Co-pyrolysis of corn stalks and plastic waste: Chemical composition of the pyrolyzates as a base for producing environmentally sustainable fuels

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Abstract

In this study pyrolysis and co-pyrolysis experiments involving lignocellulosic corn stalks (CS) samples and selected plastic waste fractions (high density polyethylene (HDPE) and polystyrene (PS)) were conducted at various mixing ratios. The main objective was to evaluate how the composition of the feedstock affects the yield and composition of the resulting pyrolysis products, by developing a sustainable method for the management of both biomass and plastic waste through the production of valuable oils and chemicals. This study contributes to a transitional approach for plastic waste management, given the anticipated reduction in the usage of plastic materials in the future. The co-pyrolysis mixtures demonstrated synergistic effects between the feedstocks, with plastic waste serving as hydrogen donors and enhancing the yield of CS pyrolysis products. Moreover, the products from plastic waste exhibited a significant predominance over those from CS, constituting ca. 66.6 and 85.6 % in the 1:1 CS/HDPE and CS/PS mixtures, respectively. This is particularly beneficial considering the elevated oxygen content in the CS products, which can contribute to heightened acidity and corrosion in the resulting synthetic bio-oil. This study reveals valuable insights into the formation of synthetic bio-oils by designing the chemical composition and optimising the pyrolysis yield.

Keywords: Biomass waste; high density polyethylene; polystyrene; synthetic bio-oil; gas chromatography-mass spectrometry.

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1. INTRODUCTION

The extensive use of fossil fuels has given rise to a significant global environmental issue, characterized by the substantial emission of greenhouse gases such as carbon dioxide (CO_2), nitrogen oxides (NO_x), and sulfur oxides (SO_x) [1,2]. These emissions induce extensive consequences on the environment, climate, and human health. Therefore, there is a growing need to investigate alternative feedstocks to replace fossil fuels.

In recent decades, various forms of lignocellulosic biomass waste have been studied as a more sustainable and renewable alternative to fossil fuels [3-6]. Most studies have been carried out on woody residues; however, any form of biomass waste can be considered for bio-oil production [7,8]. Due to its abundance, renewable nature, and low price, lignocellulosic biomass stands as a promising resource for both the chemical industry and energy production. Thus, the context of using biomass waste such as agricultural residues as a raw material for fuel production to replace fossil fuels, hold a special significance. Furthermore, improper managing of biomass waste can lead to substantial environmental problems, since after harvesting, the remaining biomass is often treated only as discarded material. It is either left in fields, creating solid waste, or burned, resulting in substantial air pollution [9]. Therefore, the use of biomass waste as a replacement for fossil fuels can prevent environmental pollution from its discharge and contribute to sustainable environmental protection, as the resulting bio-oil and biochar have the potential to be used as fuels.

Corn holds paramount significance as an agricultural feedstock in Serbia. According to the Serbian Ministry of Agriculture, in year 2022 a record of 8 million metric tons of corn was produced [10]. The byproducts stemming from corn production are being improperly managed, often subjected to landfill disposal or incineration, thereby culminating

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in pronounced atmospheric contamination. Hence, a more logical approach for corn waste management would be to use the lignocellulosic parts of the corn waste for energy production.

However, a prominent disadvantage of bio-oils is significant content of oxygen originating from the biomass source material [11]. This results in a reduced calorific value, coupled with challenges encompassing corrosion and instability [11]. To address these limitations in an effective manner, a promising approach could be co-pyrolysis of biomass with plastic wastes. Significantly, due to their substantial carbon and hydrogen contents, plastic materials such as polyethylene (PE) and polystyrene (PS) can play an important role as valuable substrates for generating synthetically derived bio-oils. Furthermore, the improper disposal of plastic waste stands as one of the foremost environmental problems of our time. Therefore, co-pyrolysis of biomass with plastic waste introduces a sustainable approach for waste recycling, leading to the creation of valuable oils and chemical compounds. Oils derived from plastic waste are not considered bio-oils as they are produced from synthetic materials. However, for reasons of practicability, oils derived from co-pyrolysis of biomass and plastic waste will be referred to as synthetic bio-oils in this paper.

Some research has been already conducted to explore co-pyrolysis of diverse forms of biomass waste in combination with plastic waste. It was demonstrated that co-gasification of polyethylene and woodchips using high-temperature steam in a semi-batch reactor exhibited synergistic effects, leading to superior syngas yield, hydrogen yield, and apparent thermal efficiency compared to the weighted average properties of individual components [12]. In another study co-pyrolysis of agricultural biomass and plastic wastes, specifically polyethylene terephthalate (PET), polypropylene (PP), and polyvinyl chloride (PVC) was investigated showing that rapeseed stalk and PP exhibited a synergistic effect, enhancing the production of aliphatic hydrocarbons and alcohols [13]. Furthermore, Liu *et al.* [14] systematically investigated the synergistic effects during co-pyrolysis of pinewood and PP in a fixed-bed reactor. Their results revealed significant improvements in syngas yield, hydrogen yield, and carbon monoxide yield, with the increases of 27, 80 and 63 %, respectively, compared to the weighted averages obtained by pyrolysis of individual components. Also, in another study it was shown that the addition of PS to cellulose clearly improved the quality of the obtained oil, resulting in decreased acid number, pour point and density [15]. Furthermore, addition of PS to Sargassum macroalgae pyrolysis was reported to improve the oil potential heating value and decreased its potential for producing air pollution when combusted, by lowering its nitrogen content [16]. Co-pyrolysis of low-density polyethylene (LDPE) and biomass was investigated in another study reporting that the LDPE addition can effectively improve the selectivity for naphthalene family products (1-methylnaphthalene and 2-methylnaphthalene) in the catalytic pyrolysis of biomass and decrease the content of aromatic hydrocarbons larger than C_{10} [17].

