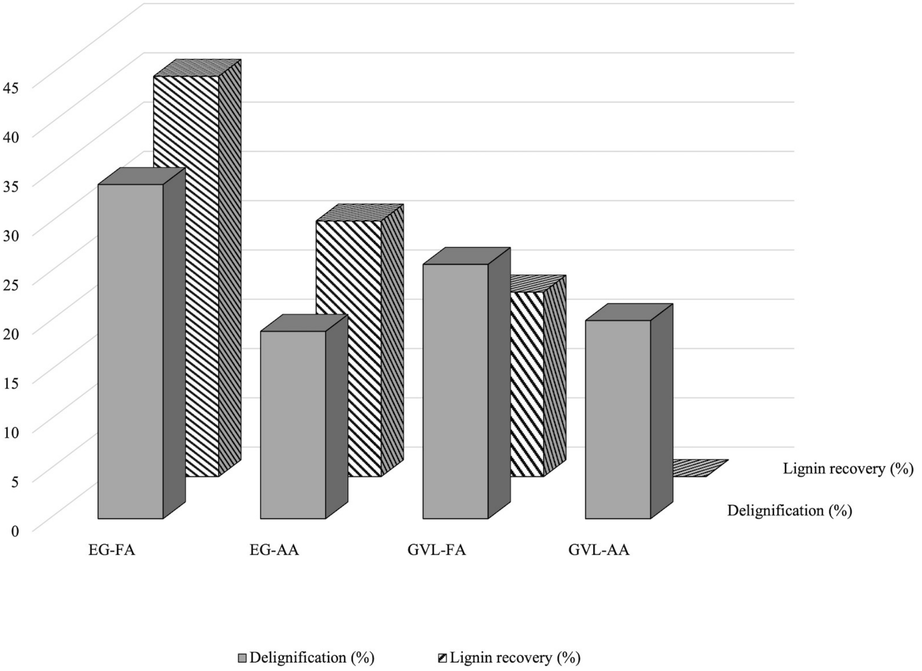

Figure 1: Delignification efficiency and lignin recovery in EG-FA, EG-AA, GVL-FA, GVL-AA solvent-catalyst pairs.

The FT-IR spectra of EGFAL, EGAAL and GVLFAL samples in the wavelength range of 650-4000 cm^{-1} are shown in Figure 2. Published studies on lignin were used for defining the FTIR bands (Ibrahim and Kruse, 2020; Lin et al., 2015; Khongchamnan et al., 2021; Zhuang et al., 2020). FTIR spectra of EGFAL, EGAAL and GVLFAL presented almost the same peaks with different intensities, which were all comply with the FTIR spectra of lignin. The O-H stretching vibration of hydroxyl groups in aromatic and aliphatic structures was appearing at 3250-3333 cm^{-1}. C-H stretching vibration of alkyls and C-H asymmetric vibration of methylene group were observed at 2923 cm^{-1} and 2853 cm^{-1}, respectively. The intensity of the C-H peaks in EGAAL and GVLFAL samples was considerably higher than that of EGFAL. The peak at 1710 cm^{-1} was due to C=O non-conjugate stretching vibration of carbonyl groups (such as ketone, carboxylic acid, and ester). Lignin specific peaks appearing at 1607 cm^{-1}, 1510 cm^{-1}, 1448 cm^{-1}, 1266 cm^{-1}, 862 cm^{-1} and 818 cm^{-1} indicated C=O stretching vibration conjugated to aromatic skeletal vibration of lignin, aromatic ring vibration in lignin, C-H deformation in lignin, C-O stretch of the guaiacyl ring of lignin, aromatic C-H out of plane bending in lignin and C-H bending of syringyl unit, respectively.

