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Enhancing Pyrolytic Oil Quality from Wood Biomass using Different Types of Carbonates as Catalysts

Poboljšanje kvalitete pirolitičkog ulja iz drvene biomase primjenom različitih vrsta karbonata kao katalizatora

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ABSTRACT • The investigation examined woody biomass vacuum pyrolysis to understand the yield and quality of the resulting py-oil. The product characteristics and chemical composition were evaluated at varying pyrolysis temperatures and with different carbonate catalysts, including CaCO_3 , K_2CO_3 , Na_2CO_3 , MgCO_3 , and NaHCO_3 . In the absence of catalysts, the highest biomass yield was 48.58 wt.% at 500 °C. The use of carbonate catalysts has been proven to have a notable impact on py-oil yield and its elemental composition under thermal conditions. Notably, the heating value for non-catalytic py-oil was computed at 20.11 MJ/kg, with heating values of 22.49, 22.82, 23.00, 23.83, and 24.17 MJ/kg obtained upon upgrading with CaCO_3 , NaHCO_3 , MgCO_3 , Na_2CO_3 , and K_2CO_3 , respectively. Deoxygenation is the main reaction promoted by K_2CO_3 , during which the oxygen content decreased from 32.64 % to 23.30 %. In addition, the catalyst level was strongly related to the catalyst pH and the increase in py-oil heating value (HHV). GC/MS analysis demonstrated that phenolic compounds can be significantly elevated in the py-oil due to K_2CO_3 and Na_2CO_3 , indicating that this fuel is of high quality and has potential as a chemical resource. In this work, carbonate-based catalysts for the transformation of wood waste into phenolic-enriched py-oil are proposed to minimise environmental impact and possibly enhance py-oil quality in a vacuum pyrolysis process.

KEYWORDS: wood biomass; vacuum pyrolysis; carbonate catalysts; py-oil quality; phenolic enrichment

SAŽETAK • U radu je istražena vakuumska piroliza drvene biomase kako bi se utvrdili prinos i kvaliteta dobivenoga pirolitičkog ulja. Svojstva i kemijski sastav produkata procjenjivani su pri različitim temperaturama pirolize te uz primjenu različitih karbonatnih katalizatora, uključujući CaCO_3 , K_2CO_3 , Na_2CO_3 , MgCO_3 i NaHCO_3 . Bez primjene katalizatora najveći prinos tekućih produkata iz biomase iznosio je 48,58 masenog postotka pri temperaturi od 500 °C. Dokazano je da primjena karbonatnih katalizatora u zadanim termičkim uvjetima znatno utječe na prinos pirolitičkog ulja i njegov elementarni sastav. Gornja ogrjevna vrijednost pirolitičkog ulja dobivenoga nekatalitičkim postupkom iznosila je 20,11 MJ/kg, dok su vrijednosti od 22,49; 22,82; 23,00; 23,83 i 24,17 MJ/kg postignute poboljšanjem kvalitete primjenom CaCO_3 , NaHCO_3 , MgCO_3 , Na_2CO_3 i K_2CO_3 . Deoksigenacija je glavna reakcija koju potiče K_2CO_3 , pri čemu se udio kisika smanjio s 32,64 % na 23,30 %. Osim toga, aktivnost katalizatora bila je usko povezana s njegovom pH-vrijednošću i povećanjem gornje ogrjevne vrijednosti (GOV) pirolitičkog ulja. Analiza plinskom kromatografijom sa spektrometrom masa (GC/MS) pokazala je da se udio feno-

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lnih spojeva u pirolitičkom ulju može znatno povećati primjenom K_2CO_3 i Na_2CO_3 , što upućuje na visoku kvalitetu toga goriva i njegov potencijal kao kemijske sirovine. U ovome se radu za pretvorbu drvnog otpada u pirolitičko ulje obogaćeno fenolima predlaže primjena katalizatora na bazi karbonata, čime se smanjuje utjecaj na okoliš i poboljšava kvaliteta produkata u procesu vakuumske pirolize.

