

Upgrading co-pyrolysis products from ternary biomass: An investigative study of commercial and locally-made catalysts

Sabah Mariyam, Mohammad Alherbawi, Tareq Al-Ansari, Gordon McKay

Item type

Journal Contribution

Terms of use

This work is licensed under a [CC BY 4.0](https://creativecommons.org/licenses/by/4.0/) license

This version is available at

https://manara.qnl.qa/articles/journal_contribution/Upgrading_co-pyrolysis_products_from_ternary_biomass_An_investigative_study_of_commercial_and_locally-made_catalysts/27677607/1

Access the item on Manara for more information about usage details and recommended citation.

Posted on Manara – Qatar Research Repository on

2024-12-01



Upgrading co-pyrolysis products from ternary biomass: An investigative study of commercial and locally-made catalysts

Sabah Mariyam^{*}, Mohammad Alherbawi, Tareq Al-Ansari, Gordon McKay

Division of Sustainable Development, College of Science and Engineering, Hamad Bin Khalifa University, Qatar Foundation, Doha, Qatar

ARTICLE INFO

Keywords:

Co-pyrolysis
Biomass
Bio-oil
Product
Yield
Characterization

ABSTRACT

Catalysts play a pivotal role in influencing product yields and compositions in pyrolysis processes, offering significant advantages for biomass conversion. This study investigates the impact of natural and commercial catalysts on the co-pyrolysis of ternary biomass at two different temperatures (550 °C and 750 °C). At higher temperatures, secondary decompositions become prominent, leading to increased gas yields and decreased char and liquid oil yields. The introduction of catalysts generally enhances char yields across both temperature regimes. Notably, CaCO_3 exhibits the highest bio-oil yield, while $\text{Ca}(\text{OH})_2$ shows the lowest, with reversed trends observed for gas yields. The influence of catalysts extends to gas composition, with $\text{Ca}(\text{OH})_2$ and zeolite notably increasing CH_4 and CO_2 concentrations at 750 °C. Each catalyst type exerts specific effects on gas production and composition, underscoring the intricate interplay between catalysts and reaction pathways. Additionally, catalysts significantly alter the composition of bio-oil, with calcium-based catalysts reducing acid content and increasing aromatics, while zeolites exhibit contrasting trends at different temperatures. Noteworthy compounds identified in the resulting bio-oil include bisphenol A, levoglucosan, phenols, and p-cresol, offering potential applications in plastics, biofuels, resins, and more. Overall, catalysts offer the potential to enhance specific compound yields, reduce corrosiveness, and optimize bio-oil and char composition for diverse industrial applications, highlighting the need for further research into synergistic effects when combining different catalysts.

1. Introduction

Biomass pyrolysis, the thermal decomposition of organic materials in the absence of oxygen, holds immense promise as a renewable energy conversion process. Through pyrolysis, biomass can be transformed into valuable biofuels, biochemicals, and bioproducts, contributing to the transition towards a sustainable energy future [1]. However, biomass pyrolysis's efficiency and product distribution are often limited by factors such as high tar content, low bio-oil quality, and undesired byproduct formation [2].

Different reactors have been investigated for biomass pyrolysis reactions [3]. Continuous feeding pyrolysis technologies have gained significant attention for their ability to enhance biomass conversion efficiency and facilitate scalable biofuel production. Among these, fluidized bed reactors are widely recognized for their excellent heat transfer and uniform temperature distribution, making them ideal for processing various feedstocks. Rotary kilns offer versatility in processing different biomass types, with their ability to handle larger feedstock sizes while maintaining consistent pyrolysis conditions. Additionally,

fixed bed reactors hold significant importance in biomass pyrolysis due to their unique properties. Often constructed with a solid catalyst, fixed bed reactors enhance product yields and allow for the modification of process conditions, making them a vital choice in this field. Lastly, auger reactors provide a continuous feeding mechanism with precise control over reaction parameters, further enhancing the efficiency of the pyrolysis process. Together, these technologies represent a promising pathway for advancing biomass pyrolysis and producing sustainable energy resources.

Catalytic pyrolysis, wherein catalysts are employed to enhance reaction kinetics and modify product selectivity, offers a viable solution to address these challenges [4]. In recent years, significant research efforts have focused on developing novel catalysts to improve the efficiency and selectivity of biomass pyrolysis. These catalysts, often derived from abundant and inexpensive materials, aim to optimize biomass conversion into high-value products while mitigating the formation of undesirable compounds [5]. Catalysts facilitate the enhancement of bio-oil quality by promoting specific bond cleavage reactions like deoxygenation, cracking, decarbonylation, and other similar processes, with bulk

^{*} Corresponding author.

E-mail addresses: sabah.sooppi2@gmail.com, samariyam@hbku.edu.qa (S. Mariyam).

<https://doi.org/10.1016/j.biombioe.2024.107471>

Received 29 April 2024; Received in revised form 28 October 2024; Accepted 28 October 2024

Available online 4 November 2024

0961-9534/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

and supported acid or base catalysts playing a crucial role in customizing the production of premium bio-oil [6].

Zeolites, like H-ZSM-5-40, enhance aromatization and olefin production [7], while nMFI promotes furan formation [8]. Catalyst combinations (HZSM-5 and HY – different types of zeolites) yield diverse products, including BTEXs and phenol [9]. Feedstock composition also influences yields, with unique conditions favouring specific compounds [10]. Calcium-based catalysts have garnered significant attention due to their potential to modulate reaction pathways and enhance product yields [11].

Given the plentiful presence of calcium resources in nature, such as limestone and marble, particularly in the form of calcium waste like CaO, its utilization in biomass co-pyrolysis is cost-effective when compared to alternative catalysts [12]. Similarly, in the presence of Na₂CO₃, gas yield increased and in contrast, liquid yield decreased compared to non-catalytic pyrolysis at the same temperatures. In-situ catalysts are introduced directly into the reaction environment, interacting with the reactants during the process. In contrast, ex-situ catalysts are applied externally to the reaction mixture, typically in a separate reactor or vessel. In-situ catalysts provide improved control over reaction kinetics and selectivity due to their close interaction with the reactants, potentially leading to enhanced catalytic activity and higher yields of bio-oil, while utilizing catalysts within a single reactor offers additional operational advantages [13,14].

This study delves into in-situ catalytic biomass co-pyrolysis, focusing on the comparative effects of four catalysts involving three specific calcium-based catalysts and zeolite. Calcium-based catalysts, such as CaCO₃, CaO, and Ca(OH)₂, possess high surface area and reactivity, making them effective in facilitating thermochemical reactions during pyrolysis. Similarly, zeolites exhibit remarkable catalytic activity and selectivity in biomass conversion reactions with their well-defined pore structures and acidic sites. Concurrently, soda lime (Ca(OH)₂) and ZSM-5 (a type of zeolite) are commercial catalysts, readily available in the market, being explored in this article. This paper also aims to bridge the gap by comparing commercial and newly developed catalysts – CaCO₃ and CaO derived from seashells - in biomass co-pyrolysis. By systematically evaluating the performance of both commercial and developed catalysts, we seek to elucidate their respective effects on bio-oil, char, and gas yields and the composition and quality of the resulting products.

Furthermore, we aim to identify the key factors driving the observed differences in product distribution and characteristics between the two types of catalysts. This exploration sheds light on the intricate interactions between catalysts and biomass constituents and contributes to developing innovative pathways for sustainable biofuel and chemical production.

