

Influence of plastic content on synergistic effect and bio-oil quality from the co-pyrolysis of waste rigid polyurethane foam and sawdust mixture

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ABSTRACT

Current disposal of end-of-life plastics by landfilling or incineration raises serious environmental concerns, simultaneously representing an irretrievable loss of valuable resources. Especially this is evident for materials that have a complex structure, like polyurethane foams. In this work, co-pyrolysis with sawdust was carried out to analyze and evaluate the product quality for further utilization as alternative fuels. The introduction of polyurethane increased the oil yield but in a limited range since no significant difference was observed between the mixture with 25 and 75% of polyurethane content. In addition, the chemical analysis showed that small addition of polyurethane is sufficient to eliminate most of the oxygenated compounds derived from sawdust. Nevertheless, the obtained liquid products are mostly benzenamines that do not meet the criteria for fuel composition. Analysis of the synergistic effect shows that the strongest impact is visible for a small branch of plastic content where liquid yield was promoted at the expense of gas. With a further increment of plastic content, this effect fades away, except for the solid residue which remains constant. Finally, a brief analysis of the gaseous fraction showed that obtained products are preferred in syngas composition, with notable hydrogen yield as the most valuable constituent.

KEYWORDS

co-pyrolysis, polyurethane, sawdust, product analysis, chemical composition, utilization possibility

ABBREVIATIONS

GC	Gas chromatography	PUR	Rigid polyurethane foam
HHV	High heating value	SD	Sawdust
MDA	3,4-Methylenedioxyamphetamine	TGA	Thermogravimetric analysis
PAHs	Polycyclic Aromatic Hydrocarbons	$W_{SD/PUR}$	Share of component
PE	Polyethylene	Y_{cal}	Calculated value
PP	Polypropylene	Y_{exp}	Experimental value
PS	Polystyrene	ΔY	Synergy level
PU	Polyurethane		

1. INTRODUCTION

Polyurethane foams (PU) are widely used polymers, with about 18 million tons produced in 2016, utilized for various applications in the automotive industry and as insulation or structural material for different appliances [1]. They are made in rigid, flexible, and viscoelastic forms [2]; therefore, their properties might vary significantly, greatly influencing their end-of-life treatment. Landfilling and incineration are the most used methods to deal with this problem, resulting in the inevitable loss of valuable resources and raising environmental issues. Simon et al. [3] brought a detailed review of potential methods for chemical recycling of waste polyurethane foams, emphasizing that recycled materials have limited application possibilities. Pyrolysis or gasification might be a promising alternative since it can convert waste materials into valuable fuels and chemicals, as mentioned in a review by Kemono and Piotrowska [4]. Nevertheless, while the rest of the polymers, such as polystyrene (PS) [5-6], polypropylene (PP) [7], or polyethylene (PE) [8-9] were widely investigated for alternative fuel production, the studies which are dealing with PU treatment by thermochemical conversion methods are seldom.

Most of the studies found in the literature deal with the investigation of kinetics or thermal degradation mechanism rather than the product compounds analysis. Garrido et al. [10] investigated the pollutant emissions from the pyrolysis of flexible polyurethane foam, focusing on the formation and yield of PAHs, furans, and chlorine-containing compounds. At 850 °C, the formation of such compounds was highest, implying potential constraints for the gasification as the recycling method. Garrido and Font [11] investigated the thermal decomposition of flexible PU in nitrogen and air atmosphere, finding that this parameter influences the number of steps in which decomposition occurs. In the case of the inert atmosphere, the process consists of two steps, while three steps are observed for the oxidative environment. This observation is even more valuable when put in the context that the rest of the polymers have a single-step decomposition mechanism. Yao et al. [12] performed pyrolysis on rigid PU from waste refrigerators in an inert atmosphere using nitrogen. They found out that decomposition consists of three stages: the initial stage at 38 to 400 °C, the second stage between 400–550 °C, and the last stage ranges between 550–1000 °C. This shows that the thermal decomposition mechanism of PU strongly depends on its type (rigid or flexible), which is a direct consequence of its chemical structure, usage of additives, and production process. Furthermore, the fact that PUs have a three-step decomposition mechanism is important for co-pyrolysis since biomass and PU could directly interact when decomposed.

Nishiyama et al. [13] analyzed the derived products from the pyrolysis and concluded that they are primarily linear hydrocarbons or oxygenated, benzene-containing species. The nitrogen-containing products (4-amino-4'-isocyanate diphenyl methane - MAI, 4,4'-Methylenedianiline - MDA) expressed the highest intensity, which is expected since they are used during the synthesis. The yield of linear hydrocarbons is favored for fuel purposes, but the yield of benzene-containing species should be minimized. One of the possible solutions might be co-pyrolysis with biomass, where feedstock interaction coupled with process parameters can reduce the yield of potentially harmful compounds [14]. An additional benefit of such practice is resolving problems related to

biomass-derived fuels like poor thermal stability, lower heating value, high viscosity or acidity, and similar [15]. Moreover, due to the limited biomass availability and geographical distribution, it is necessary to find alternative exploitation routes to maximize its potential in future energy systems while simultaneously maintaining consumption within sustainable boundaries [16].

Hassan et al. [17] provided a comprehensive review of progress in the field of biomass pyrolysis. The study emphasized the importance of co-pyrolysis with hydrogen-rich feedstock such as waste plastics to improve product properties. Biomass feedstock was widely investigated and, even more, used to produce high-quality bio-oils that are currently blended with conventional gasoline. Even though the drawbacks mentioned above constrain wider biofuel deployment or its usage in the aviation sector. Arregi et al. [18] performed pyrolysis of pine sawdust and high-density polyethylene for hydrogen-rich gas production. The results from the ultimate and proximate analysis of pine sawdust are similar to the sawdust mixture used in this study, even though the type of wood is entirely different. Yet, the product distribution is completely different, suggesting the importance of the structural composition of the biomass sample. Ahmed et al. [19] pyrolyzed *Acacia* sawdust for bio-oil production at temperatures between 400-600 °C. The highest oil yield was noticed for 500 °C, which dramatically decreased with the temperature increment to 600 °C, mostly to yield a higher share of non-condensable gases. This observation suggests that at least 500 °C is required to enhance bio-oil yield. Further increment of temperature is beneficial to reduce solid residue, but secondary cracking will occur and increase gaseous yield at the expense of liquid fraction. Liu et al. [20] performed catalytic pyrolysis over the pine sawdust with almost the same composition as the one used in this study. They found out that the addition of catalyst has a limited impact on product distribution, while it might promote the secondary reactions at higher temperatures to increase the gas yield. Kai et al. [21] performed the co-pyrolysis of corn stalk and high-density polyethylene. They concluded that the strongest synergy between biomass-plastic samples is achieved for small plastic content (<20%), and the blending ratio has a low impact on the evolution of gaseous products. The strongest synergistic effect for small plastic content is also detected in a study carried out by Ephraim et al. [22], where polystyrene and polyvinyl chloride were used.