KLJUČNE RIJEČI: drvna biomasa; vakuumska piroliza; karbonatni katalizatori; kvaliteta pirolitičkog ulja; obogaćivanje fenolima

1 INTRODUCTION

1. UVOD

Biomass is widely acknowledged as a renewable energy source. Among the various forms of biomass, woody biomass, which includes wood chips, sawdust, shavings, and bark, is generated in millions of tons each year by the forestry sector. Approximately 25 % of the raw material output from wood processing is waste that is usually discarded or incinerated. There are four main thermochemical processes for transforming biomass into energy: combustion, pyrolysis, gasification, and liquefaction. Pyrolysis specifically refers to the thermal breakdown of biomass at temperatures between 300 °C and 700 °C in an oxygen-free environment. This method yields solid charcoal (biochar), liquid (py-oil), and gaseous products. Pyrolysis is recognised as a commercially viable technique for converting biomass (Balat and Ayar, 2005; Anderson *et al.*, 2013; Jahirul *et al.*, 2012; Bridgwater, 2012; Zhang *et al.*, 2010; Wyman, 2013; Özbay, 2015).

Py-oil is primarily a product of pyrolysis and has a high heating value (HHV), making it a suitable precursor for producing liquid fuels or other valuable compounds. It comprises a variety of organic compounds (such as phenols, aldehydes, ketones, alcohols, esters, and organic acids), giving it a diverse chemical composition. Due to their higher acidity (corrosive nature) and chemical instability during storage, these oxygenated compounds are not well-suited for commercial use. In the transport industry, it is crucial to achieve substantial improvements in py-oil quality to enable its use as a replacement for petroleum-based fuels. Hence, research efforts focus on upgrading techniques and developing suitable engine configurations, while addressing corrosion concerns and optimising combustion performance (Li and Suzuki, 2009; Oasmaa and Kuoppala, 2003; Abou *et al.*, 2021; Bridgwater, 2012; Lian *et al.*, 2017).

An increasing number of studies have been conducted to improve the quality of py-oil produced by the pyrolysis of woody biomass using various catalysts. Notably, zeolites and their derivatives (Adjaye and Bakhshi, 1995; Nokkosmäki *et al.*, 2000; Horne and Williams, 1996; Lappas *et al.*, 2002; Zhang *et al.*, 2013), dolomite (Myrén *et al.*, 2002; Charusiri and Vitidsant, 2017; Ly *et al.*, 2018), metal basic oxides

(Pütün, 2010; Yuan and Shen, 2019; Cao *et al.*, 2020), nickel-based catalysts (Ji *et al.*, 2017; Yang *et al.*, 2019; Cho *et al.*, 2020), and acidic or basic inorganic materials (Patwardhan *et al.*, 2010; Guo *et al.*, 2012; Zhao *et al.*, 2013; Zhou *et al.*, 2018; Chen *et al.*, 2020) have been studied. Additionally, various combinations of these catalysts have also been explored (Li *et al.*, 2014; Wu *et al.*, 2020; Yang *et al.*, 2020). The findings from these investigations indicate that catalyst type significantly influences both product yield and chemical composition. Thus, catalytic upgrading is recognised as one of the most effective methods for enhancing py-oil performance. To assess final product yields, both catalytic and non-catalytic pyrolysis experiments were conducted using pinewood sawdust at varying temperatures. A range of carbonate catalysts, specifically $CaCO_3$, K_2CO_3 , Na_2CO_3 , $MgCO_3$, and $NaHCO_3$, were tested for improving the quality of py oil. Subsequently, the py-oils obtained from both the non-catalytic and catalytic processes were analysed by ultimate analysis and GC/MS.

2 MATERIALS AND METHODS

2. MATERIJALI I METODE

2.1 Biomass and catalysts

2.1. Biomasa i katalizatori

Scots pine (*Pinus sylvestris* L.) is widely used in Turkey, mainly for furniture and construction, and this study used sawdust waste as a biomass feedstock. The feedstock was ground and sieved to a particle size of 0.600 – 1.000 mm, then dried at 105 °C for 12 hours to remove moisture prior to pyrolysis. Samples were subjected to proximate analysis in accordance with ASTM standards and to fixed-carbon content determination to assess variability. The chemical composition of the feedstock was examined using methods reported by Wise and Karl (1962) and Rowell *et al.* (2005), along with the relevant TAPPI recommendations (T-257, T-222, and T-204). Elemental analysis was performed with the LECO CHNS-932 elemental analyser. The findings from the fundamental characterisation of the pinewood waste are summarised in Table 1.