This study investigates the impact of catalysts on the pyrolysis of a ternary biomass mixture comprising date pits (DP), cow dung (CD), and coffee waste (CW). These biomass feeds were selected due to their abundance in Qatar and their potential as sustainable feedstocks for biofuel production. Previous research by the authors has examined the kinetic and thermodynamic characteristics of these materials in both non-catalytic [15] and catalytic [4] contexts, as well as their capabilities for bio-oil production [16], and char production predictions [17]. A mixed biomass feedstock is more representative of real-world waste management scenarios, where various organic materials are often processed together. This reflects the complexity of biomass sources and can provide insights into how different feedstock components interact during pyrolysis. Notably, mixing these three waste materials has been shown to significantly increase volatiles by up to 69 % [4]. The DP composition is particularly rich in cellulose and hemicellulose [16], which enhance its thermal degradation properties, while CD contributes to the overall yield and quality of bio-oil, with reports indicating that it contains major non-polar components similar to those found in crude oil, gasoline, and diesel [18]. CW, a byproduct of the coffee industry, not only serves as an environmentally friendly feedstock but also contains substantial organic content that can be converted into valuable

resources, including biodiesel, bio-oil, and biochar [19,20]. Co-pyrolysis of these feedstocks improves process efficiency, as demonstrated in a previous study [4], which found lower activation energy and pre-exponential factor values for the ternary feed compared to single feeds. By analyzing a ternary mixture, the authors observed how the unique chemical properties of each biomass influence the overall reaction pathways, product yields, and composition of bio-oil. This can reveal important information about the effectiveness of the catalysts in a more complex matrix, which may not be apparent when studying single biomass samples. Additionally, the use of natural waste catalysts enhances thermal efficiency and reaction spontaneity, highlighting the importance of feedstock blending in optimizing biomass utilization, and economic feasibility.

This investigation further spans two critical temperatures, 550 °C and 750 °C, which were selected based on their significance in influencing the yield and quality of pyrolysis products. At 550 °C, the conditions are conducive to maximizing the production of bio-oil, as this temperature allows for optimal volatile release while minimizing the formation of char. This aligns with the findings that the volatile content is highest at lower to mid-range temperatures, making it ideal for capturing liquid products [4,17]. Conversely, 750 °C is employed to investigate the effects of higher thermal energy on the decomposition of organic materials, as elevated temperatures can enhance the breakdown of complex biomass structures, resulting in an increased yield of gas products and improved oil quality (high hydrocarbons and low oxygenated compounds) [21]. The contrasting thermal conditions of 550 °C and 750 °C not only enable a comprehensive understanding of the thermal degradation mechanisms but also elucidate the catalytic influence on product distribution. By exploring both temperatures, this study aims to provide insights into optimizing the pyrolysis process for each feedstock, thereby contributing to the development of more efficient biomass-to-energy conversion strategies.

Specifically, we seek to analyze the role of different catalysts (calcium-based catalysts, and commercial zeolite) in enhancing char yields, altering bio-oil composition, and modifying gas production, including the concentrations of gases like CH₄ and CO₂. The comparison between calcium catalysts (base catalysts) and zeolite (acid catalysts) was made to provide a comprehensive understanding of how different catalytic properties affect product distribution in biomass pyrolysis. This comparison allows for a more nuanced analysis of catalyst performance and highlights the importance of selecting appropriate catalysts based on desired pyrolysis outcomes, offering insights into how catalyst chemistry influences bio-oil production and composition. Additionally, the study aims to identify specific bio-oil compounds that hold potential for upgrading and industrial applications. By elucidating the temperature-dependent dynamics and catalytic effects on the formation of beneficial compounds, we aspire to optimize catalytic pyrolysis systems and propose future research on synergistic catalyst combinations and reaction mechanisms. Ultimately, this research contributes to advancing the field of biomass pyrolysis and promoting sustainable energy solutions.

2. Materials and methods

A tube furnace (MTI Corporation, model OTF-1200X) was employed to conduct the pyrolysis process and analyze its resulting products. A schematic of the laboratory setup for collecting pyrolysis products is depicted in Fig. 1. Samples of 3.0 ± 0.1 g held in quartz crucibles were heated under high-purity nitrogen (99.99 %) at a flow rate of 100 mL/min for 20 min at room temperature. The pyrolysis experiments were carried out at 550 °C and 750 °C, at a heating rate of 10 °C/min and the char, gas and bio-oil were collected in the crucible, tedlar bag, and acetone from the tube and condensation system, respectively. The collected liquid yield was subsequently rotary evaporated at 556 mbar and 60 °C for 2 h to remove the acetone completely. Product yields were determined using equations (1)–(3).

Exactly 20 wt% of the catalyst was physically added and mixed to the

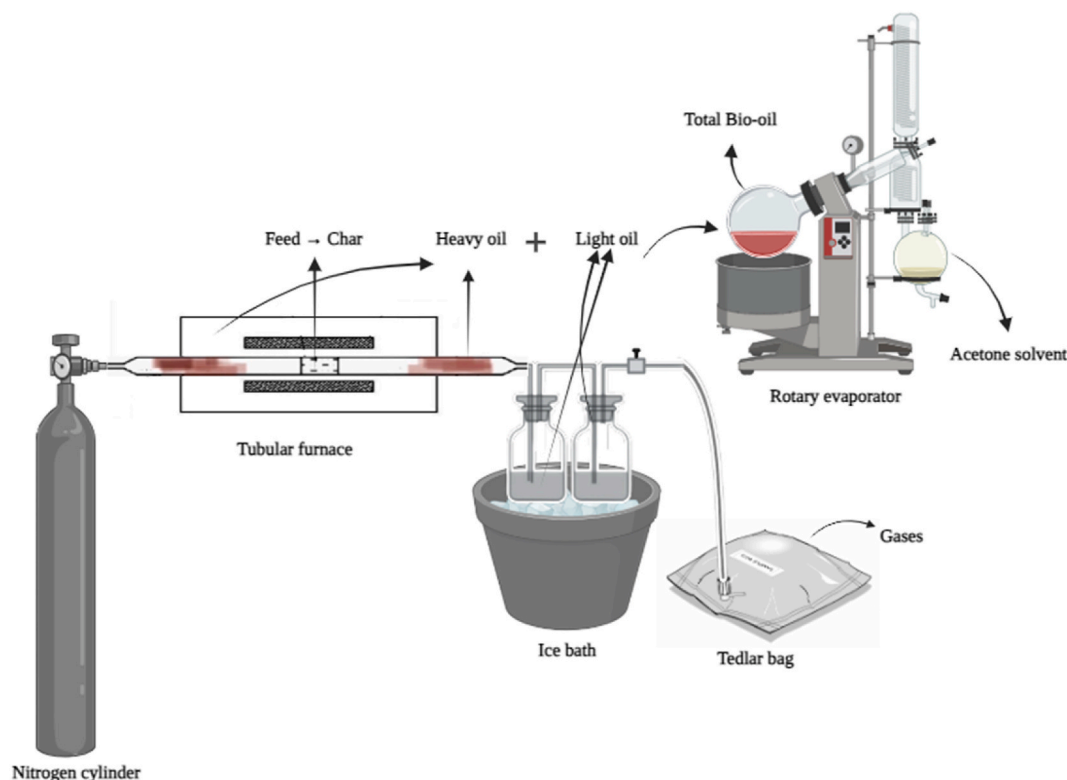


Fig. 1. Diagram of the laboratory setup for collecting pyrolysis products using a tube furnace.

ternary biomass feeds (DP, CD, CW at equal proportions) in the quartz boat. The ternary feed pyrolysis used to validate yield was further investigated in this chapter for gas, bio-oil, and char characterization. However, the feeds have been previously characterized in articles published by the authors [16]. As mentioned before, four catalysts are investigated in this study: CaCO_3 , CaO , Ca(OH)_2 , and zeolite. The former two are catalysts developed in laboratory using natural waste. Seashells (SS) have previously been investigated as potential catalysts for biomass co-pyrolysis due to their high CaCO_3 content, considering both kinetic and thermodynamic investigations [4,22]. The CaO was made by calcinating CaCO_3 (SS) at 900°C for 2 h in a muffle furnace following the methodology described by Wongsakulphasatch et al. [23]. The catalytic materials, Ca(OH)_2 (Soda-lime; Batch No: CBD1015) and zeolite (ZSM-5; CASS: 308081-08-5), were purchased from Bee Chems, Uttar Pradesh, India and Thermo Fisher Scientific, USA, respectively.