However, systematic studies of co-pyrolysis regarding molecular compositions and their relevance for designing bio-oils are scarce. Therefore, in this study the general approach to copyrolyse plastic waste and agricultural residues has been tested for an optimal bio-fuel design. Therefore, pyrolysis and co-pyrolysis gas chromatography-mass spectrometry (GC/MS) experiments were conducted using corn stalks (CS) together with high density polyethylene (HDPE) and 'polystrene (PS) plastic waste at different ratios. The overall goal of this study was to investigate the influence of PS and HDPE addition to CS pyrolysis and the corresponding molecular compositions. Therefore, the specific goals of this study were: (i) to identify and quantify distinct pyrolysis products derived from these feedstocks, and (ii) to investigate potential interactions between these samples during the pyrolysis process. Additionally, the study aimed to assess whether specific waste ratios could induce synergistic effects, influence production of particular products or giving rise to the formation of novel compounds.

2. EXPERIMENTAL

2. 1. Chemicals and reference compounds

Standard reference materials for the natural and synthetic polymers comprising cellulose, lignin, PE, and PS were purchased from Geyer Th. GmbH & Co. KG, Germany. Organic solvents required for the pyrolysis and fractionation experiments, namely acetone, dichloromethane (DCM), and methanol, were also obtained from Geyer Th. GmbH & Co. KG, Germany. Corn stalks were gathered in the vicinity of the city of Šabac in Serbia. Plastic waste materials such as food packaging, containers for food and cosmetics, plastic furniture, plastic bottles, *etc.*, were collected from multiple households in Aachen, Germany.

2. 2. Sample preparation

2. 2. 1. Agricultural waste samples

Corn stalks with leaves were cut off about 5-10 cm above the ground. They were then coarsely chopped with a knife and air dried. The samples were then ground and sieved to a specific particle size of approx. 1-2 mm suitable for pyrolysis experiments.

2. 2. 2. Plastic waste samples

After collecting the plastic waste, the material was washed with water and left to dry in air. The material was then cut into smaller particles (about 2 cm) by using scissors and shredded into particles smaller than 5 mm. The shredding was carried out under a flow of nitrogen, which was used to cool the samples and prevent melting and thermal degradation.

2. 3. Continuous flow off-line pyrolysis experiments

The pyrolysis and co-pyrolysis experiments were carried out in a model MTF 10/15/130 tube furnace (Carbolite, UK). The samples were placed in an aluminium foil vessel located in the middle of a quartz tube 150 mm long and 15 mm in diameter. The quartz tube was connected at one end to a continuous nitrogen stream, while the other end was connected to a flask tube filled with acetone that was cooled with dry ice and ethanol. To minimize the risk of secondary reactions during the heating process, the samples were placed directly into a preheated oven, consequently, the experiments were carried out without heating rate at a constant temperature of 450 °C for 30 min. The temperature of 450 °C was selected based on the optimization of experimental conditions. Experiments were conducted at the following temperatures: 400, 450, 500 and 550 °C. Based on the semi-quantitative evaluation of the pyrograms in terms of yield, 450 °C was determined to be the most efficient temperature for the thermal degradation of the samples as also suggested in a former study [18].

The co-pyrolysis experiments using corn stalk CS with one of the synsthetic polymers HDPE or PS, respectively, were carried out with the following ratios of pyrolysis educts: 4:1 (100 mg CS : 25 mg HDPE or PS); 4:2 (100 mg CS : 50 mg HDPE or PS); 4:3 (100 mg CS : 75 mg HDPE or PS); 1:1 (100 mg CS : 100 mg HDPE or PS); 3:4 (75 mg CS : 100 mg HDPE or PS); 2:4 (50 mg CS : 100 mg HDPE or PS); 1:4 (25 mg CS : 100 mg HDPE or PS). All experiments were carried out in duplicates.

The resulting pyrolyzates were left to evaporate until they reached about 2 mL and were then dried with anhydrous Na_2SO_4. Then, the samples were subjected to fractionation by liquid chromatography with a micro glass column with 2 g of activated silica gel (Baker, UK). Elution was performed by 8 mL of DCM (1st fraction), followed by 8 mL of methanol (2nd fraction). To both fractions 50 µL of surrogate standard containing fluoracetophenone (5.8 ng/µL), d20-benzophenone (6.3 ng μL^{-1}), and d_{34}-hexadecane (6.0 ng μL^{-1}) were added. The volume was reduced to approx. 200 µL prior to the GC/MS analysis.

2. 4. Gas chromatography-mass spectrometry analysis

Qualitative and quantitative analysis of all pyrolyzates was performed on a Finnigan Trace MS single quadrupole mass spectrometer (ThermoElectron, Egelsbach, Germany) coupled to a HRGC 5160 gas chromatograph (CarloErba, Milano, Italy). The gas chromatograph was equipped with a ZB-5 (Phenomenex, Aschaffenburg, Germany) capillary column (30 m length × 0.25 mm inner diammeter × 0.25 µm film). The chromatographic conditions were the following: aliquots of ca. 0.2 to 1 µL injected splitless (injector temperature 270 °C) at an initial temperature of 60 °C, isothermal time 3 min, followed by a ramp of 3 °C min^{-1} up to 240 °C, and a subsequent increase of 10 °C min^{-1} up to 310 °C. Helium was used as the carrier gas, with a flow rate set at 1.5 mL min^{-1}. The mass spectrometer measured in electron impact ionisation mode (EI+, 70 eV) with a source temperature of 200 °C, an interface temperature of 270 °C and by full scan from 35 to 500 *m*/*z*. The scan rate was set to 0.67 scans per second.