The commercial catalysts used in these experiments were supplied by Sigma-Aldrich and had chemical purities exceeding 99 wt.% for each. Their typical properties are summarised in Table 2.

Table 1 Proximate and ultimate analysis of Scots pine wood

Tablica 1. Tehnička i elementarna analiza borovine

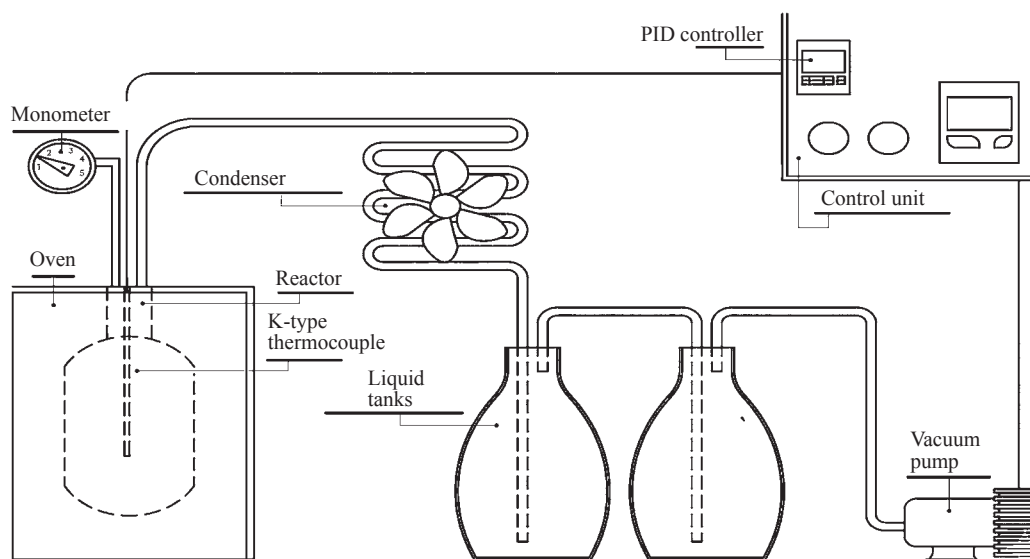
Proximate analysis (wt%, air dry) <i>Tehnička analiza (mas. %, uzorak sušen na zraku)</i>	Method <i>Metoda</i>	Value <i>Vrijednost</i>	Component analysis, % <i>Analiza komponentata, %</i>	Method <i>Metoda</i>	Value <i>Vrijednost</i>	Ultimate analysis (wt%, daf) <i>Elementarna analiza (mas. %, suha tvar bez pepela)</i>	Value <i>Vrijednost</i>
Moisture content, % <i>sadržaj vode, %</i>	(ASTM D-4442-92)	3.17	α -cellulose	(Rowell <i>et al.</i> , 2005)	48.24	Carbon <i>ugljik</i>	47.14
Volatiles <i>hlapljive tvari</i>	(ASTM E-897-88)	81.74	Holocellulose	(Wise and Karl, 1962)	78.51	Hydrogen <i>vodik</i>	5.77
Ash <i>pepeo</i>	(ASTM D-1102-84)	0.39	Lignin	(TAPPI T 222 om-02)	28.17	Nitrogen <i>dušik</i>	0.01
Fixed carbon <i>vezani ugljik</i>	calculated from the difference	14.70	Extractive	(TAPPI T 204 cm-97)	5.26	Oxygen <i>kisik</i>	47.08
						HHV ^a (MJ/kg)	12.90

^a HHV of pine sawdust was calculated according to the Dulong-Berthelot Correlation (Channiwalla and Parikh, 2002). / ^aHHV piljevine od borovine izračunan je prema Dulong-Berthelotovoj korelaciji (Channiwalla i Parikh, 2002.).