Thermogravimetric, kinetic and thermodynamic analysis of PU and sawdust (SD) mixture was carried out in our previous work as the first step to evaluating the potential of selected feedstock for the co-pyrolysis [23]. In this work, the three-step decomposition mechanism is observed for PU, which also overlaps with the SD decomposition area, suggesting that the feedstock might interact significantly when decomposed. Since the chemical properties and thermal decomposition of PUs are pronouncedly different from the rest of typical polymers and more similar to biomass feedstock, it is interesting to investigate how this interaction reflects on final product distribution. Up to now, there have been no attempts to utilize waste rigid polyurethane foam and biomass in the co-pyrolysis to produce alternative fuels. Therefore, this work aims to provide an in-depth analysis of the chemical composition of obtained pyrolytic oil, which is not found in the literature. Besides, a brief analysis of obtained syngas fraction will be given, even though the research focuses on maximizing liquid yield. Furthermore, the influence of plastic content on product

quantity and quality is evaluated by observing the synergistic effect between investigated feedstocks. Finally, the appropriate conclusions regarding the PU potential for alternative fuel production are driven.

2. MATERIALS AND METHODS

Under this section, the used materials are presented with their origin, sample preparation procedure, and the preliminary results obtained from the ultimate and proximate analysis. This is followed up by a detailed explanation of used experimental methods to ensure the reproducibility of results. The experiments and liquid fraction sampling for chemical characterization have been duplicated to ensure the accuracy of the results.

2.1. Material characterization

Samples investigated in this study were waste rigid polyurethane foam (PUR) obtained from the discharged refrigerator and used as an insulation material. Biomass feedstock was a sawdust mixture of beech, oak, and fir wood with the unknown shares obtained from a local sawmill. Samples were prepared by shredding, grinding, and sieving into finer particles (0.125-0.25 mm) to ensure the mixture's homogeneity. Besides, in the previous work where utilization properties of PUR were investigated, it was found that this particle size is the most promising one for thermochemical processes since the lowest amounts of harmful compounds are detected in that range [24].

PUR was obtained with the known ultimate and proximate analysis values. The sawdust properties are investigated according to ISO 17225-1:2021 [25]. The heating values are measured using the bomb calorimeter and following the procedure determined in the standard ISO 18125:2017 [26]. As can be seen, the heating value for PUR is pronouncedly higher than that of SD but still dramatically lower compared to the heating values of the majority of other plastics like PS, PP, or PE, which are above 40 MJ/kg [27]. Moreover, a high share of nitrogen (~7%) is detected in the PUR sample, which is not the case for other conventional polymers. Finally, from the proximate analysis of the PUR sample, a high share of volatile matter can be noticed, which is beneficial for the yield of liquid and gaseous fractions. Nevertheless, almost 6% of ash in the composition suggests that a high yield of solid residue can be expected at the end of the process. The results are summarised in Table 1.

Table 1 - Ultimate and proximate analysis of PUR and sawdust samples

	C (%)	H (%)	N (%)	O (%)	Ash (%)	Volatile matter (%)	Moisture (%)	Fixed carbon (%)	HHV (MJ/kg)
PUR	63.9	6.5	6.8	22.8	5.8	82.0	2.7	9.5	26.7
Sawdust	47.3	6.0	0.3	46.4	1.4	73.0	7.4	18.2	17.3

2.2. Thermal decomposition investigation

Thermogravimetric analysis (TGA) was carried out using TGA/DSC 2 Thermoanalyzer Mettler Toledo. The TGA is an inevitable step in the experimental investigation of the thermal decomposition mechanism, and it is often used to determine optimal process conditions for pyrolysis [28]. Samples were investigated individually and in mixtures with different shares: PUR/SD 25-75%, PUR/SD 50-50%, PUR/SD 75-25%. Samples of about 10 mg were heated

in Al₂O₃ crucibles of 70 μl, from room temperature to 600 °C, at a heating rate of 10 °C/min. As a carrier, gas nitrogen was used with a flow rate of 20 ml/min. The final temperature is selected based on previous research presented in the Introduction section. While Ahmed et al. [19] pointed out that the highest liquid yield is obtained at 500 °C, the process was further extended to 600 °C to minimize the final solid residue. This is because previous studies conducted on PU samples show that the significant mass loss is still evident after 500 °C.

2.3. Pyrolysis conditions and product analysis

The pyrolysis experiments were performed in a stainless-steel fixed bed reactor. A detailed description of the experimental setup and reactor components used in this work has been described by Hlavsova et al. [29] in their original research. The experiments were conducted under a nitrogen atmosphere with an 80 ml/min flow rate. Approximately 2 g of the sample was placed in the reactor and heated at 10 °C/min to a final temperature of 600 °C. The final temperature was maintained for about 30 min or until the complete release of pyrolysis gases. The moderate heating rate of 10 °C/min was selected based on our previous kinetic analysis, which showed no significant differences in the decomposition mechanism for the applied heating rates [23]. Samples were examined individually and in mixtures with the shares as mentioned above. The yield of the solid fraction was calculated by weighing the sample mass before and the residual mass after the pyrolysis. The output of pyrolysis gas was calculated at N₂ free-vol.%, and it is based on the volume fractions obtained from gas chromatography (GC) and densities of individual gas components. Condensable gases were cooled down using an ice bath and collected in liquid form at the end of a reactor. The share of the liquid fraction was calculated by the difference. A detailed description of the gas chromatography and mass spectrometry properties and conditions can be found in our previous work, where co-pyrolysis of polystyrene and biomass sawdust was investigated [6].

3. RESULTS

In this section in-depth analysis of liquid fraction was carried out to determine feedstock potential for alternative fuel production. Besides, a preliminary examination is performed for gaseous fraction, and the main observation from TGA are summarized at the beginning of the interpretation of the results. Finally, the synergistic effect that occurs during the feedstock interaction is evaluated at the end of this section.

3.1. Thermogravimetric and derivative thermogravimetric analysis

Another study presents a detailed thermogravimetric analysis of individual samples and respective mixtures [23]. Nevertheless, prepared samples were subjected to TGA before the pyrolysis to compare the accuracy between investigations (Figure 1). As expected, for the SD sample, moisture evaporation goes up to 110 °C, accounting for 5% of mass loss. The primary decomposition step starts at ~240 °C, with the peak at 350 °C, and ends immediately at 380 °C. The last stage, where mostly lignin is decomposed, takes a linear pathway until 600 °C, and the final residue is approximately 20%. The majority of polymers like PS, PE, or PP have a single-stage decomposition mechanism [30], while in the case of PUR, three stages can be observed. In the first

drying stage, the mass loss is negligible. At ~ 280 °C, the primary decomposition stage begins, with the main peak at 340 °C, similar to SD. At this temperature, almost half of the sample is decomposed. The second slight peak can be observed at 450 °C, indicating that PUR has a broader temperature range in which decomposition occurs than SD. The last stage of decomposition starts at 480 °C, and until 600 °C, about 10% of the sample is decomposed, and the final mass is slightly below 30%. As can be observed, the decomposition mechanism has three stages, also found in the study by Jao et al. [12], even though the temperature ranges slightly differ.

The thermal decomposition of investigated mixtures shows similar behavior to the analysis of the individual samples. The mixture, where the sawdust is a dominant compound, has a visible mass loss due to evaporation and expresses a more intensified curve breakdown at 360 °C, observed for the biomass decomposition as well. The second decomposition stage for all mixtures happens in a broader temperature range, except for the sample where SD is the main constituent. In that case, the second stage ends slightly above 400 °C, while the rest of the mixtures goes up to 500 °C. Similar behavior is also observed for PUR decomposition, probably due to the decomposition of halogenic compounds. The final mass is around 30%, similar to the PUR sample and other mixtures. These final masses are still considerably high, even though the process was extended to 600 °C. Nevertheless, a further increment in temperature would initiate secondary crackings and promote the yield of the gaseous fraction, which is not an objective of this study.