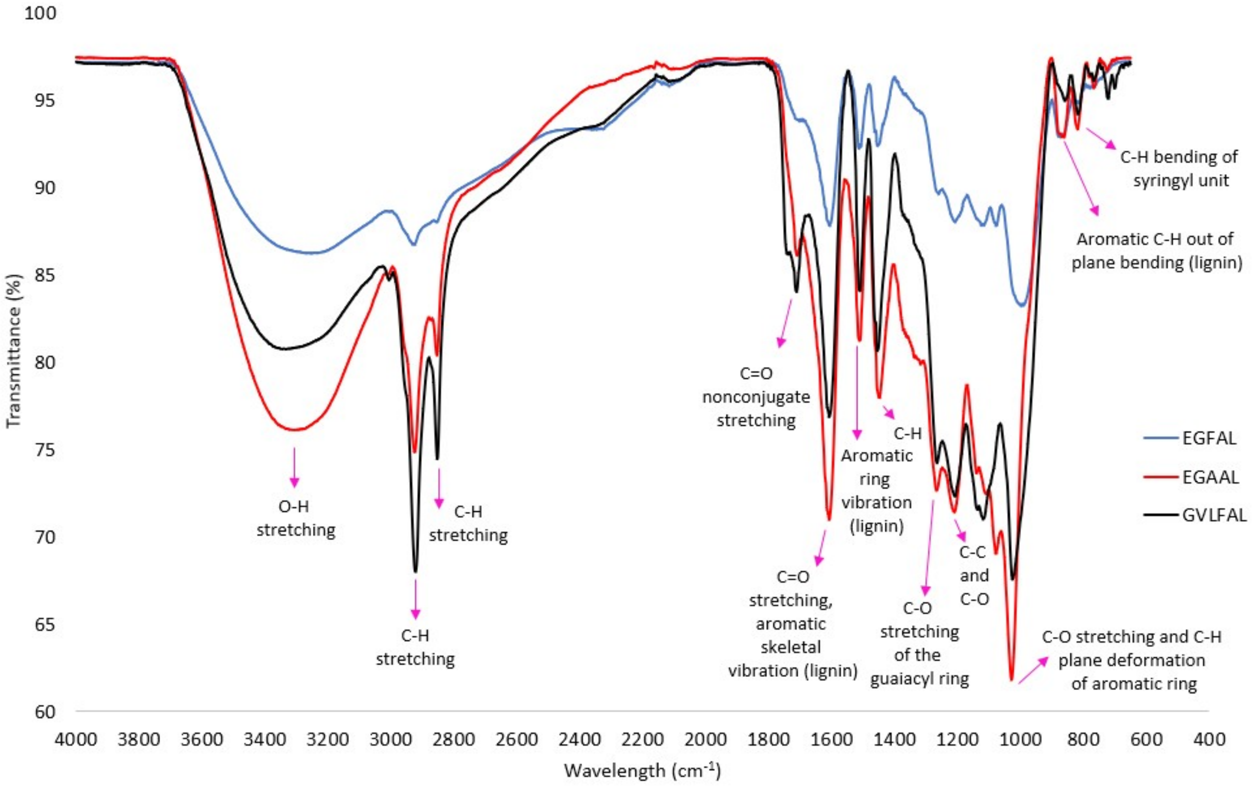

Figure 2: FT-IR spectra of EGFAL, EGAAL and GVLFAL.

Figure 3 (a) shows the thermogravimetric analysis curves of EGAAP, EGFAP, GVLAAP and GVLFAP. Thermal decomposition of EGFAP, EGAAP, GVLAAP and GVLFAP started with removal of moisture and light gases (such as CO, CO_2) below 100 °C. The mass loss in this first step ranged between 2.86% (GVLAAP) and 5.22% (EGAAP). Second stage, which occurred in a wider temperature change (150-600 °C), was due to mass loss during thermal decomposition of hemicellulose, cellulose, and residual lignin. Main mass loss was observed in this stage. In GVLAAP, GVLFAP and EGAAP, a small peak observed (attached to the main peak) around 250 °C due to hemicellulose decomposition. In the thermogravimetric curve of EGFAP, the decomposition of hemicellulose (almost 4.6% mass loss) was observed as a single degradation at temperatures between 150-200 °C. The cleavage of 1,4 glycosidic bond in glucose during cellulose decomposition was observed around 310-350 °C (Bessa et al., 2023). T_{max} (the temperature of the maximum mass loss rate) of EGFAP, EGAAP, GVLAAP, and GVLFAP were 330.6 °C, 362 °C, 369.3 °C, and 348.2 °C, respectively. The thermal decomposition of char was observed in the third stage (600-800 °C) with a less mass loss. The overall mass loss percentage due to thermal decomposition of EGFAP EGAAP, GVLFAP and GVLAAP was 76%, 78%, 76.5% and 73.3%, respectively.