Table 2 Some typical properties of the catalysts

Tablica 2. Tipična svojstva katalizatora

Properties / <i>Svojstvo</i>	CaCO ₃	K ₂ CO ₃	Na ₂ CO ₃	MgCO ₃	NaHCO ₃
Solubility in water, g/L / <i>topljivost u vodi, g/L</i>	0.017	138	220	0.0139	9.4
Melting point, °C / <i>talište, °C</i>	825	891	851	990	3000
Molecular mass, g/mol / <i>molekulska masa, g/mol</i>	100.09	138.205	106	84.31	84.01
Density, g/cm ³ / <i>gustoća, g/cm³</i>	2.93	2.43	2.54	2.96	2.2
pH value / <i>pH-vrijednost</i>	8	11-13	11	9.3	8.4


Figure 1 Experimental scheme of the vacuum pyrolysis apparatus

Slika 1. Shematski prikaz eksperimentalne aparature za vakuumsku pirolizu

2.2 Pyrolysis experiments

2.2. Provođenje pirolize

Pyrolysis was conducted under vacuum in a fixed-bed reactor. An outline of the experiment is shown in Figure 1. The reactor is a stainless-steel cylinder with an internal diameter of 24 cm and a height of 36 cm. A 200 g sample was added to the reactor for non-catalytic tests. In the catalytic experiments, the biomass was mixed with selected catalysts at a 5 wt – %

loading and introduced into the reactor. Heating was applied using an electric furnace with target temperatures of 450, 500, and 550 °C, and the temperature was closely controlled by a PID (Proportional-Integral-Derivative) controller. The temperature within the internal bed was recorded using a K-type thermocouple at one-minute intervals. The temperature was maintained at the prescribed level for 30 minutes during the isothermal stage in each experiment. The pyrolysis products

consisted of three main components: bio-oil (py-oil), biochar, and non-condensable gas. Condensable products were collected by a condenser attached to the reactor outlet. The solid biochar yield was determined from the gravimetric mass of the remaining reactor residue at each test iteration, while the gas yield was predicted using mass-balance calculations.

2.3 Characterisation of py-oil

2.3. Karakterizacija pirolitičkog ulja

The liquid product extraction was carried out using an equal volume of diethyl ether. Extraction of ether extracts for gas chromatography-mass spectrometry (GC/MS) and elemental analysis were carried out. Elemental analysis (LECO CHNS-932 analyser) was performed to quantify the carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) content in the pyrolysis oil; the oxygen (O) content was determined by difference. The higher heating value (HHV) was estimated using the Dulong–Berthelot correlation reported by Channiwala and Parikh (2002). In contrast, pyrolysis oil was quantified using an Agilent 6890 GC coupled to an Agilent 5973 mass spectrometer to determine its chemical composition. Separation was performed on an HP-5 capillary column (30 m × 0.25 mm i.d., film thickness: 0.25 µm) with helium as the gas carrier (at a flow rate of 1.2 mL/min). The temperature program was as follows: hold at 40 °C for 10 minutes, ramp up at 2 °C/min to 170 °C, and hold for 5 minutes. This was followed by a repeated ramp-up to 250 °C (8 °C/min, held for 15 minutes), before a final ramp-up to 300 °C (10 minutes). The injector was run in split mode at 250 °C with a split ratio of 1:10. Mass spectrometer conditions were set to electron impact (EI) ionisation mode, and compound identification was performed by comparison with the NIST mass spectral library using G1035A software.

3 RESULTS AND DISCUSSION

3. REZULTATI I RASPRAVA

3.1 Yields of pyrolysis products

3.1.1. Prinosi produkata pirolize

Figure 2 depicts the percentages of products produced by pyrolysis at different temperatures, in non-catalytic and carbonate-catalysed processes. For non-catalytic pyrolysis, the maximum py-oil yield was around 48.58 wt.% at 500 °C, then decreased at 550 °C; however, the biochar yield decreased consistently from 39.28 wt.% at 450 °C to 36.71 wt.% at 550 °C, and the gas yield increased at high temperature. This is consistent with the literature, which shows a temperature effect on product distribution. The best py-oil yield from woody biomass, as shown in Figure 2, occurs at 500 – 550 °C, with a significant effect of the carbonate catalyst on gas, liquid, and char yields between 450 – 550 °C. The optimal yield was approximately 47 wt.% at 500 °C with CaCO₃ as the catalyst. Notably, it was determined that at these temperatures, lower py-oil yields were obtained than in non-catalytic pyrolysis when K₂CO₃ and Na₂CO₃ were used as catalysts. The marginal decline in py-oil yield with K₂CO₃ (from 48.58 wt.% to 43.3 – 45.0 wt.%) is part of an inherent technical trade-off for catalytic pyrolysis. As alkaline catalysts promote gas and char formation in chemistry, the liquid yield is lower, but the deoxygenation process improves the quality of the py-oil. As Mahasweta (2025) has stated, the reduced liquid yield can be technically and economically acceptable, as the improved stability and energy density of the upgraded py-oil will be more economical. In the current study, a further ~20 % increase in HHV (to 24.17 MJ/kg) and a significant decrease in oxygen content (from 32.64 % to 23.30 %) result in a much stronger fuel. These results are reflected in similar studies that demonstrate signifi-