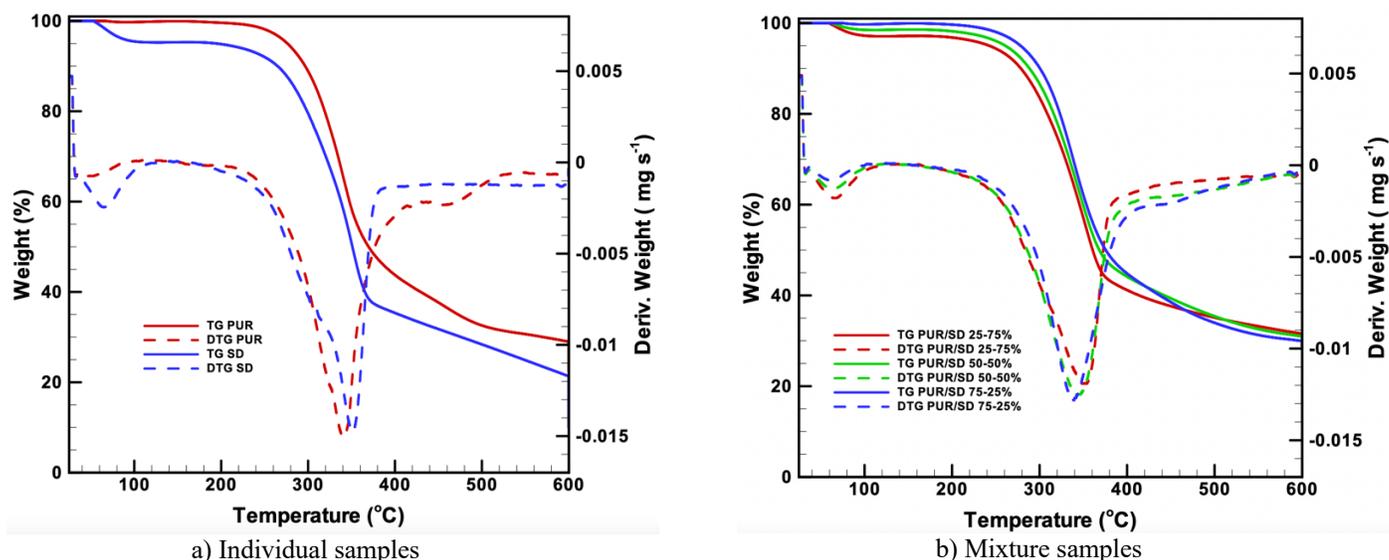


Figure 1 - TG and DTG curves for individual samples a) and mixtures b) thermal decomposition

3.2. Pyrolysis product analysis

Individual pyrolysis of investigated samples shows a similar share of solid residue in the range of 20-22%. Nevertheless, the distribution of volatiles, gas, and liquid fractions shows completely different trends (Figure 2). In the case of the SD sample, the dominant fraction is syngas with a share of 48%, followed by bio-oil yield with $\sim 31\%$. From PUR pyrolysis, the predominant product is an oil with a yield of 61%, even though a notable amount of gaseous fraction (17%) is detected

as well. The oil yield from PUR is pronouncedly lower than conventional polymers like PS, where the yield of a liquid fraction can go up to 96% [6]. A high share of syngas from SD pyrolysis may be attributed to cellulose decomposition, which is the main driver for yielding non-condensable volatiles with low carbon numbers ($<C_4$). Such results might indicate that cellulose is the principal constituent of the used biomass sample. Nevertheless, to confirm this hypothesis, deconvolution of the TGA curve should be carried out to determine the structural composition of the sawdust sample [31].

For the mixtures pyrolysis, the yield of a solid fraction is slightly higher than individual samples (~27%) but more-less constant for all investigated mixtures. In general, the solid residue is a consequence of fixed carbon and ash content, and obtained values for individual samples are expected. Nevertheless, in the case of mixtures, the share of solid residue is increased, probably due to the feedstock interaction during the process and their mutual influence that hinders complete decomposition and release of volatiles. The yield of liquid fraction is extensively promoted by introducing PUR to the fuel mixture, from 31% for the SD sample to around 50% for all investigated mixtures. This was achieved at the expense of the gaseous fraction, which yields decreased to only 20% for the mixture with 75% of PUR content. The introduction of only 25% of PUR halved the yield of gases compared to results from sawdust pyrolysis. Once again, this confirms the hypothesis that waste plastics can significantly enhance the liquid yield from co-pyrolysis [32]. Nevertheless, it is interesting to observe the potential for improving the oil yield by introducing PUR into the mixture. Even in the case of 75% of PUR content, the oil yield barely surpasses 50%. In addition, the difference in oil yield between the mixture with 25% and 75% of PUR content is below 4%. Such observation indicates that the polyurethane potential for an increment of oil yield is greatly limited. This can be confirmed by comparing previous work where PS was investigated [6], since only 25% of PS in the mixture doubled the yield of liquid fraction, and further increment of PS content had a visible impact on final product distribution, promoting the oil yield. Even more, the share of the solid fraction was reduced with the increment of PS content. At the same time, this study found that mixtures have an even higher share of a solid residue than individual samples, and the mixing ratio does not play an important role. Similar was also found for the co-pyrolysis of corn stover with PP [33]. The addition of PP has a visible effect on promoting the yield of the liquid fraction at the expense of others. Nevertheless, in that case, the yield of a gaseous fraction remains relatively high (42-48%) since individual polypropylene pyrolysis yields about 40% of gases. A detailed analysis of liquid and gaseous products is given in the following sections.

Furthermore, through the analysis of the synergistic effect, the influence of PU content on final product distribution will be discussed. The solid fraction is not further investigated since the utilization possibilities are relatively low. A promising solution for its utilization might be as an additive to enhance wood pellets' quality [34].

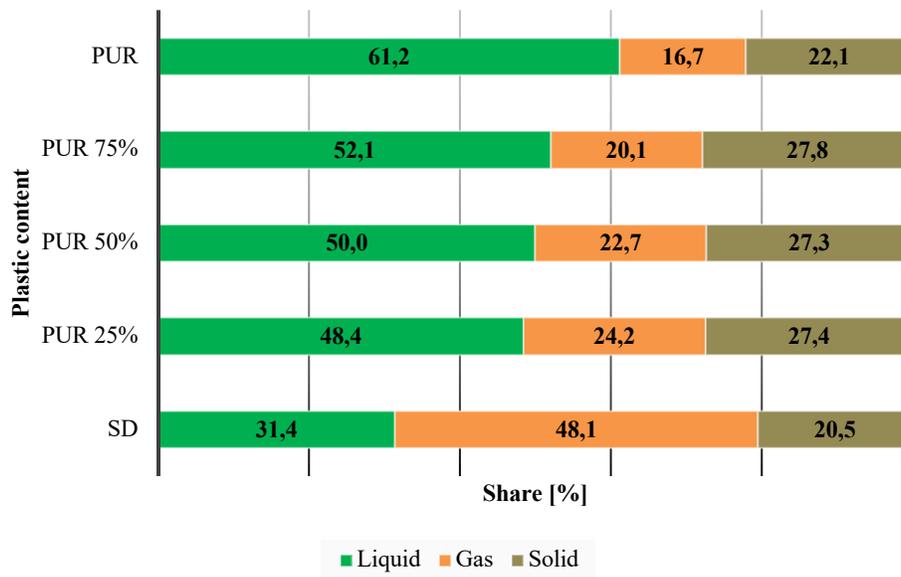


Figure 2 - Product yield from individual pyrolysis and PUR/SD blends co-pyrolysis