The char is characterized using Scanning Electron Microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) to examine the surface morphology and elemental composition. The sample powders were dispersed onto carbon tape, with any excess removed using compressed air. A 5 nm gold layer was then sputtered onto the sample to enhance electrical conductivity for SEM analysis using a Quorum Q150 sputtering system. SEM imaging was conducted at 5 KV with an ETD secondary electron detector using a Quanta 650FEG FEI SEM system. Elemental microanalysis was performed at 15 KV using a Bruker Quantax EDS detector.

The bio-oil composition was analyzed using GC-MS (Shimadzu GCMS-QP2020 NX, Kyoto, Japan). Approximately 1 ml of the bio-oil sample was injected into the GC-MS port, with an initial temperature set at 50°C and a residence time of 100 s. Helium served as the carrier gas at a flow rate of 215 mL/min. The GC-MS was equipped with a Restek Rxi-5ms column (30m length, 0.25 mm diameter, and thickness, 0.25 μm) with a split ratio of 25:1. The GC-MS operated in scan mode at a detector voltage of 0.7 kV in the mass range of 20–400 m/z , with a scan speed of 555 amu/s. The study reported bio-oil composition as GC-MS peak area percentages, with compounds having areas higher than 2 %

considered. This method provides a detailed profile of the bio-oil components by identifying and quantifying the relative abundance of different compounds. The peak areas represent the proportional concentrations of these compounds within the bio-oil. The experimental results presented in this study are mean values derived from multiple trials. The measurement errors associated with these results were consistently below 2 %, indicating a high level of consistency and reliability in the data collected. Non-condensable gases, including CO_2 , CH_4 , H_2 , and CO , were quantified using spectrometric curves from a fixed gas analyzer (CDS model 5500), with calibration gases purchased from Buzwair Scientific and technical gases, Qatar.

$$\text{Char yield (\%)} = \frac{\text{Mass of residue}}{\text{Mass of feedstock}} * 100 \quad [1]$$

$$\text{Bio-oil yield (\%)} = \frac{\text{Mass of liquid}}{\text{Mass of feedstock}} * 100 \quad [2]$$

$$\text{Gas yield (\%)} = 100 - (\text{Char yield} + \text{Bio-oil yield}) \quad [3]$$

3. Results and discussion

3.1. Feed characterization

The analysis of biomass feeds in previous studies has examined their proximate and ultimate composition [4,17]. The proximate and elemental analyses of the three biomass feeds—DP, CW, and CD—reveal distinct differences in their compositions. CW has the highest moisture at 8.6 % and volatile content at 76 %, while CD shows the highest ash at 19 % and fixed carbon content at 18 %, indicating its potential for char production. DP stands out with the lowest ash content 0.28 % and a high hydrogen content 6.2 %, which could enhance bio-oil yields. In terms of elemental composition, DP has the highest carbon 46 % and nitrogen content 4.3 %, suggesting a more energy-dense feedstock, while CW has the highest oxygen content 46 %, which may influence the type of bio-oil

produced. CD's relatively high ash and fixed carbon content make it distinct from the other two, which are more volatile-rich, influencing the efficiency of co-pyrolysis processes. These compositional differences make each feedstock valuable for different aspects of the pyrolysis process.

A detailed SEM-EDS analysis was conducted for the feeds, and the SS was utilized to develop the catalysts CaCO_3 and CaO [4]. SEM results (refer [4]) depicted CW with a uniform, dense, and smooth surface, while DP and CD appeared rougher and non-uniform. The catalyst SS (CaCO_3) exhibited distinct particle shapes compared to biomasses. EDS data revealed differences in carbon and oxygen content among the biomasses, with DP having the highest carbon content and CW having the highest oxygen content. Other elements like sodium, magnesium, aluminium, silicon, phosphorus, sulfur, chloride, potassium, calcium, iron, and copper were present in varying concentrations across all biomasses, potentially influencing their applications. Notably, CD showed a higher magnesium concentration, suggesting a different composition and potential use, while differences in the presence of elements like iron and copper indicated variations in biomass composition.

3.2. Effects of catalysts on product yields and gas composition

Fig. 2 shows the product and gas yields at 550 °C and 750 °C. At higher temperatures (>600 °C), secondary decompositions dominate, increasing the gas product yields at the expense of char and liquid oil yields [24]. The low reduction in char yield from 550 °C to 750 °C in the non-catalytic study can be explained by the limited thermal decomposition of more stable components at higher temperatures. Although higher temperatures typically lead to further breakdown of biomass, in this case, the composition of the feedstock underwent significant devolatilization at 550 °C, leaving behind a more resistant char fraction. The analysis of char yields revealed interesting trends across different catalysts and temperatures. Comparing the ternary feed with and without catalysts, it is evident that catalysts generally led to increased char yields at 550 °C and 750 °C. Notably, the highest char yield was observed when CaO was used as a catalyst at 550 °C. The tendency for gas and oil to increase and decrease respectively over temperature is well-known in literature and has been discussed previously [25]. The case is similar in the presence of catalysts as well. It is essential to highlight that calcium ions have previously exhibited high reactivity when it comes to enhancing the development of char, the transformation