2. 5. Identification and quantification of the pyrolysis products

Pyrolysis products were identified based on the comparison of the obtained mass spectra with the NIST 14/Wiley registry mass spectral data bases [19], detailed interpretation of the mass spectra, comparison with reference material as well as published literature data. The relative quantification of the obtained degradation products was based on the integration of specific ion chromatograms and corresponding peak areas, corrected using the surrogate standard.

3. RESULTS AND DISCUSSION

3. 1. Pyrolysis experiments

To evaluate the initial composition of the pyrolysis oils and to relate it to the products, pyrolysis experiments were conducted using individual samples of the synthetic polymer waste, and reference materials of cellulose and lignin, as well as the CS sample. The specific pyrolysis products for HDPE and PS have been previously identified and are presented in detail in our former study [18]. Briefly, pyrolysis experiments on HDPE revealed a distinct pattern, characterized by a sequence of triplets. Each triplet consists of alkadienes, *n*-alkenes, and *n*-alkanes, with a systematic increase in the carbon number as given by the homologues series [18]. Contrary, pyrolysis of PS produced only aromatic products, with styrene dimer and styrene trimer having the highest abundance [18].

Pyrolysis of CS produced dark oil as the predominant pyrolysis product. The GC/MS analysis of the resultant pyrolyzate revealed a complex mixture of oxygenated compounds, including phenols, aldehydes, fatty acids, furans, and alcohols. This spectrum of degradation products is characteristic for lignocellulosic materials, highlighting the contribution of components coming from the thermal degradation of both lignin and cellulose [20]. The pyrolysis products were identified and assigned to their specific compound group (see Table 1). All identified pyrolysis products were quantified. However, the quantification represents only a fraction of all peaks observed in the chromatogram obtained. As listed in Table 1, the predominant group of degradation products observed are phenolic compounds derived from the lignin content present in CS. Phenols comprised 44.6 % of the obtained pyrolizate. The most abundant compound is methoxy-vinylphenol, constituting 13.5 % of the total pyrolizate, followed by methoxyphenol at 8 %, and dimethoxyphenol, representing up to 7.8 % of the composition. The cellulose derived compounds in CS were determined at 18.8 %, including compounds such as furanone, furyl methyl ketone, methylfurfural, ethenylfuran, methyl-cyclopentanedione and 1,4:3,6-dianhydro-α-d-glucopyranose. The given compounds were also identified in corn stalk samples in literature [20].

Table 1. Identified degradation products obtained in the pyrolysis experiments using CS samples

Compound group	Content, %
Phenolyc compounds	
2-Methoxyphenol	8
4-Ethyl phenol	6.3
2-Methoxy-6-methylphenol	2.3
4-Ethyl-3-methylphenol	0.7
4-Ethyl-2-methoxyphenol	4.2
2-Methoxy-4-vinylphenol	13.5
2,6-Dimethoxyphenol	7.8
2-Methoxy-4-allylphenol	0.6
1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	0.9
2,6-Dimethoxy-4-(2-propenylphenol)	0.3
Aldehydes	
3-Methoxy-4-hydroxybenzaldehyde	2.4
4-Hydroxy-3,5-dimethoxy-benzaldehyde	0.7
5-Methylfurfural	0.9
Acidic compounds	
4-Hydroxy-3-methoxybenzoic acid (Vanillic acid)	1.3
Hexadecanoic acid	0.2
Oleic acid	0.1
Octadecanoic acid	0.1

Compound group	Content, %
Ketones	
Furanone	4.8
2-Furyl methyl ketone	0.8
Methyl-cyclopentanone	9.6
3-Methyl-1,2-cyclopentanedione	6.3
Alcohols	
3-Methoxy-1,2-benzenediol	< 0.1
1-(2,4,6-Trihydroxyphenyl)-2-pentanone	0.9
Others	
3-Ethyl-2-hydroxycyclopent-2-en-1-one	2.1
1,4:3,6-Dianhydro-α-d-glucopyranose	3.4
Unknown	14.6
Unknown	4.0
2-Ethenylfuran	2.6
2.3-Dihydroinden-1-one	0.6
Isopropyl myristate	<0.1

3. 2. Co-pyrolysis experiments

Co-pyrolysis experiments involving mixtures in different ratios of CS and HDPE resulted in a blend of the distinct degradation products from both feedstocks (Fig. 1). Subsequent fractionation of the pyrolyzates effectively separated these products.