3.3. Chemical characterization of the liquid fraction

Analysis of liquid fraction composition showed that bio-oil from SD pyrolysis consists of 90 compounds, while 94 are detected in the liquid from PUR pyrolysis. In the case of mixtures, the number of identified compounds with visible shares is 94. It should be emphasized that some other compounds may be present in traces, but their significance can be neglected in this case. Identified compounds belong to different organic groups like aromatic amines (benzenamines), aromatic hydrocarbons, phenols, alcohols, PAHs, ketones, acids, and aldehydes. The share of organic groups in the obtained oils is given in Figure 3. For better visibility in the given figure, the term *Rest* encompasses toluene, indole, sugars, and furans, which are present with a minor share.

As can be seen, in the case of bio-oil from SD pyrolysis, the dominant are oxygen-containing compounds like phenols (24%), ketones (22%), and aldehydes (12%), which is expected and already reported in the literature [28-29]. Besides, a significant amount of acids and PAHs are detected (~9% and ~10%, respectively), which is not beneficial for fuel purposes. The formation of PAHs from biomass pyrolysis occasionally occurs through the acetylene addition mechanism, where acetylene reacts with naphthalenes to promote the yield of PAHs [37]. Since the share of acetylene and naphthalene is relatively low in bio-oil, it can be presumed that the acetylene addition mechanism has occurred here. Lin et al. [38] suggest torrefaction of biomass sample before the pyrolysis to reduce the yield of unwanted compounds like furans, aldehydes, and acids. This technique improves the bio-oil quality, even though it reduces its quantity. On the other hand, the benzenamines (~72%) are the dominant compounds from PUR pyrolysis, followed by aromatic hydrocarbons (~8%). In addition, a significant amount (~6% each) of phenols and alcohols is detected as well, most probably as a consequence of PUR synthesis [2].

When it comes to mixtures, it can be seen that the share of PUR has a significant influence on liquid product distribution. Only a small introduction of PUR almost wholly removed the

aldehydes and sugars, while it significantly reduced the yield of ketones, acids, and most importantly, PAHs below 3%. It is especially interesting to observe the creation of PAHs, which are only present in traces for individual PUR pyrolysis. This is probably because the significant generation of PAHs from polyurethane starts at 700 °C [24], with the highest yield above 1000 °C, where soot and char are formed [39]. Therefore, at 600 °C, the generation of such compounds is hindered for a liquid fraction, while various benzenamines (42%) and aromatic hydrocarbons (13%) are promoted. In the case of phenols, for this mixture with 25% of PUR, the reduction was almost negligible, which can be attributed to the fact that PUR oil also yields these compounds; therefore, a complete removal is not possible.

Further increment of PUR content almost completely removed the ketones and acids, significantly influencing the yield of phenols. For the mixture with 50% PUR, the yield of phenols is halved, while further increment of PUR content to 75% reduced the yield to only 3%. Removing phenols is strongly preferred since they can cause jet-fuel surface deposits and corrosion [40].

Simultaneously, with the reduction of oxygen-containing organic groups, the formation of benzenamines was promoted, and they are the dominant constituents of the mixture's oils. Nevertheless, benzenamines are not preferred in the fuel composition, and even more, by observing the organic groups of derived oils, it can be stated that their potential for further refinement to fuel is minimal. They could be better utilized elsewhere in the chemical industry.

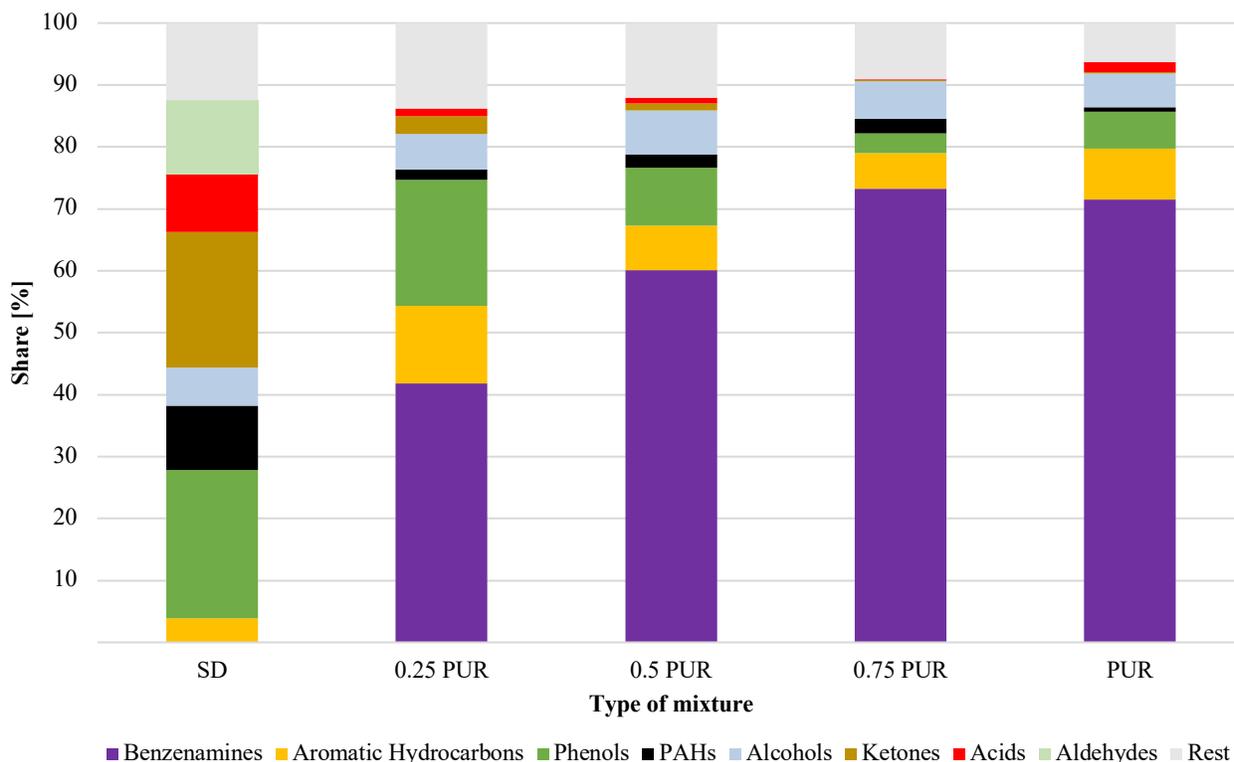


Figure 3 - Identified organic groups in the obtained bio-oils

Detailed compound analysis was conducted by setting the threshold, which excluded those with a yield lower than 1.5% from further investigation. As shown in Figure 4, most identified compounds are found with the yield below this threshold, indicating that the obtained oils have a strongly heterogeneous composition. For the bio-oil from SD, 69 such compounds account for 43.8% of the oil composition, and their number increases with the increment of PUR content. For the PUR-derived oil, 86 compounds present in traces with a share below 1.5%, representing only 25.2% of all identified compounds, suggesting a more homogenous structure than bio-oil. Liu et al. [38] suggest higher final temperatures to achieve a higher level of homogeneity in bio-oil composition.