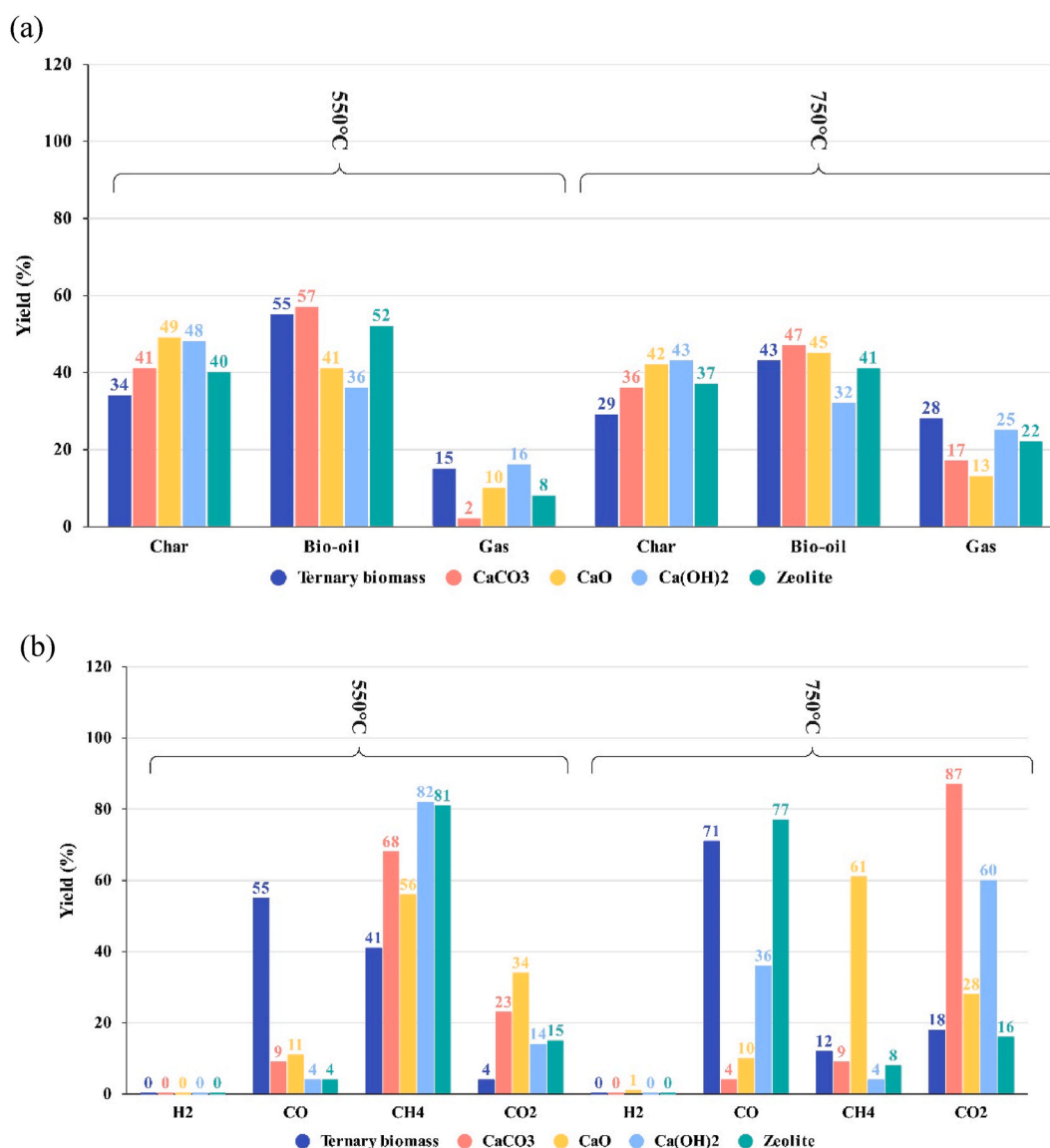


Fig. 2. Product (a) and gas yields (b).

of lignin into light oxygenates and furans, and the conversion of 5-(hydroxymethyl) furfural into smaller furans like furfural [26]. The reduction is not significantly lower at higher temperatures due to the secondary pyrolysis char production. Catalysts based on calcium have also been documented to substantially enhance the secondary reactions of tar, leading to a rise in the production of gases and char. The calcium has little impact on primary pyrolysis, it significantly promotes the secondary reactions of nascent tar, leading to increased char formation. Calcium species engage in repeated bond-breaking and bond-forming processes with tar and coke, which enhances the polymerization of tar forming more solid char rather than converting the volatiles into gas. At higher temperatures, calcium is released as an atomic species, which further promotes tar polymerization and can also enhance cracking. However, the overall effect of the catalyst leans more towards favouring char formation due to the reduction in energy activation for polymerization being more significant than for cracking reactions [27]. This explains the increased char yield and reduced gas yield, even though catalysts usually promote cracking and gas formation. The impact of catalysts on bio-oil yields was marked by distinct product variations, primarily due to the increased char yields. At 550 °C, CaCO_3 and zeolite showed relatively marginal effects on bio-oil yields, while CaO and $\text{Ca}(\text{OH})_2$ led to slight decreases compared to the feed without catalysts. CaO has been previously reported to reduce bio-oil yields during pyrolysis of sewage sludge [28]. Interestingly, at 750 °C, CaCO_3 and CaO exhibited an increasing trend, whereas $\text{Ca}(\text{OH})_2$ and zeolite contributed to notable reductions in bio-oil production. This suggests that the presence of certain catalysts can potentially alter the distribution of reaction pathways, resulting in divergent bio-oil yields.

The overall gas yields depended on both catalyst type and temperature. Using catalysts significantly impacted gas production, with varying degrees of influence. In most cases, the addition of catalysts resulted in alterations to the composition and quantity of gas phase products. While all catalysts reduced total gas yields, $\text{Ca}(\text{OH})_2$ increased at 550 °C; the same catalyst also provided the highest CH_4 content amongst all the catalysts.

Also, at the pyrolysis temperature of 550 °C, introducing catalysts yielded distinct alterations in H_2 , CO, CH_4 , and CO_2 concentrations compared to the ternary feed without catalysts. The subsequent discussion is contingent on the relative gas percentages and does not necessarily imply an accurate representation of the absolute production of each gas. Using CaCO_3 exhibited minimal impact on H_2 levels, causing a 46 % reduction in CO concentrations. Remarkably, CH_4 concentrations surged by 27 %, and CO_2 concentrations saw a substantial increase of 19 %. The CO_2 resulting from the decomposition of CaCO_3 could likely be the reason for the rise, facilitating the intensified thermal decomposition of VOCs formed during pyrolysis, thereby contributing supplementary carbon and oxygen sources [29]. Similarly, including CaO led to unchanged H_2 levels, a 44 % reduction in CO concentrations, a 15 % increase in CH_4 , and an impressive 30 % escalation in CO_2 .

Regarding the generation of carbon dioxide (CO_2), its primary source is attributed to carboxyl and carboxylate groups at lower temperatures. In contrast, at elevated temperatures, its origin is linked to ether linkages, quinones, or oxygen-containing heterocycles [30,31]. In terms of methane (CH_4) formation, its production is associated with demethylation reactions, encompassing processes like the fragmentation of aliphatic and aromatic hydrocarbons and the cleavage of methyl, oxy-methylene, and poly-methylene constituents [32,33].

Elevating the temperature to 750 °C showcased analogous trends. Notably, CaO introduced a 1.0 % augmentation in H_2 concentrations while causing a reduction of 45 % in CO. Furthermore, CH_4 concentrations saw a 49 % increase, while CO_2 experienced a notable 10 % rise. $\text{Ca}(\text{OH})_2$ and zeolite led to undeviating H_2 levels and a further increase in CO concentration. Similar results were yielded when various calcium-based catalysts found that CaO increased H_2 via carbonation, water shift, Boudouard, and thermal cracking reactions, which increased CH_4 , light hydrocarbons, and hydrogen [34]. CH_4 concentrations, however,

witnessed a decrease of 8.0 % and 4.0 %, respectively. The hydrogen yields are lower than anticipated; this is considered to be due to the low catalyst-to-biomass ratio applied in this study. According to Chen et al. (2017), if the CaO ratio is lower than 0.20, there is a reduction in acids and an increase in ketones, but between 0.20 and 0.40, the reaction absorbs CO_2 , owing to water shift reactions and improved H_2 generation, and further than 0.40, the reactions increase esters and anhydro-sugar contents in the bio-oil [35]. Therefore, a detailed study to understand the increased catalyst percentage is further required.

On the other hand, CO_2 concentrations are lowest amongst the catalysts, at 550 °C, owing to its superior CO_2 capture abilities. Wongsakulphasatch et al. [23] found that $\text{Ca}(\text{OH})_2$ precursor provided a better adsorption capacity than CaO and CaCO_3 precursors, indicating that $\text{Ca}(\text{OH})_2$ can enhance CO_2 capture. The catalysts $\text{Ca}(\text{OH})_2$ and zeolite brought about unaltered H_2 concentrations and a notable decrease of 51 % in CO. At 750 °C, the CO_2 and CO concentrations are substantially higher than CaO and CaCO_3 ; the catalyst promoted the water gas reaction after 650 °C, which forms CaCO_3 , and which further decomposes to CO_2 and CO. Another comparative study showed lower CO contents while utilizing K_2CO_3 and MgO rather than $\text{Ca}(\text{OH})_2$ [36,37]. Interestingly, both catalysts spurred a remarkable boost in CH_4 levels by ~41 %, and a considerable 10 % and 11 % rise in CO_2 concentrations, respectively. $\text{Ca}(\text{OH})_2$, by inducing substantial increases in CH_4 production due to the cracking of methyl groups and C–C bond breakage at 550 °C, presents intriguing possibilities for methane-rich gas generation [38].