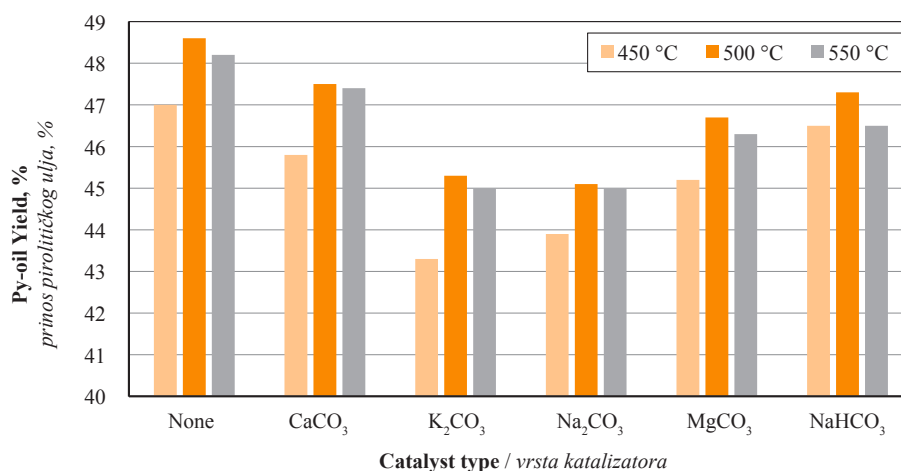


Figure 2 Comparison of product yields and py-oil production using carbonate catalysts at different temperatures
Slika 2. Usporedba prinosa produkata pirolize i proizvodnje pirolitičkog ulja u ovisnosti o temperaturi i vrsti karbonatnog katalizatora

cant differences in the distribution of lignocellulosic biomass-derived pyrolysis products among catalysts (Tirapanampai *et al.*, 2019; Fan *et al.*, 2020; Bagi and Baseri, 2021).

3.2 Py-oil characterisation

3.2. Karakterizacija pirolitičkog ulja

The elemental compositions of the produced py-oils are summarised in Table 3. It was observed that the presence of carbonate catalysts significantly modified the elemental distribution of the liquids. Among the tested catalysts, K_2CO_3 was identified as the most effective, reducing the oxygen content from 32.64 % (non-catalytic) to 23.30 % while increasing the carbon content to 68.74 %. The superior deoxygenation performance of alkali carbonates (K_2CO_3 and Na_2CO_3) compared to alkaline earth carbonates ($CaCO_3$ and $MgCO_3$) was attributed to their higher alkalinity and solubility, as reported in Table 2. The catalytic performance in this study was further compared with modern catalytic systems, such as zeolites (e.g., ZSM-5), which were frequently cited in recent literature (Mahasweta, 2025; Fan *et al.*, 2020). While acidic zeolites are highly effective in aromatics production through severe deoxygenation, they often promote extensive dehydration, leading to significant carbon loss as coke and a

substantial decrease in liquid yield. This resulted in a maximum liquid yield (~45 wt.%) and a significantly improved HHV of 24.17 MJ/kg. Specifically, the HHVs for py-oils generated with $CaCO_3$, $NaHCO_3$, $MgCO_3$, Na_2CO_3 , and K_2CO_3 were 22.49, 22.82, 23.00, 23.83, and 24.17 MJ/kg, respectively. These findings demonstrate a strong correlation between the catalyst alkalinity (pH) and the energy density of the resulting py-oil. This suggests that carbonate-based vacuum pyrolysis offers a more balanced and viable route for producing stable, oxygen-reduced py-oils with lower operational and hydrogen-conversion costs than high-surface-area synthetic zeolites.