Most compounds with a yield between 1.5 and 5% are found in bio-oil (18), following the decreasing trend with the increment of PUR content, and only 4 of them are detected in the oil from individual PUR pyrolysis. The same trends are noted for their share in the obtained oils. Compounds in that range represent more than 37% of the bio-oil composition, but their yield is decreased to only 11% for individual PUR pyrolysis. In the case of bio-oil, phenols and ketones are the most prominent groups detected in that range, but there is also the presence of PAHs and acids, which yield should be carefully monitored.

Finally, the threshold for a significant share was set at 5%, and almost all obtained oils have three compounds that are detected above this threshold, while only PUR-derived oil has four of such compounds. Even though their total number is pronouncedly lower, their shares in derived oils are significant. For the bio-oil, they represent more than 18% of the composition, rapidly increasing with PUR content increment to the final value of almost 64% for individual PUR pyrolysis. As expected, all such compounds from PUR oil belong to benzenamines, while in bio-oil, they are furans, ketones, and PAHs.

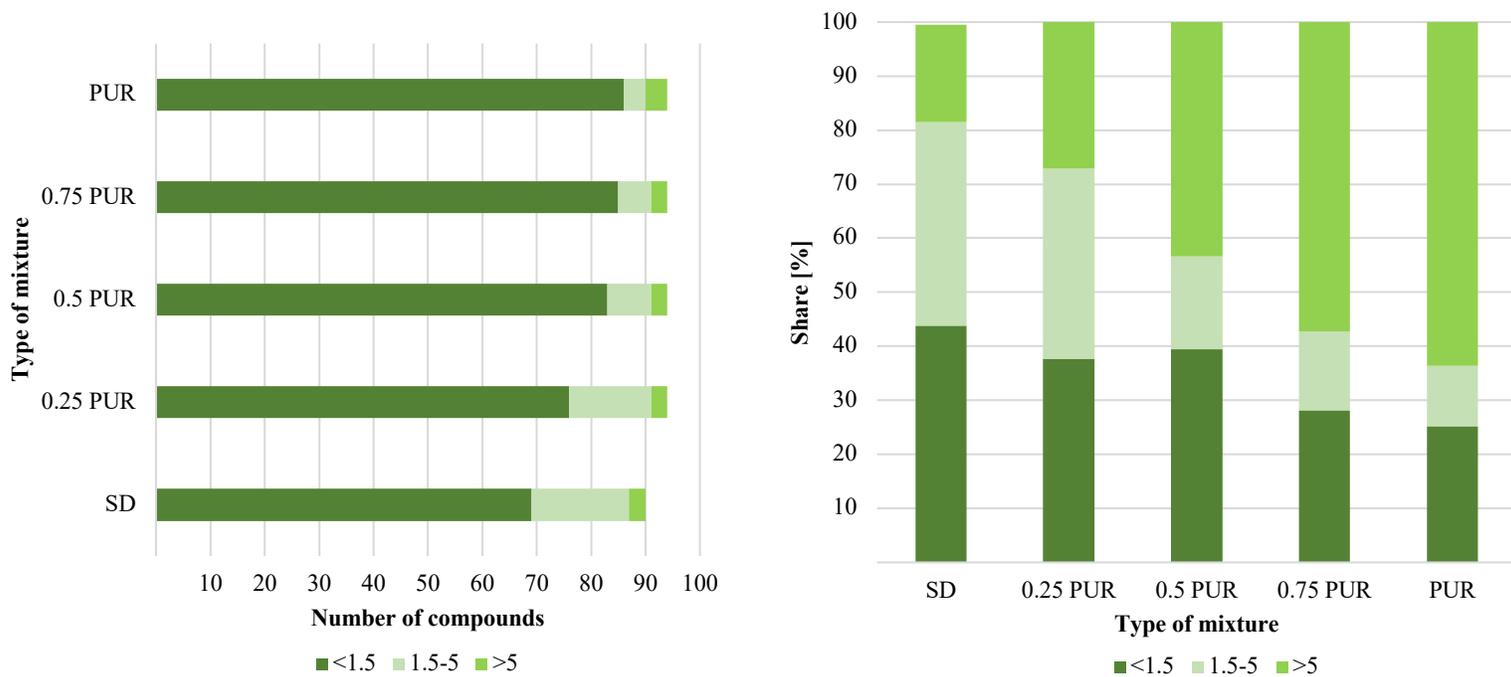


Figure 4 - Number of identified compounds (left) and their share in the derived oil (right)

Identified compounds in bio-oil are similar to those found in work by Yuan et al. [41]. Furfural, acetophenone, and 1,2,3,4-tetrahydro-2-phenyl-naphthalene have the highest share (~6%), while the yield of the other selected compounds (18 of them) is between 1.5 and 3%. For the PUR-derived oil, 4,4'-methylene bis-benzenamine, also known as 4,4'-Methylenedianiline (MDA), has the highest yield, accounting for almost 39% of oil composition. The high share of MDA is also reported in the study by Nishiyama et al. [13]. The MDA is a colorless or white solid with a low melting point, used as a precursor for polyurethane synthesis; therefore, its higher share is not unexpected [42]. Besides, it is classified as a potentially carcinogenic compound, and its presence in the fuel is not allowed. Another compound with a significant share is 3-methyl-benzenamine (m-toluidine), with a yield of 11.5%. It is a viscous liquid classified as the aromatic amine used to produce dyes [43]. The 2,3-dimethyl-benzenamine and aniline also have a significant share of almost 7%, and the rest of the selected compounds are in the range between 1.6-4.5%. From Table 2, it is visible that PUR yields more homogenous oil since eight selected compounds are responsible for almost 75% of oil composition, while in the case of bio-oil, 21 selected compounds account for only 56% of the composition.

Table 2 - Selected compounds from individual pyrolysis of SD and PUR

Selected compounds detected in bio-oil	Share [%]	Selected compounds detected in PUR derived oil	Share [%]
1,2-cyclopentadiene	1.6	[1,1'-Biphenyl]-4,4'-diamine, 3,3'-dimethyl-	2.5
1,6-Anhydro-β-D-glucopyranose (levoglucosan)	2.1	1,1':3',1''-Terphenyl, 5'-phenyl-	4.5
2,6-Dimethoxytoluene	2.1	1,3-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	1.6
2-Methoxy-4-vinylphenol	1.9	1-propoxy-2-Propanol	2.7
2-Methoxyphenol	2.7	Aniline	6.8
2-Pentanone	2.6	2,3-dimethyl-benzenamine	6.7
4-Methoxyphenol	2.4	3-methyl-benzenamine	11.5
Acetic acid	1.9	4,4'-methylene bis-benzenamine (MDA)	38.7
Acetophenone	5.9		
Dodecanoic acid	2.2		
Furfural	5.8		
Naphthalene	1.9		
1,2,3,4-tetrahydro-2-phenyl- naphthalene	6.8		
2,6-dimethoxy-phenol	1.6		
2,6-dimethoxy-4-(2-propenyl)- phenol	1.5		
Propanone	2.1		
Pyrocatechol	1.5		
Styrene	1.9		
Tetradecanoic acid	1.9		
Toluene	2.9		
Vanillin	2.9		
Share of selected compounds	56.2	Share of selected compounds	74.9