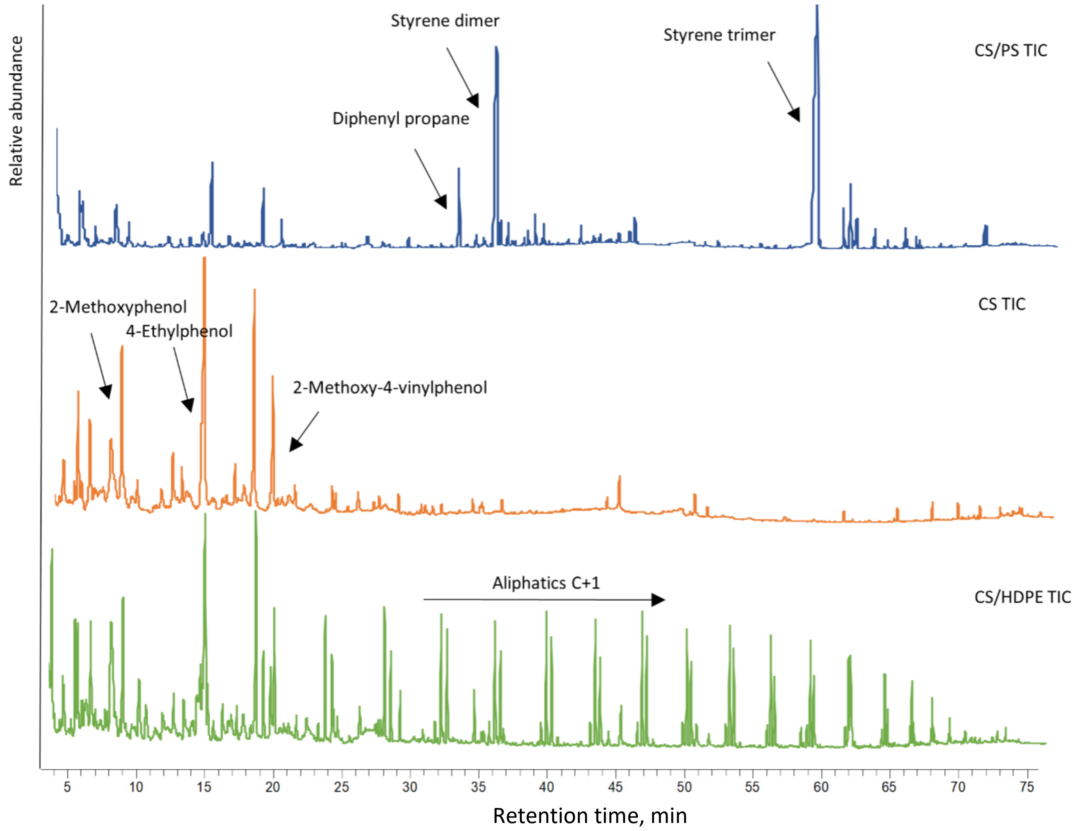

Figure 1. total ion chromatograms (TIC) obtained from the pyrolysis of CS samples and co-pyrolysis experiments on CS/PS and CS/HDPE mixtures in the 1:1 ratio

GC/MS analysis of the fractions revealed that, in contrast to the methanol fraction containing only CS degradation products, DCM fractions contained predominantly products derived from HDPE degradation, with only trace amounts of CS-derived products.

Co-pyrolysis of the CS/PS mixture resulted in a mixture of specific products as already observed in the CS/HDPE experiments. In contrary to the CS/HDPE experiments, in the DCM fraction, in all the observed ratios, products from the CS degradation were not identified, and only products coming from PS thermal degradation were observed. Consequently, the CS pyrolysis products were identified in the methanol fraction.

3. 2. 1. Co-pyrolysis of corn stalks / high density polyethylene mixtures

The effects of CS/HDPE ratios, ranging from 4:1 to 1:4 in the co-pyrolysis experiments were evaluated by the composition pattern based on calculated percentages of CS and HDPE products in the total products (as illustrated in Figure 2). According to Figure 2a, thermal degradation of both CS and HDPE was inhibited during CS/HDPE co-pyrolysis, resulting in significantly lower product yields compared to those obtained from individual pyrolysis processes. Already a very low amount of 25 mg of HDPE addition to CS pyrolysis has influenced the degradation process of CS. The fact that co-pyrolysis of biomass with different plastics differs from the individual pyrolysis of biomass was already proven in the literature [21,22].

However, further addition of the polymer into the mixture led to a linear increase in the amount of the obtained CS degradation products. Figure 2b demonstrates a linear correlation between the specific pyrolysis products and the amount of CS and HDPE in the pyrolysis mixtures. The respective pyrolysis product groups exhibited a yield increase from the CS/HDPE ratio of 4:1, reaching their maximum at the 1:1 ratio, followed by a decrease in ratios from 1:1 to 1:4. Only glucose derivatives reached their maximum at the 4:3 ratio (Table 2). In the 1:4 mixture, CS products constituted only 2.6 % of the resulting pyrolysis liquids (Figure 2b). This is in line with the study of Fan *et al.* investigating pyrolysis of lignin and PE mixtures in different ratios [22]. They reported that the addition of PE to lignin pyrolysis experiments led to the production of higher yields of lignin products, reaching the maximum at the ratio of 1:1 [23].

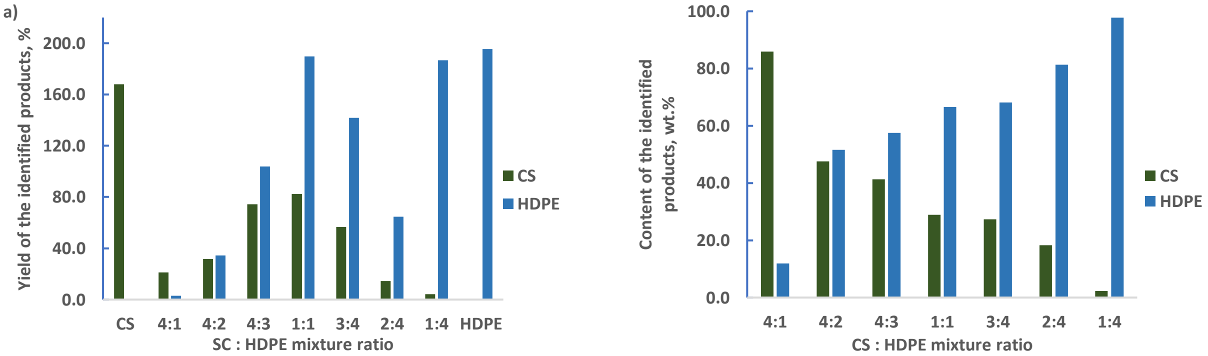

Figure 2. Co-pyrolysis of CS/HDPE mixtures: a) yields of the total identified CS and HDPE products; b) content of the total identified CS and HDPE products in the overall co-pyrolysis products