The abundance of oxygen-containing functional groups was assessed by GC/MS analysis. The py-oil from non-catalytic pyrolysis shown in Table 4 primarily consists of oxygenated compounds such as aldehydes, ketones, phenols, organic acids, benzenes, and alcohols. Phenolic compounds were identified as the most prevalent. The identified phenolic compounds were phenol, 2-methylphenol, 4-methylphenol, 2-methoxyphenol (guaiacol), 2-methoxy-4-methylphenol, and 4-ethyl-2-methoxyphenol. The identified compounds also corresponded to the previously reported chemical characterisation of pyro-oil obtained from biomass pyrolysis (Kanaugia *et al.*, 2013; Özbay, 2015; Nhuchhen *et al.*,

Table 3 Elemental composition and HHV of py-oils^a

Tablica 3. Elementarni sastav i gornja ogrjevna vrijednost pirolitičkih ulja^a

	C	H	N	O ^b	HHV (MJ/kg)
None	61.16	7.18	0.02	32.64	20.11
$CaCO_3$	65.17	7.85	0.05	26.93	22.49
K_2CO_3	68.74	7.88	0.08	23.30	24.17
Na_2CO_3	68.26	7.67	0.08	23.99	23.83
$MgCO_3$	66.72	7.46	0.06	25.76	23.00
$NaHCO_3$	66.45	7.37	0.05	26.13	22.82

^a Dry basis, ^bCalculation from difference / ^aSuha tvar; ^bizračunano iz razlike

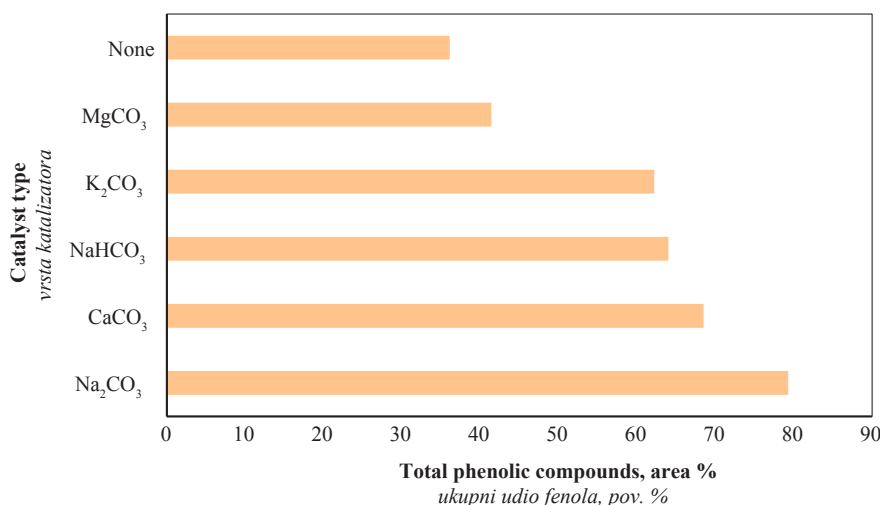


Figure 3 Comparative analysis of total phenolic compound concentrations (area %) in py-oils obtained from non-catalytic and carbonate-catalysed vacuum pyrolysis

Slika 3. Usporedba koncentracije ukupnih fenolnih spojeva (pov. %) u pirolitičkim uljima iz nekatalitičke i katalitičke vakuumske pirolize s karbonatima

Table 4 Main organic components of py-oils with GC-MS analysis**Tablica 4.** Glavne organske komponente pirolitičkih ulja dobivene GC-MS analizom