Like the thermogravimetric curves of cellulose-rich pulps, the thermal decomposition of EGAAL, EGFAL and GVLFAL are given in Figure 3(b). Since the lignin was not precipitated from GVL-AA solvent-catalyst pair, GVLAAL is not seen in Figure 3(b). Compared to cellulose-rich pulps, EGAAL, EGFAL and GVLFAL decomposed in a wider temperature range (up to 700 °C). First stage, which was due to removal of moisture and light gases, occurred before 100 °C. In the second stage (150-700 °C), thermal decomposition each EGAAL, EGFAL and GVLFAL showed two or more peaks showing that precipitated lignin had no uniform structure. While EGFAL showed three peaks at 217 °C, 305 °C (T_{max}) and 415.8 °C, EGAAL showed two peaks at 313 °C (T_{max}) and 403.7 °C. A shift of the peak temperature to a lower value indicates the decomposition of lower molecular weight compounds in lignin fraction (Ramezani and Sain, 2018). T_{max} values of both EGFAL and EGAAL are lower than that of soda and Kraft lignins (Domiguez-Robles et al., 2017). In the decomposition of GVLFAL, thermogravimetric curve showed two peaks at 372.7 °C (T_{max}) and 419 °C. GVLFAL obviously included high molecular weight compounds in the lignin fraction. Similar observation was done by Jampa et al. (2019), where lignin precipitated from GVL-H_2SO_4 solvent-catalyst pair showed a T_{max} around 400 °C. Thus, GVLFAL is the most thermally stable lignin in this study. Total mass loss due to thermal decomposition was 52%, 62% and 63% for EGFAL, EGAAL and GVLFAL, respectively.

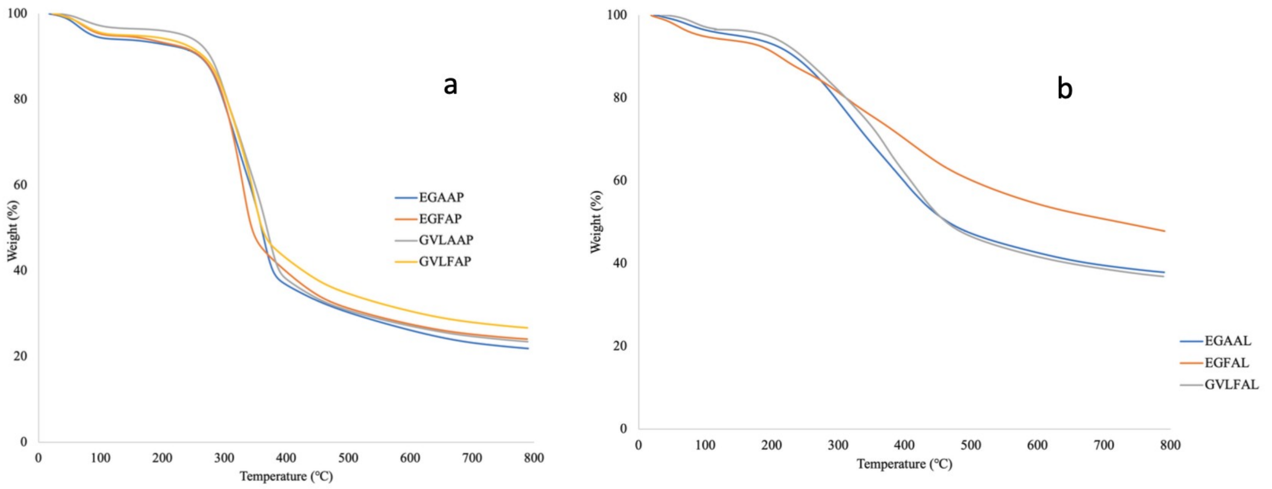

Figure 3: Thermogravimetric curves of pulps (a) and lignins (b).

The DSC curves of EGAAP, EGFAP, GVLAAP and GVLFAP are shown in Figure 4 (a). All the pulp samples showed endothermic and exothermic changes during heating from room temperature to 800 °C. The endothermic change due to moisture evaporation was observed at a temperature interval of 80-150 °C (peak at 100 °C). EGAAP, GVLAAP, and GVLFAP exhibited highly exothermic reactions due to cellulose decomposition (Kurian et al., 2015) at a temperature interval of 300-450 °C, where EGFAP showed less energy release due to decomposition at temperatures around 350-450 °C.

The DSC curves of EGAAL, EGFAL and GVLFAL are illustrated in Figure 4(b). Similar to pulps, lignins also showed an endothermic change due to moisture removal at around 100 °C. Exothermic decomposition of lignin occurred in a wider temperature range (250-550 °C).