When it comes to mixture analysis, it can be seen from Table 3 that most of the identified and selected compounds are these also found from individual PUR pyrolysis. This indicates that the plastic fraction is the main driver for the liquid yield, but also it directly influences the selectivity of the compounds inside the derived oil. The 4,4'-Methylenedianiline (MDA) is once again the compound with the highest yield, and its share increases with the increment of PUR content. Like PUR-derived oil, 3-methyl-benzenamine and aniline are compounds with a significant share among all investigated mixtures. The difference in their yield for investigated mixtures is less pronounced than MDA. Like bio-oil composition, the mix with 25% PUR content has a higher heterogeneity level than others. The 18 selected compounds with a share above 1.5% account for 62.3% of oil composition. At the same time, in a PUR-dominant mixture, nine selected compounds are responsible for almost 72% of oil composition. In general, it can be stated that compounds identified in the derived oil from the individual pyrolysis and mixture co-pyrolysis are predominantly valuable chemicals rather than compounds preferred in the composition of alternative liquid fuels [44]. This is because they have attached either oxygen or nitrogen atom in their structure, limiting utilization possibilities. While the former often causes thermal instability, the bottom one may promote the formation of nitrogen oxides (NO_x) [45], and both dramatically lower the heating values [46]. Besides, several acidic chemicals suggest that such bio-oil has higher acidity, which may also cause corrosion.

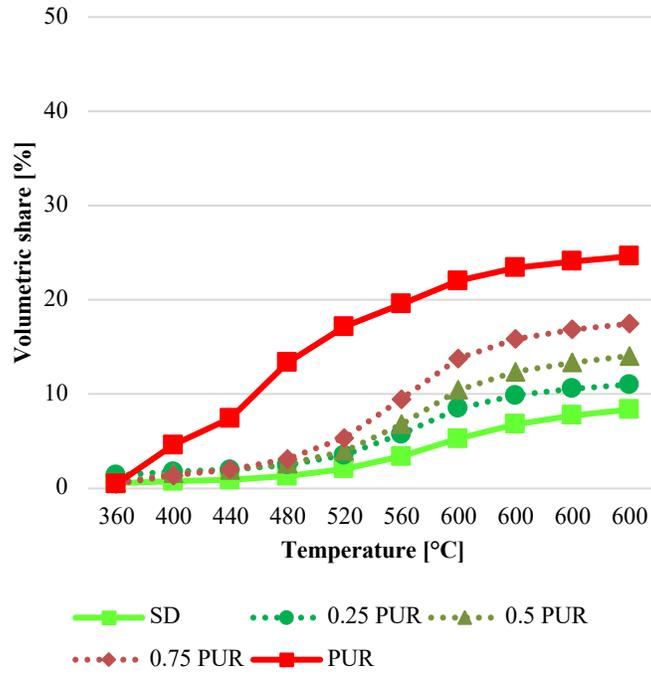
Table 3 - List of selected compounds from mixture analysis

Selected compounds from mixture analysis	0.25 PUR	0.5 PUR	0.75 PUR
Aniline	9.9	10.6	11.9
2,3-dimethyl-benzenamine	3.9	3.1	5.0
3-methyl-benzenamine	9.6	12.0	15.8
4,4-methylenebis-benzenamine (MDA)	7.5	20.7	29.5
1,1':3',1''-Terphenyl, 5'-phenyl-	3.6	1.7	1.7
2-(2-hydroxypropoxy)-1-propanol	1.6	1.5	1.8
2-(phenylmethyl)-benzenamine	3.0	4.1	2.7
1H-Indole, 2,6-dimethyl-	1.8		1.5
3,4-dimethyl- benzenamine	2.2		2.0
4-ethyl-2-methoxy-phenol	2.7	1.9	
Diphenylmethane		1.9	
Catechol		1.6	
2,3-Dimethyl-4-biphenylamine		1.5	
1,1'-Biphenyl, 2-methyl-	2.4		
1-(4-methylphenyl)-1H-Pyrrole	2.6		
2-hydroxy-3-methyl-2-Cyclopenten-1-one	1.6		
methyl-cyclopentane	1.8		
2-methoxy-phenol	2.6		
trans-Isoeugenol	1.8		
2,6-dimethoxy-4-(2-propenyl)-phenol	2.0		
2,6-dimethoxy-phenol	1.7		
Share of selected compounds [%]	62.3	60.5	71.9

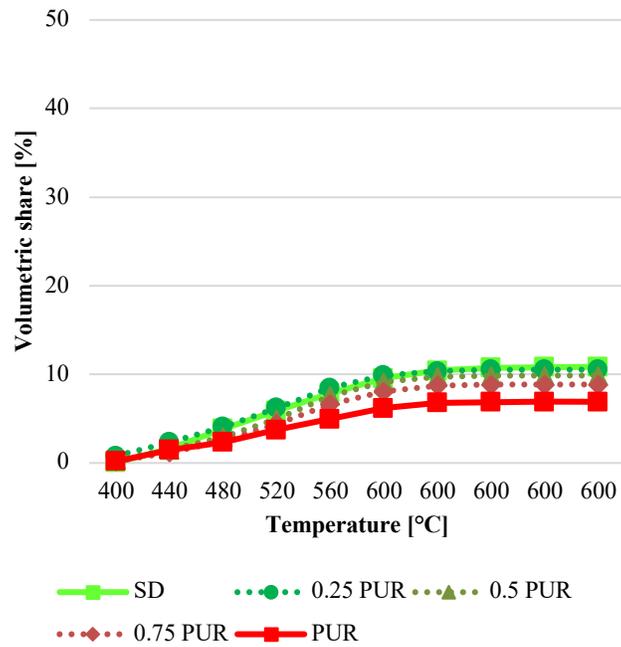
3.4. Syngas composition

In the following subsection, the evolution of gaseous compounds: carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), methane (CH₄), and higher hydrocarbons (C_xH_y) from the copyrolysis of sawdust and waste rigid polyurethane foam is analyzed (Figure 5). The evolution of gases starts at 360 °C, where primarily CO₂ is identified, which remains the dominant product during the whole process for all investigated samples. The volumetric share of CO₂ varies between 39% (mixture with 0.25 of PUR) to 46% for pure PUR pyrolysis (Figure 5d). Removal of CO₂ can be achieved by amine scrubbing, a standard biogas upgrading method [47]. Interestingly, the residence time did not significantly impact the evolution of syngas species because the composition didn't change significantly after reaching the final temperature. The same trend is noticed for the rest of the investigated non-condensable gases. The residence time is represented in Figure 5 by three repeating values of 600 °C, which was the final temperature at which samples were held for 30 minutes.