RT, min	Name of compounds <i>Ime spoja</i>	Area / Površina, %						Category
		None	CaCO ₃	K ₂ CO ₃	Na ₂ CO ₃	MgCO ₃	NaHCO ₃	
5.58	Propanoic acid	0.21	3.69	–	–	0.12	–	Acid
7.28	Cyclopentanone	–	1.42				1.88	Ketone
7.76	Butanoic acid	0.14	2.54					Acid
8.67	Furancarboxaldehyde	0.45	2.44	0.11		0.16		Aldehyde
9.68	1,3-Dimethyl-benzene	–	1.67			0.11		Benzene
9.69	Furanmethanol		–		0.72		2.04	Alcohol
10.57	1,3-Dimethyl-benzene	–	1.20				9.49	Benzene
11.46	2-Methyl-2-cyclopenten-1-one	0.32	1.17	0.14	1.53	0.11	2.16	Ketone
12.69	1,3-Dimethyl-1-one-cyclopentene	–	2.07		1.16		0.72	Ketone
13.40	1-Ethyl-2methyl-benzene					0.05	0.88	Benzene
14.00	5-Methyl-2-furancarboxaldehyde	0.31	4.52	0.97		0.05		Aldehyde
14.70	Phenol	5.36	13.54	8.02	8.93	7.54	8.92	Phenol
15.11	Benzofuran	0.11	0.55	1.16		1.45		Furan
15.50	2,3-Dimethyl-1-one-cyclopentene		0.47	0.20	1.38		1.22	Ketone
16.19	2-Ethyl-3,4-dimethyl-benzene			0.14		0.17	3.41	Benzene
16.36	Limonene						0.84	Benzene
17.24	Indene	–	0.79	0.06	0.84	0.21	0.80	Benzene
17.25	1-Ethyl-3methyl-benzene	0.18	1.72	1.24	0.73	1.18		Benzene
17.60	1,3-Dimethyl-1-one-cyclopentene			0.22	1.48			Ketone
18.00	2-Methyl-phenol	4.79	8.29	4.22	6.94	4.43	5.86	Phenol
18.44	Ethenone			0.11	2.03			Ketone
18.58	Acetophenone	–	1.08					Ketone
19.06	4-Methyl-phenol	9.52	14.56	14.68	15.95	9.86	11.55	Phenol
19.51	2-Methoxy-phenol	7.62	11.97	11.40	12.10	8.24	11.69	Phenol
20.01	2-Methyl-benzofuran	0.08	–			0.07		Furan
20.30	2,6-Dimethyl-phenol	0.20	1.72	1.06		0.12	1.35	Phenol
22.35	2,4-Dimethyl-phenol	0.61	5.37		0.92		7.22	Phenol
22.10	1-Methyl-1H-indene				0.89	0.08	1.40	Benzene
23.35	3-Ethyl-phenol	0.27	1.75	0.12	0.58	0.13	3.46	Phenol
23.74	2,3-Dimethyl-phenol			2.18	1.94	0.39	1.42	Phenol
23.75	Benzoic acid	–	4.14					Acid
23.76	Naphthalene	0.67	0.69			0.10		Benzene
24.87	2-Methoxy-4-methyl-phenol	4.80	7.54	6.65	9.82	5.30	5.73	Phenol
24.78	3,4-Dimethyl-phenol	0.09		4.20	4.38		1.21	Phenol
26.41	4-Ethyl-3-methyl-phenol	0.11	0.51	6.32	7.93			Phenol
26.42	3-(1-Methyl)-Phenol			2.44	1.29			Phenol
28.13	4-Ethyl-2-methoxy-phenol	2.49	3.24		6.13	5.23	4.73	Phenol
28.69	2-Methyl-naphthalene	0.28		0.06	0.75	0.09	0.87	Benzene
29.43	1-Methyl-naphthalene	0.16	1.09		0.72	0.06	0.61	Benzene
31.53	2-Methoxy-4-(2-propenyl)-phenol	0.24		0.88	2.30	0.14	0.84	Phenol

2018; Khuenkao and Tippayawong, 2020; Li *et al.*, 2025). When carbonate catalysts were used for wood pyrolysis (K₂CO₃ and Na₂CO₃), the composition of the pyro-oil changed substantially with an increase in phenolic content. This trend was also observed with other carbonates (Figure 3).