Table 2. Composition of the CS/HDPE co-pyrolysis products expressed as content of the compound groups for different CS/HDPE mass ratios

Compound group	CS/HDPE mass ratio						
	4:1	4:2	4:3	1:1	3:4	2:4	1:4
	Content, %						
Phenols	32.8	14.5	19.4	16.5	16.7	7.7	0.2
Aldehydes	1.7	2.9	1.6	0.8	0.8	2.2	0.3
Acids	0.3	0.2	0.7	0.7	0.7	0.2	0.0
Ketones	11.2	8.4	8.9	7.3	7.1	7.8	1.8
Diols and triols	0.7	0.8	1.3	0.9	1.1	0.2	0.0
Glucose derivatives	39.2	20.6	9.4	2.7	0.8	0.1	0.0
Alkadienes	0.0	3.1	3.4	7.6	7.7	6.1	9.0
n-Alkenes	0.0	14.0	22.2	30.4	32.8	31.7	43.5
n-Alkanes	11.9	34.5	31.9	28.6	27.7	43.5	45.3
Others	2.2	0.9	1.2	4.5	4.6	0.4	

Furthermore, in the CS/HDPE = 4:1 ratio (see subchapter 2.3), alkadienes and alkenes were not observed, and only alkanes from C_{13} to C_{31} were identified, constituting 11.9 % of all pyrolysis products for this experiment (Figure 2b).

However, as the proportion of HDPE in the feedstock increased, a linear increase in the amount of detected HDPE products occurred, including alkadienes, *n*-alkenes, and *n*-alkanes. *n*-Alkenes and *n*-alkanes dominated the pyrolizates in the ratios from 4:3 to 1:4, indicating a pronounced prevalence over CS products.

The 1:4 ratio resulted in a substantial production of HDPE products reaching 97.7 % (Figure 2b). The introduction of lower amounts of CS (25 mg) during HDPE pyrolysis suppressed the generation of n-alkanes. However, it resulted in increased production of n-alkenes and alkadienes (see Table 2). Moreover, the CS/HDPE ratio of 2:4 led to a noteworthy reduction in the total generated aliphatic products compared to 1:4 ratio (Figure 2a). However, with the further addition of CS in the feedstock, HDPE products experienced an increase starting from the 2:4 ratio and reaching their maximum at the 1:1 ratio.

The ratio of CS to HDPE was observed to significantly influence the composition of the pyrolytic liquids (Table 2). Co-pyrolysis of HDPE and CS resulted in the production of synthetic bio-oils characterized by lower oxygen content compared to the bio-oils obtained from the CS degradation, and a significant aliphatic contribution particularly those ranging from 4:3 to 2:4. These ratios revealed chemical compositions of the obtained oils beneficial for synthetic bio-oil production exhibiting a favourable balance of aliphatic and oxygen-aromatic compounds with content of 57.5 to 81.3 % of the aliphatic compounds (sum of alkanes, alkenes and alkadienes; see Table 2) within the specified range. This aliphatic composition is comparable to that found in commercial fuels like diesel, indicating substantial promise for future applications.

Table 2. Composition of the CS/HDPE co-pyrolysis products expressed as content of the compound groups for different CS/HDPE mass ratios

Compound group	CS/HDPE mass ratio						
	4:1	4:2	4:3	1:1	3:4	2:4	1:4
	Content, %						
Phenols	32.8	14.5	19.4	16.5	16.7	7.7	0.2
Aldehydes	1.7	2.9	1.6	0.8	0.8	2.2	0.3
Acids	0.3	0.2	0.7	0.7	0.7	0.2	0.0
Ketones	11.2	8.4	8.9	7.3	7.1	7.8	1.8
Diols and triols	0.7	0.8	1.3	0.9	1.1	0.2	0.0
Glucose derivatives	39.2	20.6	9.4	2.7	0.8	0.1	0.0
Alkadienes	0.0	3.1	3.4	7.6	7.7	6.1	9.0
n-Alkenes	0.0	14.0	22.2	30.4	32.8	31.7	43.5
n-Alkanes	11.9	34.5	31.9	28.6	27.7	43.5	45.3
Others	2.2	0.9	1.2	4.5	4.6	0.4	

3. 2. 2. Co-pyrolysis of corn stalks /polystyrene mixtures

As noticed above in Figure 1, in the CS/HDPE co-pyrolysis experiments the CS products were identified in the methanol fraction. Moreover, the comprehensive outcomes from the CS/PS pyrolysis experiments demonstrated a significant predominance of PS products over CS degradation (Figure 3a). The most abundant group of pyrolysis products in all co-pyrolysis experiments were benzene derivatives coming from the PS degradation, followed by phenols, glucose derivatives and ketones.

The relative proportions of the identified products given as content of the respective compound groups are given in Table 3. In the 1:1 ratio, acids, aldehydes and alcohols were detected at a minimal level of 0.4, 0.8 and 0.3 %, respectively. Ketones and glucose derivatives appeared at a range of 2.2 and 1.3 % respectively. The phenol formation decreased from 44.6 % in the individual CS pyrolysis to 8.4 % in the CS/PS 1:1 ratio. Moreover, at the 1:1 ratio benzene derivative dominated the pyrolizate with 85.6 %. Here, benzene derivatives include compounds like styrene oligomers, cyclopropyl benzene, biphenyl, diphenylmethane, diphenylethylene, diphenyl propane and diphenyl hexadiene. Styrene oligomers, styrene dimer and styrene trimer were identified as the most abundant pyrolysis products. Even at the 4:2 ratio, PS products showed overall prevalence over the products from CS degradation comprising 69.4 % of the obtained pyrolizate (Fig. 3b). It is suggested that lignocellulosic biomass sources typically exhibit a low hydrogen content, reflected in an H/C ratio ranging from 0 to 0.3. In contrast, plastic waste possesses a significantly higher H/C value when compared to biomass sources, resulting in higher yields of products with petrochemical characteristics [24].