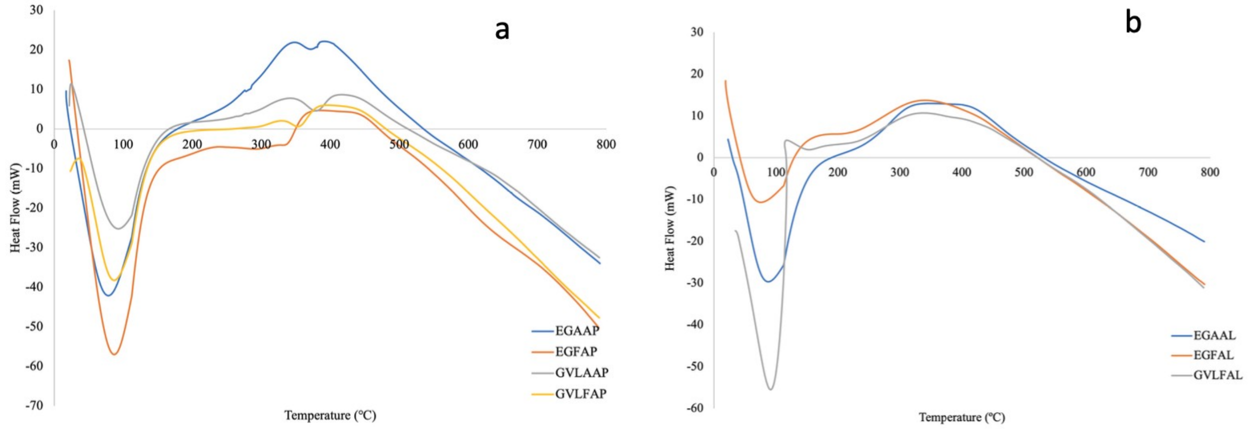

Figure 4: DSC curves of pulps (a) and lignins (b).

The major fast pyrolysis products of EGFAL, EGAAL and GVLFAL were identified using Py-GC/MS. The chromatograms of EGFAL, EGAAL and GVLFAL identified 64 peaks, 88 peaks, and 71 peaks, respectively. Figure 5-7 show the common compounds identified by Py-GC/MS. Commonly, lignin pyrolysis yields phenolic compounds, carbonyl compounds (like aldehydes, acids, esters), and other hydrocarbons (Lin et al., 2015; Liu et al., 2016). However, the method of isolation of lignin and the lignin structure of the biomass has a great influence on the pyrolysis volatiles of lignin (Wang et al., 2015; Margellou et al., 2021).

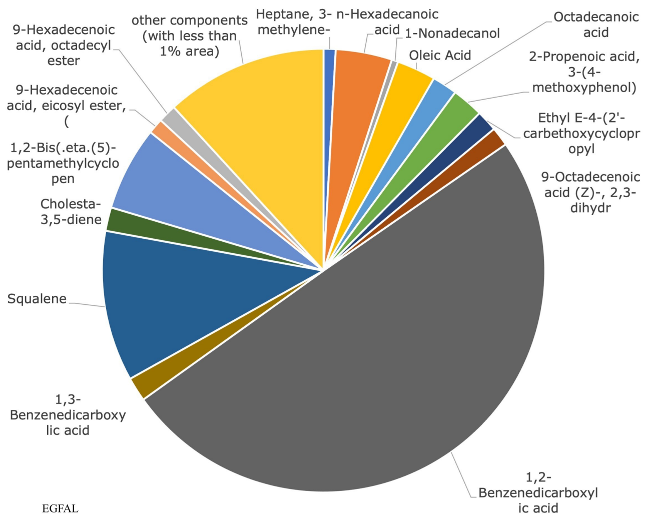

Figure 5: Relative composition of pyrolysis volatiles of EGFAL (which are represented as the percentage of the total chromatographic peak area).

All three of the pyrolysis products of EGFAL, EGAAL and GVLFAL had components in common: 3-methylene heptane, n-hexadecanoic acid, 1-nonadecanol, oleic acid, octadecanoic acid, 3-(4-methoxyphenol)2-propenoic acid, 1,3-benzenedicarboxylic acid, squalene, cholesta-3,5-diene. The chromatograms were quite different from that of other lignins (Brebu et al., 2013; Qian et al., 2023). This is mainly due to biomass type, lignin structure in the biomass, organosolv severity and precipitation conditions. Lignin is used in various areas such as constructions (Jędrzejczak et al., 2021) and buildings (Agustin et al., 2021), energy storage systems (Wang et al., 2023), wastewater (Sun et al., 2021), biomedical applications (Liu et al., 2020), adhesives (Gao et al., 2020) etc. Therefore, once the lignin is precipitated and separated, it has a vast range of end-use.