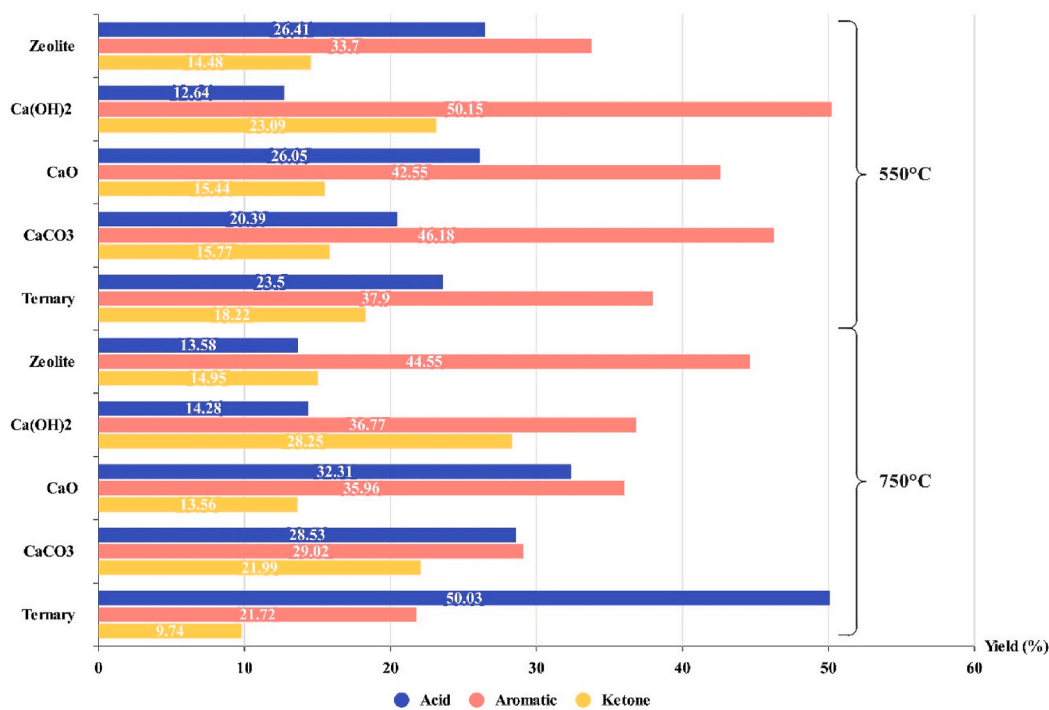
Similarly, zeolite produced more CH_4 at 550 °C and higher CO at 750 °C. A previous study reported CH_4 as the main gas component when MSW was pyrolyzed in the presence of zeolites at 500 °C at around 45 % [38]; unlike our study, the relative concentrations of gases were calculated up to C_5H_{12} rather than the four main permanent gases. Zeolites are reliable adsorbents with extensive surface areas; however, they present difficulties concerning gas desorption and require regeneration. Additionally, temperature has a significant impact on the CO_2 adsorption capacity of zeolites [39]. Also, zeolites are known to cause an increase in hydrogen yields in some cases; however, there is no increase in our case, probably due to the low ratio of the catalyst or the lower total gas yield produced, which could create difficulty in detecting lighter gases. In our case, the ZSM-5 converted the oxygenated compounds to CO and CO_2 at 750 °C up to 77 and 16 %. A previous study on DP reported the same behavior in pyrolytic gases under the application of ZSM-5, which also improved the viscosity due to lowered H_2O content, otherwise present at lower temperatures [40]. Future studies should focus on analyzing the gases other than the four analyzed, to accurately understand the heating value of the gases.

3.3. Effect on bio-oil composition

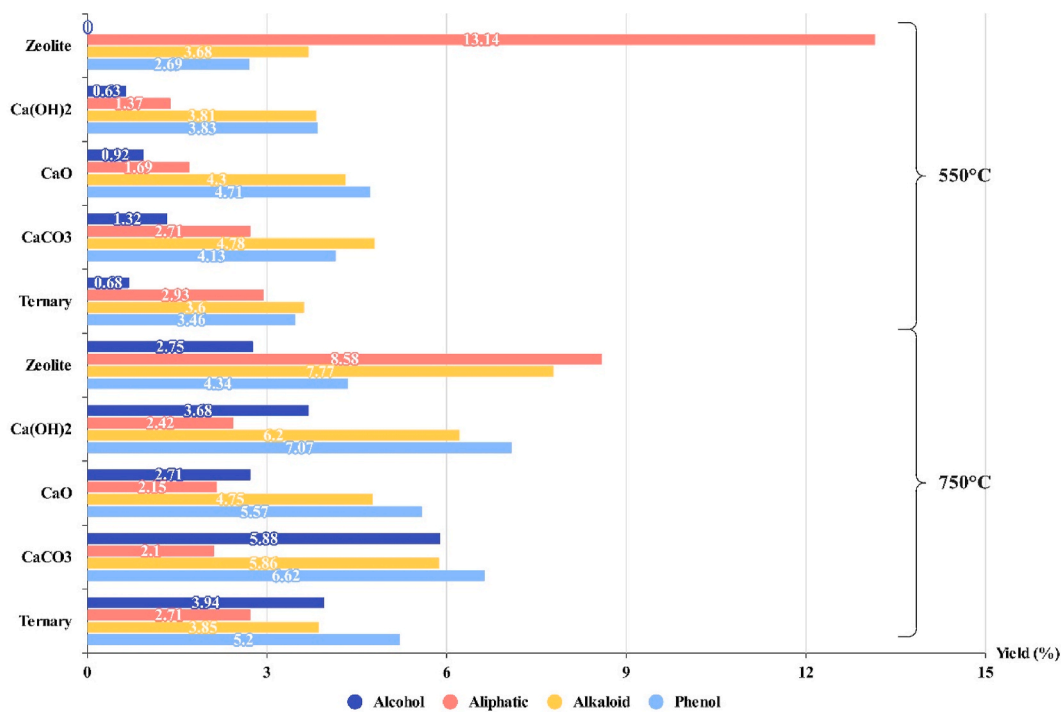
This section discusses the trends observed in the bio-oil composition due to the addition of catalysts. The characterization of the bio-oil obtained from the pyrolysis of ternary biomass (date pits + coffee waste + cow manure) at 550 °C and 750 °C. The volatiles characterization from ternary biomass using the pyroprobe was discussed in an article published by the authors [16]. However, this section distinguishes from it since the bio-oil collected from the tube furnace was characterized, thereby having a more distinct depiction of the characteristics. Additionally, the other analysis was conducted at 10 °C/s heating rate and 500 °C, while this study has much slower heating rates and two distinct temperatures (550 and 750 °C). The use of catalysts on the bio-oil characteristics is also conducted for the first time.

3.3.1. Trends in familial classifications

In the presence of various catalysts CaCO_3 , CaO, $\text{Ca}(\text{OH})_2$, and zeolite, the bio-oil has been analyzed, and the familial classification is presented in Table S1 and Fig. 3. The addition of catalysts during the pyrolysis of the ternary biomass resulted in notable variations in the composition of the bio-oil, as discussed below.