The fact that phenolic compounds are remarkably enriched indicates that alkali carbonates are useful for the selective cleavage of lignin in this molecule. Li *et al.* (2015) and Tang *et al.* (2025) have reported that the transformation of lignin into aromatic compounds is caused by the depolymerisation of its polymer structure, in which β-O-4 ether linkages are the most abun-

dant and most vulnerable targets for catalytic treatment. In this work, CO₃²⁻ ions were also used as the base catalyst. The alkaline environment facilitates the deprotonation of the phenolic hydroxyls in lignin, thereby enabling reactions with quinone methide molecules. At the same time, the intermediates accelerate the fragmentation of the β-ether bonds. In the process, the macromolecule is decomposed into one of its monomeric components, such as guaiacols or methylphenols. In addition, the alkali carbonates Na₂CO₃ and K₂CO₃ scavenge acidic intermediates, and they cannot be repolymerised in subsequent reactions. Thus, high pH levels of catalysts preserve the main breakdown

products in the py-oil, yielding high-value volatile phenols. This catalytic enhancement is crucial, given that abundant phenolics indicate a strong potential for alternative fuel production. These findings are consistent with the literature on the chemical composition of py-oil from the alkaline-catalysed pyrolysis of woody biomass (Rutkowski, 2011; Bu *et al.*, 2012; Kabir and Hameed, 2017; Rangel *et al.*, 2023; Zhang *et al.*, 2024).

The practical and industrial value of carbonate-based catalysts is enhanced by their potential for recovery and reuse from solid residue. Alkali carbonates such as Na_2CO_3 and K_2CO_3 are highly soluble in water and can be readily recovered from biochar via a simple aqueous leaching process. Wang *et al.* (2021) reported that using K_2CO_3 in biochar and pyrolysis promotes easy recovery in water through improved porosity and environmentally friendly processing methods, and that a solution of purified water can remove the carbonate salts. Although a small percentage of catalyst can be incorporated into the ash matrix, previous research indicates that recovered carbonates are very catalytic. This process reduces overall operational costs and aligns with the principles of green chemistry by avoiding chemical waste in biomass-to-fuel conversion.

4 CONCLUSIONS

4. ZAKLJUČAK

In this study, the vacuum pyrolysis of Scots pine (*Pinus sylvestris* L.) sawdust was investigated, and the subsequent improvement of the py-oil using various carbonate catalysts was also examined. The study resulted in the following main analytical findings:

It shows that the value of the liquid products generated was strongly temperature dependent in non-catalytic vacuum pyrolysis, with the highest value of 48.58 wt.% at 500 °C, and the value at 500 °C was noted; more than 500 °C results in decreased py-oil yield as a consequence of secondary cracking reaction, which promoted gas production.

The influence of various carbonate catalysts on product distribution was found to be very strong. So, a py-oil yield of 47 wt.% was sustained by calcium carbonate (CaCO_3); gasification and char formation were favoured by alkaline carbonate catalysts (potassium carbonate (K_2CO_3) and sodium carbonate (Na_2CO_3), and a decrease in liquid yield was observed, despite an appreciable improvement in quality.

The elemental compositions of py-oil were positively modified in all tested carbonate catalysts. K_2CO_3 was found to be the most efficient catalyst for deoxygenation, where the oxygen content decreased from 32.64 % (in non-catalytic pyrolysis) to 23.30 %. Therefore, there is a significant increase in carbon content and stability in the produced py-oil.

There was a significant positive correlation between the pH values of the carbonate catalysts and the higher heating value (HHV) of the py-oil formed. The py-oil with the highest HHV (24.17 MJ/kg) was formulated from K_2CO_3 , which has higher alkalinity and is more favourable than the non-catalytic oil (20.11 MJ/kg). A gas chromatography-mass spectrometry (GC/MS) analysis showed that the concentration of phenolic compounds increases when Na_2CO_3 and CaCO_3 are used for catalytic pyrolysis. This indicates that these catalysts enhance the breakdown of complex lignin structures into simpler aromatic compounds, yielding simpler yet more significant structures.

It was concluded that combining vacuum pyrolysis with carbonate-based catalysts is a practical way of producing high-quality py-oil with low oxygen content and high energy density. The new research suggested that inexpensive carbonates can also serve as green catalysts in a biomass-to-fuel conversion system. Also, the high enrichment of phenolic compounds suggests that this py-oil could serve as a sustainable precursor for wood adhesives, resins, and preservatives in the wood-processing and furniture industries.

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