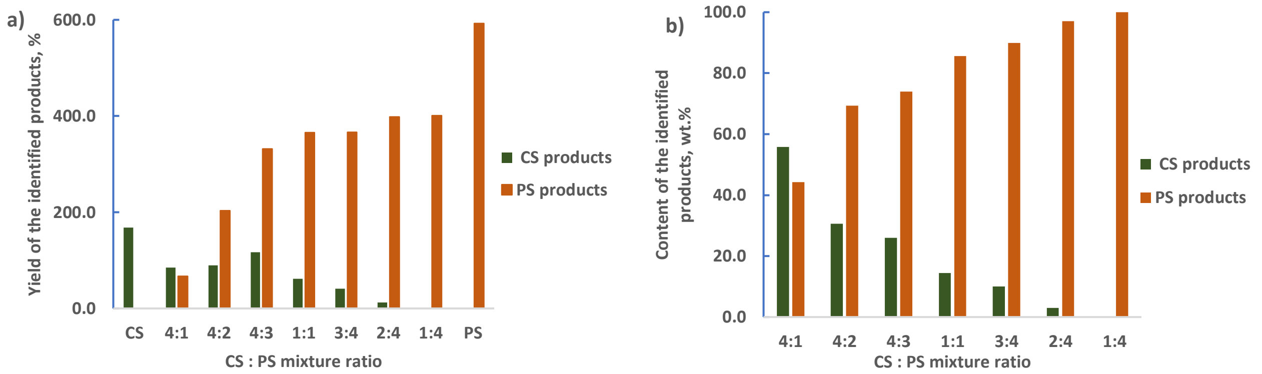

Figure 3. a) yield of the total identified CS and PS products; b) content of the total identified CS and PS products in the obtained pyrolizates

Table 3. Relative composition of the compound groups in the CS/PS co-pyrolysis experiments. Given ratios of co-pyrolysis educts correspond to subchapter 2.3

Compound classes / Co-pyrolysis experiments	Ratio of co-pyrolysis educts						
	4:1	4:2	4:3	1:1	3:4	2:4	1:4
	Relative content, %						
Phenols	13.4	16.4	10.9	8.4	6.2	0.7	0.0
Aldehydes	6.7	1.5	2.2	0.8	0.8	0.7	0.0
Acids	0.2	0.5	0.5	0.4	0.3	0.0	0.0
Ketones	4.6	5.1	8.7	2.2	1.5	0.6	0.0
Alcohols	0.9	0.7	0.3	0.3	0.5	0.1	0.0
Glucose derivatives	28.1	4.6	2.0	1.3	0.0	0.8	0.0
Benzene derivatives	44.2	69.4	74.0	85.6	89.9	97.0	100.0
Others	2.0	1.8	1.4	1.0	0.7	0.1	0.0

Furthermore, yields for both CS and PS samples were suppressed during the co-pyrolysis process as compared to the individual pyrolysis experiments. However, higher amounts of PS in the pyrolysis mixture did once again lead to higher amounts of the total CS products starting from the 4:1 ratio and reaching their maximum at the 4:3 ratio. For the 1:4 ratio, CS products were not identified. This can be explained by the prevalence of products derived from the PS degradation process, particularly styrene dimer and styrene trimer. The high abundance of these compounds might mask the presence of CS products in the chromatogram, making their detection challenging. Furthermore, the introduction of CS into PS pyrolysis resulted in reduced quantities of PS products compared to the individual PS pyrolysis. This pattern persists as the CS amount in the pyrolysis mixture increases. However, the 1:4 ratio demonstrated the most significant decrease in product yields, with subsequent additions showing only small changes in the obtained products.

3. 3. Comparison of co-pyrolysis processes of CS/HDPE and CS/PS mixtures

The co-pyrolysis of CS with different plastic wastes—HDPE and PS—demonstrated divergent pathways, both in product distribution and in the nature of biomass-plastic interactions. While both systems aimed to improve bio-oil quality by reducing oxygenated species, the underlying mechanisms and product outcomes differed.

In CS/HDPE mixtures, the co-pyrolysis resulted in liquid products with a marked aliphatic character, indicating effective hydrogen transfer and synergistic interaction. The formation of diesel-like compounds in HDPE-rich systems supports previous findings that polyolefins can enhance the deoxygenation of lignocellulosic biomass via radical neutralization and hydrogen donation [24]. Conversely, in CS/PS mixtures, the pyrolysates were dominated by compounds originating from PS degradation. The obtained CS product yields in the CS/PS mixture were much higher compared to the yields obtained in the CS/HDPE mixture. This could be due to the formation of wax, that is being produced as a solid product of the pyrolysis process during the thermal degradation of HDPE. This is a residual product that partly remains in the pyrolysis container and can thus compress the degradation of the biomass, which is not the case with PS degradation.

These contrasting behaviors suggest that plastic type plays a decisive role in directing co-pyrolysis pathways. HDPE serves primarily as a hydrogen source, enabling improved fragmentation and volatilization of biomass-derived species while PS contributes predominantly through its own decomposition, producing high-value aromatics but offering limited synergy with the lignocellulosic matrix. From an application standpoint, CS/HDPE systems are more aligned with fuel-oriented outcomes, while CS/PS may be more suited for producing specialty chemicals. Therefore, the choice of plastic co-feedstock should be aligned with the desired product spectrum.