(a)

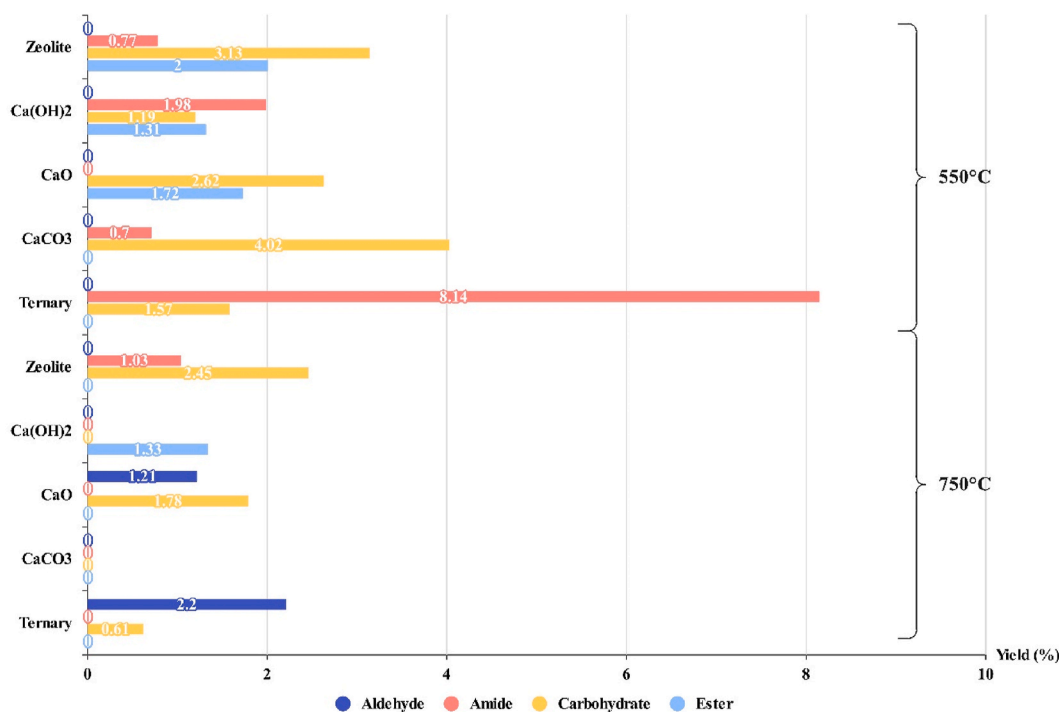


(b)

Fig. 3. Bio-oil family classification trends at 550 °C and 750 °C because of catalysts (a) Major compounds (acid, aromatic and ketone) (b) Moderate compounds (alcohol, aliphatic, alkaloid, phenol) (c) Minor (aldehyde, amide, carbohydrate and esters).

At 550 °C, the ternary feed pyrolysis exhibits a diverse composition. It contains a significant proportion of acids (50 %), indicating carboxylic acids in the reaction mixture. A lack of catalysts would result in highly

acidic bio-oil, reduced heating value, heightened corrosion, increased viscosity, and instability, thus limiting its use as a transportation fuel [41]. Additionally, there are notable amounts of alcohols (3.9 %) and



(c)

Fig. 3. (continued).

aldehydes (2.2 %), indicating the occurrence of various chemical reactions. The presence of alkaloids (3.9 %) in the feed is intriguing but expected since caffeine is a significant compound in CW [42]. The aromatic compounds (22 %) are substantial in the feed; additionally, phenols make up ~5 % of the oil composition. At 750 °C, the composition of the ternary feed undergoes significant changes. The proportion of acids decreases (34 %), indicating possible decomposition to the gaseous stage and further transformation of these compounds at higher temperatures. Alcohols and phenols also decrease (0.68, 3.5 %), suggesting their potential conversion to other products. Interestingly, amides (8.1 %) are prominent, possibly due to reactions involving the nitrogen content in the feed. On the contrary, aromatic compounds (31 %) increase significantly, likely due to the decarboxylation of acids and alcohols (refer to following discussions), yielding high CO and CO₂ levels [41]. As documented in the literature, the creation of nearly all poly-aromatics, such as pyrene, phenanthrene, anthracene, and naphthalene, takes place at elevated temperatures (>700 °C), with their levels increasing in correlation with temperature [24]. The escalation of the ultimate pyrolysis temperature prompts a secondary cracking process in functional group-containing compounds, resulting in the generation of species that exhibit greater stability.

Upon adding different catalysts to the reaction mixture, noticeable trends emerge. Adding CaCO₃ generally increases alcohol content (3.9–5.9 %), suggesting its potential role in promoting alcohol formation. CaO is the only catalyst that yields aldehydes, albeit less than the non-catalytic feed. Moreover, it has the potential to enhance the tar's quality by reducing its levels of oxygen, nitrogen, and sulfur. It stimulates the creation of lighter alkanes and augments the outputs of benzene, toluene, xylene, and naphthalene. Utilizing CaCO₃ as a catalyst also yielded reductions in the acid ratios, showing a decrease of 14 % for *Chlorella vulgaris*, 49 % for kitchen waste, and 25 % during their copyrolysis—these values were notably lower compared to the effect of CaO [43]. Also, the study presented the introduction of CaCO₃, which exhibited enhancements in aromatic hydrocarbons for *Chlorella vulgaris*

and mixed. The study's findings underscored the capacity of CaO and CaCO₃ to elevate the quality of pyrolysis products through the mitigation of oxygen-related elements like acids, nitriles, and amides, likely in the form of gases. Similarly, our study found lower acid concentrations by 22 % and 18 % at 550 °C in the presence of CaCO₃ and CaO, respectively. On opposing trends, CaCO₃ increases alkaloid and alcohol concentrations, while CaO boosts alkaloid compounds.

At 550 °C and 750 °C, Ca(OH)₂ leads to a decline in aldehydes (0 %) from 2.2 % in the non-catalytic feed at 550 °C, which has been reported previously [36]. Also, Ca(OH)₂ leads to a decline of 3.7 to 0.6 % of alcohols with increasing temperature at the expense of an increase in aromatics from 41 to 54 %. A previous biomass co-pyrolysis study with ZSM-5 transformed feedstock into aromatics (yielding up to 58 %) through olefin cyclization and aromatization due to a synergistic deoxidation effect in corn stalk and MSW [8]. This suggests that the catalyst's influence can vary depending on the reaction temperature and the specific reactions. Additionally, the acid content was lowest during the catalytic pyrolysis using Ca(OH)₂, with an astounding reduction of 36 % and 21 % at 550 °C and 750 °C, respectively. Reduction of the acid components of oil and enhancement in desirable phenolic components have been reported in the pyrolysis of empty fruit bunch pyrolysis [37] and pine wood pyrolysis [36] due to the neutralization of the carboxylic groups by the catalysts. The Ca(OH)₂ catalyst enhances aromatics, and zeolite leads to elevated aromatics, aliphatics, carbohydrates and reduced acids. At 750 °C, the Ca(OH)₂ catalyst results in higher aliphatic, amide, aromatic, carbohydrate, and ester concentrations, suggesting its role in these reactions.

Ketones exhibit exciting trends based on catalysts and temperatures. At 550 °C, the ternary feed contains 12 % ketones, while CaCO₃ and CaO catalysts boost ketones to 22 % and 14 %, respectively. This indicates that these catalysts might facilitate ketone-forming reactions, such as decarbonylation. Ding and colleagues confirmed that using CaO as the catalyst medium effectively converts acids into ketones and hydrocarbons due to neutralization reactions, thermal cracking, and catalytic

cracking [44]. At 750 °C, the ketone concentrations increased in the presence of CaO by 2 %, indicating their role in promoting decomposition reactions that generate ketones at higher temperatures.

Zeolite addition substantially increases the proportion of aliphatic compounds at both temperatures, indicating its catalytic role in promoting hydrocarbon formation. Zeolites have been previously reported to be effective in removing acids and improving the formation of aromatics and olefins through catalytic cracking, neutralization, and thermal cracking due to the unique microporous structure of ZSM-5 favours the aromatic production, but coke deposition on the surface inevitably deactivates the catalyst at higher temperatures [45,46]. Zeolites provided shape selectivity for deoxygenation and increased hydrocarbon yields. The effect of zeolites at 750 °C is similar to the calcium-based catalysts at both temperatures. Compared to non-catalytic feed, at 750 °C, zeolite decreases amides, acids and alcohols and increases aromatics, ketones, aliphatic, alkaloids, and carbohydrates, suggesting its preference for other reaction pathways. Notably, the zeolite catalyst at this temperature significantly enhances aromatics to 44 at 550 °C, suggesting its role in promoting aromatization reactions at relatively lower temperatures.