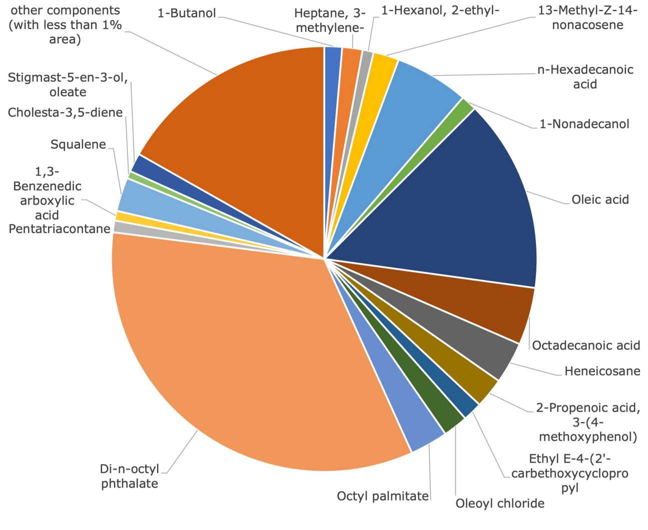

Figure 6: Relative composition of pyrolysis volatiles of EGAAL (which are represented as the percentage of the total chromatographic peak area).

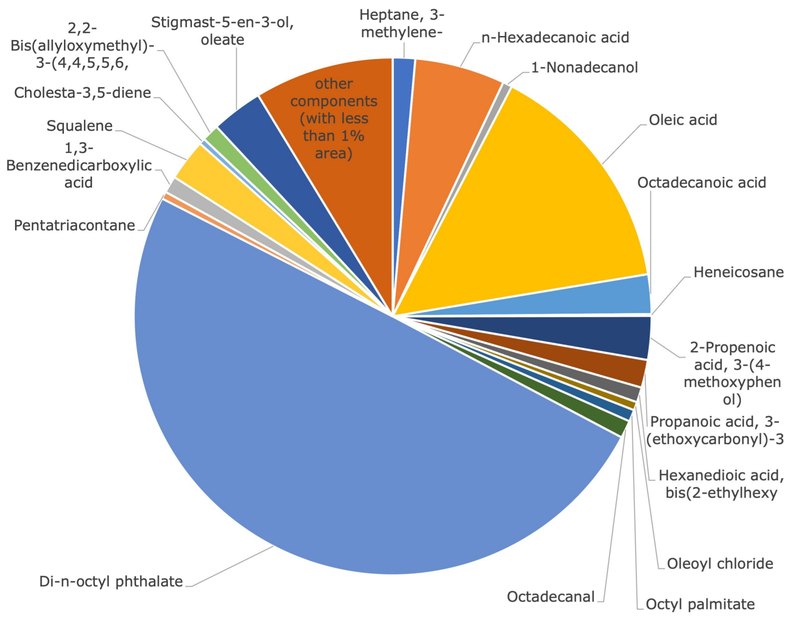

Figure 7: Relative composition of pyrolysis volatiles of GVLFAL (which are represented as the percentage of the total chromatographic peak area).

4. CONCLUSION

In the present study, hazelnut shell was subjected to organosolv treatment with different solvent (ethylene glycol and γ-valerolactone) and catalysts (phosphoric acid and acetic acid) under atmospheric conditions. Cellulose-rich pulp was separated from the solution and lignin fraction was precipitated and characterized. Based on results, the delignification yield and lignin recovery depended on the chosen solvent-catalyst system. The best performance in terms of delignification yield and lignin recovery was observed in EG-FA solvent-catalyst system. In terms of thermal stability, GVLAAP and GVLFAL fractions were the most stable cellulose-rich pulp and lignin. According Py-GC/MS results, lignins obtained by EG and GVL can be used as additives in plastics, packaging films, adhesives, surfactants, detergents, lubricants, coatings, cosmetics, and personal care products.

5. CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

6. ACKNOWLEDGMENTS

This research was financially supported by Yalova University Scientific Research Unit (Project No: 2022/YL/0019).

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