Achieving economically feasible production of high-quality bio-oil requires careful process optimization to ensure satisfactory yields. One viable upgrading strategy focuses on in situ catalytic deoxygenation during pyrolysis. Zeolite-based catalysts, particularly ZSM-5, are widely used for this purpose due to their efficiency in facilitating dehydration reactions [25,26]. Other catalysts, such as basic metal oxides (e.g., CaO and MgO), have also been explored [26], though their application may lead to increased coke formation and a decline in oil yield [26].

4. CONCLUSION

In this study, pyrolysis and co-pyrolysis experiments on corn stalk samples and HDPE and PS plastic waste samples were conducted at various ratios. The objective was to explore the influence of the feedstock composition on the obtained product yields and the selectivity of the obtained products. Synergistic effects were observed in both CS/HDPE and CS/PS mixtures. The plastic samples acted as hydrogen donors during CS degradation, resulting in increased yields of CS products as the proportion of plastic waste in the pyrolysis mixture varied from 4:1 to 1:1. Notably, both HDPE and PS products exhibited a pronounced prevalence over CS products, which is particularly advantageous given the high oxygen content in CS products. In CS/HDPE experiments, aliphatic compounds, specifically *n*-alkenes and *n*-alkanes, constituted the most abundant compounds. The total aliphatic content in the obtained pyrolyzates ranged from 57.5 % to 81.3 % for ratios ranging from 4:3 to 2:4. This range of aliphatic compounds closely resembles diesel fuel, highlighting the potential of these co-pyrolysis products for synthetic bio-oil production. In contrast, CS/PS experiments showed that benzene derivatives were the predominant compounds, constituting 85.6 % in the 1:1 ratio. This resulted in a reduction in the phenolic structures originating from the pyrolysis of CS, as opposed to the individual pyrolysis of CS.

It is important to highlight that this method signifies a transitional approach for managing plastic waste, as the utilization of plastic materials is expected to phase out in the anticipated future. However, this investigation presents insights into the behaviors of lignocellulosic biomass waste and plastic materials, revealing valuable understandings into the chemical composition of the bio oils obtained from co-pyrolysis experiments. The results represent important and general aspects as base for designing bio fuels from different waste fractions.

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REFERENCES

[1] Ryu HW, Kim DH, Jae J, Lam SS, Park ED, Park Y-K. Recent advances in catalytic co-pyrolysis of biomass and plastic waste for the production of petroleum-like hydrocarbons. *Bioresour Technol.* 2020; 310: 123473. https://doi.org/10.1016/j.biortech.2020.123473

[2] Wang G, Dai Y, Yang H, Xiong Q, Wang K, Zhou J, Li Y, Wang S. A review of recent advances in biomasspyrolysis. *Energ Fuel.* 2020; 34(12): 15557-15578. https://doi.org/10.1021/acs.energyfuels.0c03107

[3] Chen H, Lin G, Chen Y, Chen W, Yang H. Biomass pyrolytic polygeneration of tobacco waste: product characteristics and nitrogen transformation. *Energ Fuel.* 2015; 30(3): 1579-1588. https://doi.org/10.1021/acs.energyfuels.5b02255.

[4] Munawer ME. Human health and environmental impacts of coal combustion and post-combustion wastes. *J Sustain Min.* 2018; 17(2): 87-96. https://doi.org/10.1016/j.jsm.2017.12.007.

[5] Martín JVG, González JF, Martínez G. Energetic use of the tomato plant waste. *Fuel Process Technol.* 2008; 89(11): 1193-1200. https://doi.org/10.1016/j.fuproc.2008.05.011.

[6] Tsai W, Lee MK, Chang Y-F. Fast pyrolysis of rice husk: Product yields and compositions. *Bioresour Technol.* 2007; 98(1): 22-28. https://doi.org/10.1016/j.biortech.2005.12.005 .

[7] Mohan D, Pittman ACU, Steele PH. Pyrolysis of Wood/Biomass for Bio-oil: A Critical review. *Energ Fuel.* 2006; 20(3): 848-889. https://doi.org/10.1021/ef0502397.

[8] Bridgwater AV. Renewable fuels and chemicals by thermal processing of biomass. *J Chem Eng.* 2003; 91(2-3): 87-102. https://doi.org/10.1016/s1385-8947(02)00142-0.

[9] Koul B, Yakoob MY, Shah MP. Agricultural waste management strategies for environmental sustainability. *Environ Res.* 2022; 206: 112285. https://doi.org/10.1016/j.envres.2021.112285.

[10] Maslac T. Grain and Feed Annual Report (Serbia). United States Department of Agriculture - Foreign Agricultural Service, 2021. https://apps.fas.usda.gov/newgainapi/api/Report/DownloadReportByFileName?fileName=Grain%20and%20Feed%20Annual_Belgrade_Serbia_04-01-2021

[11] Omais B, Crépier J, Charon N, Courtiade M, Quignard A, Thiébaut D. Oxygen speciation in upgraded fast pyrolysis bio-oils by comprehensive two-dimensional gas chromatography. *Analyst* 2013; 138(8): 2258. https://doi.org/10.1039/c2an35597c

[12] Ahmed I, Nipattummakul N, & Gupta A, Characteristics of syngas from co-gasification of polyethylene and woodchips. *Appl Energy*, 2010; 88(1): 165-174. https://doi.org/10.1016/j.apenergy.2010.07.007

[13] Wu M, Wang Z, Chen G, Zhang M, Sun T, Wang Q, Zhu H, Guo S, Chen Y, Zhu Y, Lei T, Burra K, G & Gupta AK, Synergistic effects and products distribution during Co-pyrolysis of biomass and plastics. *J Energy Inst.* 2023; 111, 101392. https://doi.org/10.1016/j.joei.2023.101392