On the other hand, at 750 °C, the zeolite catalyst decreases aromatic compounds to 34 %, possibly due to coke formation filling the microporous structure of the zeolites, which favours aromatic production [47]. Notably, zeolite eliminates alcohol and aldehyde formation at 750 °C, possibly due to their conversion into other products. The reduction in the specific gases shows that above 550 °C, most of the compounds are converted into gases such as CO and CO₂, where the CO concentration was highest (77 %) during zeolite co-pyrolysis at 750 °C.

In conclusion, the reducing acids content with increasing temperature is echoed in the calcium-based catalysts. In these series, an elevation in temperature is generally accompanied by a decrease in acid content. Intriguingly, the zeolite series exhibits an interesting exception: the 750 °C sample possesses a slightly higher acid content (26 %) than its 550 °C counterparts (14 %), diverging from the temperature trend the calcium-based catalyst presented. This divergence beckons further investigation into the temperature-dependent dynamics within zeolite-mediated reactions. Consequently, these findings underscore that zeolite is best utilized at 550 °C since the sum of aromatics and aliphatic are highest; the percentages were 24, 31, 38, 39, 53% without catalysts, with CaCO₃, CaO, Ca(OH)₂, and zeolite respectively. The aliphatic hydrocarbons derived from the pyrolysis of specimens could serve as combustible fuels, while monocyclic aromatic hydrocarbons found widespread utility in the chemical industry as crucial foundational materials [48]. The lowest acids at 550 °C occur in the presence of zeolites (14 %), reducing corrosiveness and stability issues and increasing the calorific value in the pyrolysis oil.

Consequently, a greater abundance of aliphatic hydrocarbons and monocyclic aromatic hydrocarbons was anticipated, coupled with a reduced presence of acids. Although the combined aliphatic and aromatic yields have increased due to all the catalysts compared to non-catalytic feeds, zeolite seems to be the best option if targeting the highest yields. Also, future work should focus on combining the calcium-based catalysts with zeolites to utilize both their positives in bio-oil composition; for example, reference [49] found that the addition of CaO or MgO to ZSM-5 led to a significant improvement in the conversion of aromatic hydrocarbons.

3.3.2. Product composition

Carbohydrates exhibit intriguing behavior at different temperatures. At 550 °C, compounds like beta-D-glucopyranose, 1,6-anhydro- show increased yields in the presence of Ca(OH)₂. However, at 750 °C, the yield of this compound increases in the absence of catalysts and with all catalysts except Ca(OH)₂. The transformations of individual glucose monomers involving the rupture and subsequent reconstruction of the ring structure due to dehydration reactions lead to an increase in glucopyranose [50]. Next, we will discuss the presence of certain aromatic

compounds that make significant differences in the overall yield.

At 550 °C, the distribution of aromatic compounds reveals a distinct sensitivity to different catalysts. The compound, 3,4'-isopropylidenediphenol forms most of the bio-oil composition, which increases significantly with temperature, up to 22 % at 750 °C from 8.0 %. The percentages also increase with catalysts, except in the case of zeolites. This is a primary reason why the aromatics content was lowest in the case of zeolites at 750 °C (compared to other catalysts). It has been reported previously that high-molecular-weight, elongated compounds become broken down into individual monomers through the cleavage of carbon chains, including compounds like bisphenol A and 3,4'-isopropylidenediphenol in the presence of zeolites [51].

Additionally, another study showed that 3,4'-isopropylidenediphenol is the only compound that was detected in the presence of ZSM-5, Al₂O₃, MgO during the pyrolysis of electronic equipment [52]. The most striking trend emerges with compounds like 3,4'-isopropylidenediphenol and p-cresol, which substantially increase their formation under the influence of Ca(OH)₂ and zeolite at 550 °C. The process of dehydrogenation and transalkylation reactions within the context of the pyrolysis of tyres could lead to p-cresol in the presence of zeolite catalysts [53]. This suggests that these catalysts play a pivotal role in promoting the conversion of precursor molecules into these aromatic compounds. The slight presence of pyridine has been reported previously in the co-pyrolysis of food waste digestate and corn husk with CaO [54].

Furthermore, the compound furan-2-carbohydrazide, N₂-(1-methylhexylideno), shows a notable increase in formation when Ca(OH)₂ is introduced (0.76 %), indicating the catalytic role of Ca(OH)₂ in promoting the formation of this compound. In this scenario, a precursor compound with a furan ring and hydrazide functional group is present, but its arrangement does not naturally lead to furan-2-carbohydrazide formation. When Ca(OH)₂ is introduced as a catalyst, interactions between Ca(OH)₂ and the precursor occur, potentially through surface adsorption or acid-base interactions. Ca(OH)₂'s catalytic effect triggers the rearrangement of the precursor's functional groups, possibly involving bond cleavage, isomerization, or other changes. This rearrangement, facilitated by Ca(OH)₂, transforms the precursor into furan-2-carbohydrazide, particularly N₂-(1-methylhexylideno), increasing concentration. This highlights Ca(OH)₂'s role in promoting this compound's formation. The described pathway presents a speculative mechanism, likely involving more complex steps and interactions. The reaction's specifics require further investigation in the future for confirmation. Similarly, the compound 1,2-benzenediol, 4-methyl – an oxygenated compound – increased slightly with CaCO₃, CaO, and zeolite at 550 °C, and CaO and zeolite at 750 °C. However, the increase is not significant enough to increase the overall oxygenated compounds (all below 1.6 %). Phenolic compounds originating from lignin can experience cleavage of the oxygen-aromatic carbon bond and further cleavage of the oxygen-alkyl carbon bond, leading to benzene-diols or benzenetriols [41]. Reducing benzene-diol with increasing pyrolysis temperature was first reported during rice husk pyrolysis [55].

Additionally, naphthalene formation exhibits a noticeable enhancement under the influence of the catalysts at 750 °C in the non-catalytic and catalytic pyrolysis, up to 2.7 % in the presence of CaCO₃ - which implies that this catalyst promotes the synthesis of this polycyclic aromatic hydrocarbon. Poly-aromatics, such as pyrene, phenanthrene, anthracene, and naphthalene are known to increase at temperatures (>700 °C) [24]. Meanwhile, hydroquinone and phenol display differential responses to catalysts at 750 °C. However, hydroquinone formation remains largely unchanged under the influence of most catalysts, except for a slight increase with Ca(OH)₂. Phenol, on the other hand, demonstrates slightly increased formation, reflecting these catalysts' role in enhancing its production and, at the same time, reducing the production of phenol, 4-(1-methyl-1-phenylethyl), especially in the presence of zeolite (no detection). Importantly, phenols increase by 1.1 % in the presence of CaO.

Furthermore, about 15 and 11 ketone compounds were detected at 550 and 750 °C, respectively, for the ternary feed. At 550 °C, different catalysts exert varying effects on the formation of ketone compounds. Butyrolactone, for instance, shows a consistent trend of decreased production in the presence of CaCO_3 , CaO , and zeolite, suggesting that these catalysts demote the conversion of precursor molecules into this ketone. 1,2-cyclopentanedione, 3-methyl-, another ketone compound, exhibits an interesting pattern. Its formation is enhanced with CaCO_3 and zeolite, indicating that these catalysts contribute to its synthesis. Similarly, 2-acetyl-2-methyl-succinonitrile and 2-pentanone, 4-hydroxy-4-methyl- are more effectively formed (increase by 2 %) when CaCO_3 and zeolite are present. Also, 2-propanone, 1-hydroxy-, 2-pyrrolidinone are only present in CaCO_3 and zeolite. Furthermore, ketones of 2-cyclopentenone derivatives show selective enhancement in the presence of specific catalysts. On the other hand, ketones, 2-tridecanone, and ethanone 1-cyclododecyl- are present only the presence of Ca(OH)_2 .