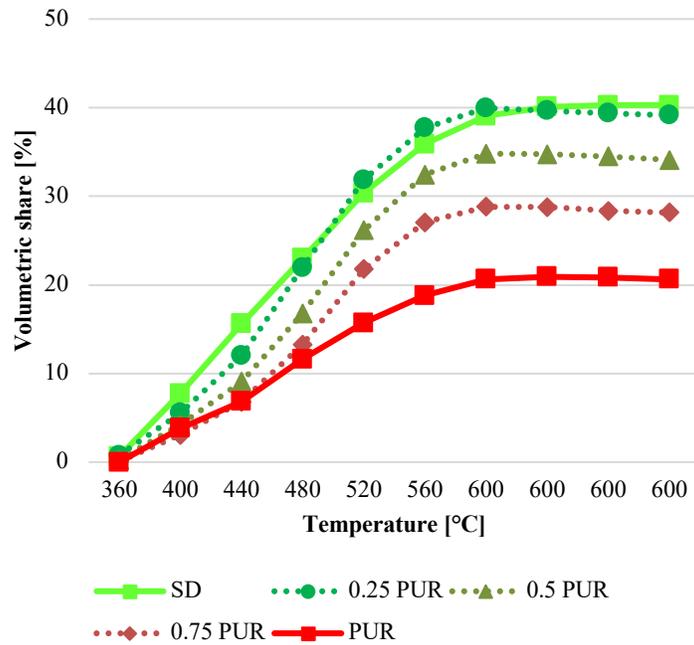
The syngas composition obtained from the pyrolysis of individual sawdust shows that around 61% vol. of identified gases are those preferred in the syngas composition (H₂, CH₄, CO). The highest yield (~40%) is noticed for CO, while the share of hydrogen and methane is around 8.4 and 11%, respectively. The share of higher hydrocarbons is almost negligible, with a yield below 2% vol. for all investigated samples; therefore, it won't be discussed further. It can only be stated that a low output of such gases can be expected since they are cracked at higher temperatures to methane and hydrogen [48]. This is supported by Figure 5 a) and b), where it can be seen that the yield of these two compounds is increasing with the temperature increment. Besides, the secondary cracking of liquid fraction also occurs, resulting in the increment of methane but even more pronounced hydrogen. As the most valuable compound, the share of hydrogen (Figure 5a) is the lowest for the sawdust sample, but it goes up to almost 25% for the pyrolysis of PUR. A high share of hydrogen (>50%) is also found in the study [39] for the temperatures 1000-1300 °C, where gasification was performed on the same sample to investigate the effect of temperature and residence time on gas yield. The hydrogen yield from the investigated mixtures is between values obtained from the individual samples and increases with the increment of polyurethane content (Table 4). The methane yield is similar for all investigated mixtures, between 8.8 and 10.6%, and it decreases with the increment of PUR content (Figure 5b). The lowest methane yield is noticed for the individual pyrolysis of PUR, with a value of 6.9% vol. The most significant difference is observed in carbon monoxide yield, as shown in Figure 5c. For the fraction where the dominant compound is sawdust, the outcome is almost the same as for the individual pyrolysis of the sawdust sample. This is expected since the cellulose and hemicellulose are responsible for the evolution of CO. With the further increment of polyurethane content, the share of CO is dramatically falling, and it is slightly above 20% for the pyrolysis of individual PUR.



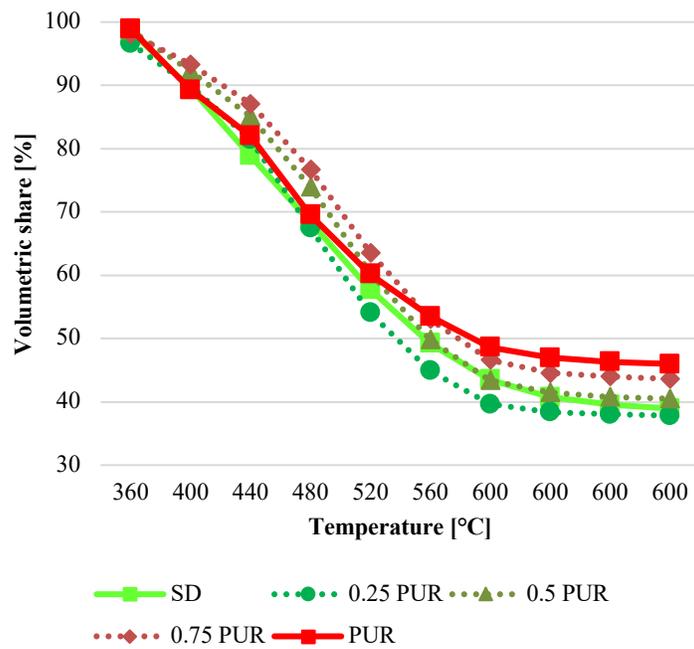
a) H₂



b) CH₄



c) CO



d) CO₂

Figure 5 - Distribution of gaseous products for all investigated samples

The yield of syngas compounds is summarised in Table 4. The presented volumetric share of observed gases is obtained at a final temperature of 600 °C and after a residence time of 12 minutes. Since no significant change is noticed, this was selected as a representative share of obtained

syngas. The only interesting observation after 30 minutes of residence time is seen for the hydrogen yield, which share was increased by approximately 2% vol. in all investigated mixtures, while the share of other compounds did not change significantly. The effect of residence time for PUR gasification is more pronounced at higher temperatures; since then, the secondary cracking of heavy hydrocarbons from the volatiles is promoted over formed soot and char particles [39]. This study found that the content of H₂ increased with time due to breaking the bonds between higher hydrocarbons to promote the formation of lighter compounds or pure H₂. Furthermore, the increase of CO content and the decrease of CO₂ is mainly because the bottom one reacts with char particles as an oxidant and promotes the formation of other compounds [48].

Table 4 – The syngas composition of investigated samples

	H ₂	CH ₄	CO	CO ₂	C _x H _y
	[% vol.]				
Sawdust	8.4	10.9	40.3	38.9	1.6
0.25 PUR	11.0	10.6	39.2	37.8	1.5
0.5 PUR	14.1	9.8	34.1	40.5	1.5
0.75 PUR	17.5	8.8	28.2	43.6	1.9
PUR	24.6	6.9	20.6	46.0	1.8

3.5. Synergistic effect

The synergistic effect is the main driver for product distribution from the co-pyrolysis of biomass and waste plastics. To determine the level of synergy, experimental results are compared to the theoretical values. Theoretical values (Y_{cal}) are calculated using the following Equation (1):

$$Y_{cal} = W_{SD}Y_{SD} + W_{PUR}Y_{PUR} \quad (1)$$

Where $W_{SD/PUR}$ stands for proportions of each component in investigated mixtures, and $Y_{SD/PUR}$ presents the values obtained from the individual pyrolysis [22]. The existence and level of synergy are determined by the difference between experimentally obtained values and calculated ones using Equation (2). According to [17], it can be stated that synergy exists when the difference between the experimental and calculated values is positive.

$$\Delta Y = Y_{exp} - Y_{cal} \quad (2)$$

Table 5 summarizes the calculated synergy levels for the three fractions concerning the plastic content inside the mixture. From the obtained values, it is evident that the main trade-off occurs between the volatiles fractions, liquid, and gas, while the synergy level is almost constant in the case of solid fractions.