[14] Liu X, Burra KG, Wang Z, Li J, Che D, & Gupta AK, On deconvolution for understanding synergistic effects in co-pyrolysis of pinewood and polypropylene. *Appl Energy* 2020*;* 279: 115811. https://doi.org/10.1016/j.apenergy.2020.115811

[15] Rutkowski P, Kubacki A. Influence of polystyrene addition to cellulose on chemical structure and properties of bio-oil obtained during pyrolysis. *Energy Convers Manag.* 2006; 47(6): 716-731. https://doi.org/10.1016/j.enconman.2005.05.017

[16] KositkanawuthK, Bhatt A, Sattler M, & Dennis, Renewable Energy from Waste: Investigation of Co-pyrolysis between Sargassum Macroalgae and Polystyrene. *Energy Fuels.* 2017; 31(5): 5088-5096. https://doi.org/10.1021/acs.energyfuels.6b03397

[17] Zheng Y, Tao L, Yang X, Huang Y, Liu C, Zheng Z. Study of the thermal behavior, kinetics, and product characterization of biomass and low-density polyethylene co-pyrolysis by thermogravimetric analysis and pyrolysis-GC/MS. *J Anal Appl Pyrol.* 2018; 133: 185-197. https://doi.org/10.1016/j.jaap.2018.04.001

[18] Jovancicevic I, Antić M, Gajica G, Schwarzbauer J. Co-pyrolysis of various plastic waste components as an environmentally sustainable source of alternative fuels. *J Serb Chem Soc.* 2024; 89(7-8): 1053-1066. https://doi.org/10.2298/jsc240207046j

[19] Wiley Registry/NIST Mass Spectral Library 2023. https://sciencesolutions.wiley.com/solutions/technique/gc-ms/wiley-registry-nist-mass-spectral-library/ (Accessed July 31, 2025)

[20] Pittman CU, Mohan D, Eseyin AE, Li Q, Ingram LL, Hassan EB, Mitchell B, Guo H, Steele PH. Characterization of Bio-oils Produced from Fast Pyrolysis of Corn Stalks in an Auger Reactor. *Energ Fuel.* 2012; 26(6): 3816-3825. https://doi.org/10.1021/ef3003922.

[21] Wang S, Lin X, Li Z, Yi W, Bai X. Thermal and kinetic behaviors of corn stover and polyethylene in catalytic co-pyrolysis. *Bioresour.* 2018; 13(2): 4102-4117. https://doi.org/10.15376/biores.13.2.4102-4117.

[22] Fan Y, Liu C, Kong X, Yue-Hong H, Lei M, Xiao R. A new perspective on polyethylene-promoted lignin pyrolysis with mass transfer and radical explanation. *Green Energy Environ.* 2022; 7(6): 1318-1326. https://doi.org/10.1016/j.gee.2021.02.004.

[23] Chu SY, Subrahmanyam AV, Huber GW. The pyrolysis chemistry of a β-O-4 type oligomeric lignin model compound. *Green Chem.* 2013; 15(1): 125-136. https://doi.org/10.1039/c2gc36332a.

[24] Chattopadhyay J, Pathak TS, Srivastava R, Singh A. Catalytic co-pyrolysis of paper biomass and plastic mixtures (HDPE (high density polyethylene), PP (polypropylene) and PET (polyethylene terephthalate)) and product analysis. *Energy* 2016; 103: 513-521. https://doi.org/10.1016/j.energy.2016.03.015.

[25] Nishu, Liu R, Rahman MdM, Sarker M, Chai M, Li C, Cai J. A review on the catalytic pyrolysis of biomass for the bio-oil production with ZSM-5: Focus on structure. *Fuel Proc Technol.* 2020; (199): 106301. https://doi.org/10.1016/j.fuproc.2019.106301

[26] Zadeh ZE, Abdulkhani A, Aboelazayem O, Saha B. Recent Insights into Lignocellulosic Biomass Pyrolysis: A Critical Review on Pretreatment, Characterization, and Products Upgrading. *Processes.* 2020; 8(7): 799. https://doi.org/10.3390/pr8070799

Hemijski sastav pirolizata dobijenih ko-pirolizom ostataka kukuruznih stabljika i plastičnog otpada kao osnova za proizvodnju ekološki održivih goriva

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(Naučni rad)

Izvod

U ovom istraživanju izvršeni su eksperimenti pirolize i ko-pirolize uzoraka otpada lignoceluloznih kukuruznih stabljika (KS) i odabranih frakcija plastičnog otpada (polietilen velike gustine (engl. high density polyethylene, HDPE) i polistiren (PS)) u različitim masenim odnosima. Glavni cilj bio je procena uticaja sastava sirovine na prinos i sastav rezultujućih piroliznih proizvoda, razvijajući održivu metodu za upravljanje kako otpadom biomase tako i plastičnim otpadom kroz proizvodnju ulja i hemikalija. Reakcije ko-pirolize dokazale su sinergističke efekte između sirovina, pri čemu se plastični otpad pokazao kao donor vodonika poboljšavanjem prinosa proizvoda KS. Osim toga, proizvodi od plastičnog otpada su pokazali značajnu premoć nad onima od KS, čineći oko 66,6 i 85,6 % u odnosu 1:1 smeša KS/HDPE i KS/PS, redom. Ovo istraživanje pruža važne uvide u formiranje sintetičkih bio-ulja kroz dizajn hemijskog sastava i optimizaciju prinosa pirolize, što je posebno značajno zbog povećanog sadržaja kiseonika u proizvodima dobijenim pirolizom KS koji može povećati kiselost i korozivnu aktivnost bio-ulja.

Ključne reči: Plastični otpad; polietilen velike gustine; polistiren; gasna hromatografija-masena spektrometrija; sintetička bio-ulja; održivi razvoj