Table 5 - Theoretical and experimental values for product yield and calculated level of synergy

Sample	Liquid fraction			Gas fraction			Solid fraction		
	Theoretical	Exp.	ΔY	Theoretical	Exp.	ΔY	Theoretical	Exp.	ΔY
0.25 PUR	38.85	48.41	9.56	40.26	24.17	-16.09	20.89	27.43	6.53
0.5 PUR	46.30	49.98	3.68	32.41	22.67	-9.74	21.28	27.35	6.07
0.75 PUR	53.76	52.06	-1.71	24.57	20.12	-4.45	21.67	27.82	6.15

The trendlines illustrate this phenomenon even better, and they are plotted in Figure 6 – Synergistic effect for investigated mixtures within the dependence of plastic content

. As can be seen, the highest synergies are achieved for the fraction with 25% of PUR content, and the level of synergy decreases with the increment of plastic content. A decrease in the synergistic effect is evident in Figure 6 since the values are approaching the horizontal axis. Kai et al. have already reported this phenomenon [21], where a mixture with 20% of high-density PE expressed the highest synergy, and Ephraim et al. [22], where the highest synergy effect is observed for a mixture where plastic content does not exceed 40%.

Interestingly, the co-pyrolysis shows a constant level of synergy for the yield of solid residue, which is approximately 6% in all investigated mixtures. The yield of a solid fraction is around 27% from all investigated mixtures, which is slightly higher than individual analysis (20-22%). Since the yield of solid fraction from individual pyrolysis is relatively similar, and theoretical yield presumes the same behavior (Table 5), the constant values obtained for synergy level are not unexpected.

Nevertheless, the most interesting is analyzing the trade-off between volatile fractions. The introduction of PUR increased the oil yield at the expense of the gaseous fraction. This can easily be confirmed by summing up the synergy values from each fraction for a particular mixture and taking into account that solid residue is almost constant for investigated mixtures. Only a little introduction of PUR reduced the gas yield by more than 16% and increased the liquid output by nearly 10%. As the plastic content increase, the level of synergy decreases, already observed in previous work for polystyrene and the sawdust co-pyrolysis [6], but also in the studies mentioned above. For the mixture where PUR is a dominant constituent, negative synergy is noticed for the yield of volatile fractions, even though it should be emphasized that the obtained experimental values are close to theoretically expected (Table 5).

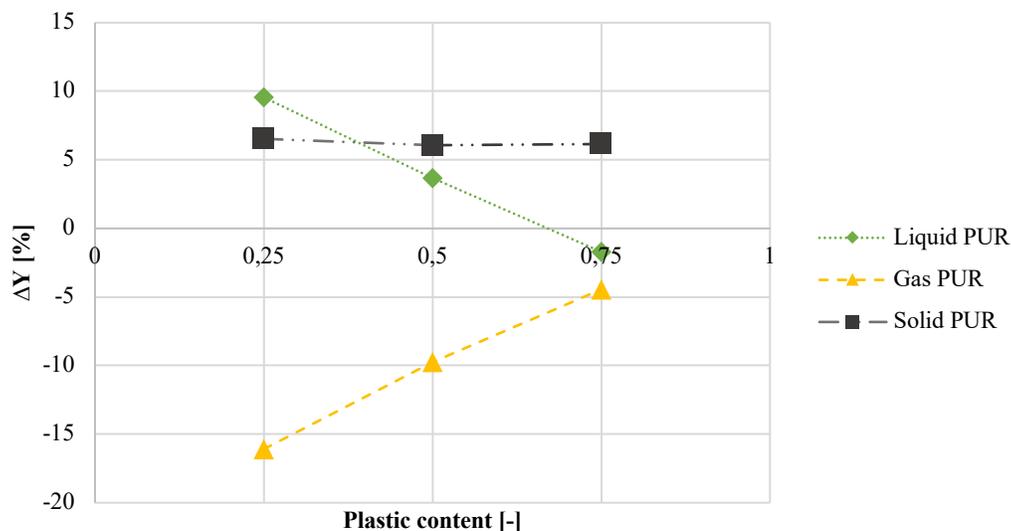


Figure 6 – Synergistic effect for investigated mixtures within the dependence of plastic content

The mixture with higher plastic content expresses better agreement with theoretically calculated yield, implying that product yield prediction from the co-pyrolysis might be more straightforward when the plastic material is the dominant compound since its decomposition mechanism is much simpler than biomass. This assumption is in accordance with the results from mixture analysis, where biomass was the predominant compound and where the highest synergy and discrepancies in calculated and experimentally obtained results are noticed.

4. CONCLUSION

The co-pyrolysis of biomass sawdust and PUR showed that valuable chemical products could be obtained from their thermal decomposition. Nevertheless, their utilization as alternative fuels in the future energy system does not look feasible due to the high share of nitrogen-containing compounds. Moreover, obtained products are rather valuable chemicals than fuel constituents that could be used to synthesize new materials and chemicals. Even though a gaseous fraction could be used to produce syngas, while char might be utilized as an additive for wood pellets production. The main findings of the work are summarized as follows:

- The TGA analysis showed that the main decomposition areas of investigated samples overlap and have similar decomposition kinetics, which is beneficial for synergistic effect. From the mixture TGA, it is visible that the share of plastic content inside the mixture does not play an essential role on the decomposition mechanism.
- The addition of PUR to the mixture can enhance the oil yield from the co-pyrolysis process. Nevertheless, its impact is limited since only a slight increment (<4%) in the yield is noticed between the mixture with 25 and 75% of PUR content. Even though only small addition of PUR reduces the yield of a gaseous fraction by 14% compared to individual SD pyrolysis. Simultaneously, for all investigated mixtures, the increment of solid residue was noted compared to individual pyrolysis, accounting for ~27% of the initial mass.
- The composition of bio-oil from sawdust pyrolysis expresses a strong heterogeneous structure with the highest share of oxygenated compounds like phenols, ketones, aldehydes, and acids. A significant share of PAHs is detected as well. On the other side, the PUR-derived oil has a more homogenous structure since more than 70% of identified compounds belong to the benzenamines group.
- With the increment of PUR content in the mixtures, the oil composition becomes more homogenous with the highest yield of benzenamines, especially MDA, 3-methyl-benzenamine, and aniline, which account for more than 55% of oil structure. Furthermore, even the mixtures with an equal share of both feedstock yield chemical compounds found in PUR-derived oil rather than bio-oil.
- Syngas evaluation shows that the introduction of PUR can significantly enhance hydrogen yield and reduce the output of carbon monoxide and methane. In general, the evolution of gases starts at 360 °C as a consequence of cellulose and hemicellulose degradation. At 600 °C, the composition of the gaseous fraction becomes permanent, implying that residence time doesn't have a significant impact.

- Greatest synergy level is observed for the mixture with 25% of PUR, and with a further increment of plastic content, the synergistic effect fades away. The most significant trade-off is noted for volatile fractions, where the liquid formation is promoted at the expense of a gaseous one. This is especially evident in the case of a mixture with 25% of PUR, where the synergistic effect for liquid yield accounts for 9.5%. The yield of solid fractions expresses a constant synergy level of 6%.
- Finally, the overall analysis showed that the small addition of plastic content to mixture composition could significantly enhance the liquid yield through a synergistic effect and remove most unwanted oxygenated compounds derived from sawdust pyrolysis. Even though obtained oil does not meet fuel requirements, plastic addition to a mixture with less than 50% share should be sufficient to enhance derived oil properties for further exploitation.

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