At 750 °C, the behavior of ketone compounds becomes even more pronounced. The majority of the ketone compounds were not detected without a catalyst. Also, most of the ketones were 2-pentanone, 4-hydroxy-4-methyl-, without any catalyst and with CaCO_3 , CaO , and zeolites. The percentage increases slightly in the presence of CaCO_3 but is lower for the others. The yields of 2-pentanone, 4-hydroxy-4-methyl-, increased significantly from 400 °C to 600 °C when organic pruning wastes were pyrolyzed [56]. Similarly, 2-heptadecanone and 2-nonadecanone exhibit a notable increase in synthesis with the addition of CaO and Ca(OH)_2 catalysts. This implies that these catalysts are crucial in forming these ketone compounds. A recent study emphasized the role of CaO is producing ketone groups, which constituted 27 % of the peak area during the pyrolysis of DP utilizing calcined dolomite [57]. It includes elongated compounds like undecanone, tridecanone, nonadecanone (around 1 %), and 2-heptadecanone (approximately 5 %). The elevated ketone content is attributed to CaO 's role as a reactant; CaO 's interaction with acids or carboxyl groups forms calcium carboxylates, breaking down into CaCO_3 and ketones. In our case, CaO produced 5 % pentanone, 4-hydroxy-4-methyl, and 4.2 % 2-heptadecanone at 550 °C, which increased to 5.6 % at 750 °C, forming most of the ketones content. Additionally, 2-pentanone, 4-amino-4-methyl-, displays enhanced synthesis in the presence of Ca(OH)_2 and zeolite, indicating that these catalysts contribute to its production.

In the alcohol family, 2-furanmethanol responds differently to the two temperatures and various catalysts. The compound 2-furanmethanol forms at relatively lower temperatures due to the decomposition of levoglucosan [58] and has been detected in bio-oil from pyrolyzed tomato plant residues [59] ironwood (4 %) [60], and fruit shells [61]. At 550 °C, the presence of CaCO_3 , Ca(OH)_2 , CaO enhances its yield, while at 750 °C, it shows increased yields with CaCO_3 and CaO . This demonstrates that temperature and catalysts impact the formation of alcohols, indicating potential pathways for bio-oil production.

In the acids family, at 550 °C, acetic acid shows a notable reduction with Ca(OH)_2 (from 8.1 to 2.9 %) and zeolite (3.4 %) catalysts, suggesting their efficient role in its conversion. Butanoic acid displays an increase with CaCO_3 , hinting at a potential catalytic effect. Propanoic acid remains relatively stable across catalysts. Specific acids like tetradecanoic acid and 9-eicosenoic acid are unique to the ternary feed, seemingly removed by all catalysts. 9-octadecenoic acid's concentration changes notably with different catalysts, indicating varying conversion rates. Similarly, n-hexadecanoic acid shows sensitivity to CaO and Ca(OH)_2 catalysts, influencing its concentration. Overall, the acid content reduces considerably. Due to decarboxylation, acids convert carboxylic acids to ketones, such as acetone, 2-butanone, 2-pentanone, and 3-hexanone [62].

At 750 °C, the presence of 9,12-octadecadienoic acid is pronounced with CaO . On the other hand, 9-octadecenoic acid and its derivatives vary with catalysts. The yields of 9-octadecenoic acid (Z)-, 2,3-bis(acetyloxy)p are highest amongst the derivatives and are notably decreased in the presence of catalysts, suggesting their role in its conversion.

Dodecanoic acid remains relatively stable, while n-hexadecanoic and tetradecanoic acid concentrations are considerably diminished by Ca(OH)_2 catalyst. Both acids have been important acid components in the bio-oil of biochemical sludge (25, 0.80 %) and sewage sludge (23.0, 0.66 %) [63]. Oleic acid – with 19 carbon atoms – with Ca(OH)_2 at both temperatures reduced considerably, as presented in other [37].

Generally, while some compounds show similar trends in their response to catalysts at both temperatures, there are instances where the effect of a catalyst at 750 °C differs from its effect at 550 °C. For example, at 750 °C, 2-pentanone, 4-hydroxy-4-methyl-, exhibits increased yields with CaCO_3 , CaO , and Ca(OH)_2 , whereas at 550 °C, the same compound shows enhanced yields primarily with CaO and Ca(OH)_2 only. These differences suggest that the temperature plays a significant role in dictating the interaction between catalysts and specific compounds. At the same time, catalysts may have differing effects on the same compound independent of the temperature. For instance, 2-nonadecanone has higher yields with CaCO_3 and Ca(OH)_2 . This indicates that specific catalysts might favour different reaction pathways or intermediate species irrespective of the temperature. Similarly, some catalysts consistently enhance the yields of specific compounds across both temperatures. For instance, 3,4'-isopropylidenediphenol consistently shows increased yields with all the calcium-based catalysts at both 550 °C and 750 °C. This suggests that certain catalysts may exhibit similar catalytic behaviours regardless of temperature due to their intrinsic activity and interaction mechanisms.

On the other hand, compounds that are sensitive to temperature-driven reactions might exhibit differing trends in response to catalysts at both 550 °C and 750 °C. For instance, pyridine was detected only at 550 °C in the presence of CaO and Ca(OH)_2 . The differences in reaction kinetics due to the reaction rate constants at different temperatures can influence the behaviour of catalysts. Catalysts may promote specific reactions more effectively at certain temperatures due to activation energy requirements. The formation and stability of intermediate species during pyrolysis can be temperature-dependent. Different catalysts may interact with these species uniquely, leading to varying product distributions. Certain reactions might compete for the same precursors at different temperatures. Catalysts can influence the relative rates of these reactions, resulting in varied product distributions.

The major compounds generated at 550 and 750 °C are shown in Fig. 4. Generally, the addition of catalysts tends to influence the production of the major compounds. For example, at 550 °C, catalysts like CaCO_3 and CaO lead to increases in certain compounds, such as 2-pentanone, 4-hydroxy-4-methyl- and 3,4'-isopropylidenediphenol, suggesting their role in promoting these reactions. Conversely, the presence of catalysts like Ca(OH)_2 and zeolite can lead to decreases in compounds like n-hexadecanoic acid and acetic acid. At 750 °C, the effects of catalysts are more diverse. While some compounds like n-hexadecanoic acid show increases in concentration with certain catalysts, others like 9-octadecenoic acid (Z)-, 2,3-bis(acetyloxy)p decrease in the presence of all catalysts. The compound 3,4'-isopropylidenediphenol show decreases, especially with zeolite. These variations indicate the complex interplay between catalysts and reaction pathways at different temperatures. Hence, understanding the trends in the total familial classification rather than the product composition seems useful. Also, the effect of physical properties due to the compound composition is a necessary study for the future.

3.3.3. Identification of valuable compounds

Various compounds were identified in the bio-oil produced from pyrolysis, each with distinct applications. The major compound, 3,4'-Isopropylidenediphenol (Bisphenol A), accounted for up to 37 % at 750 °C with CaCO_3 , and is used in polycarbonate plastics and epoxy resins for food can coatings [64]. 1,6-Anhydro-beta-D-glucopyranose (Levoglucosan) was present at 1.8 % with Ca(OH)_2 at 550 °C and can be converted into biofuels or high-value chemicals [65,66]. Other notable compounds include 4-Methylcatechol (2.0 % at 550 °C), which

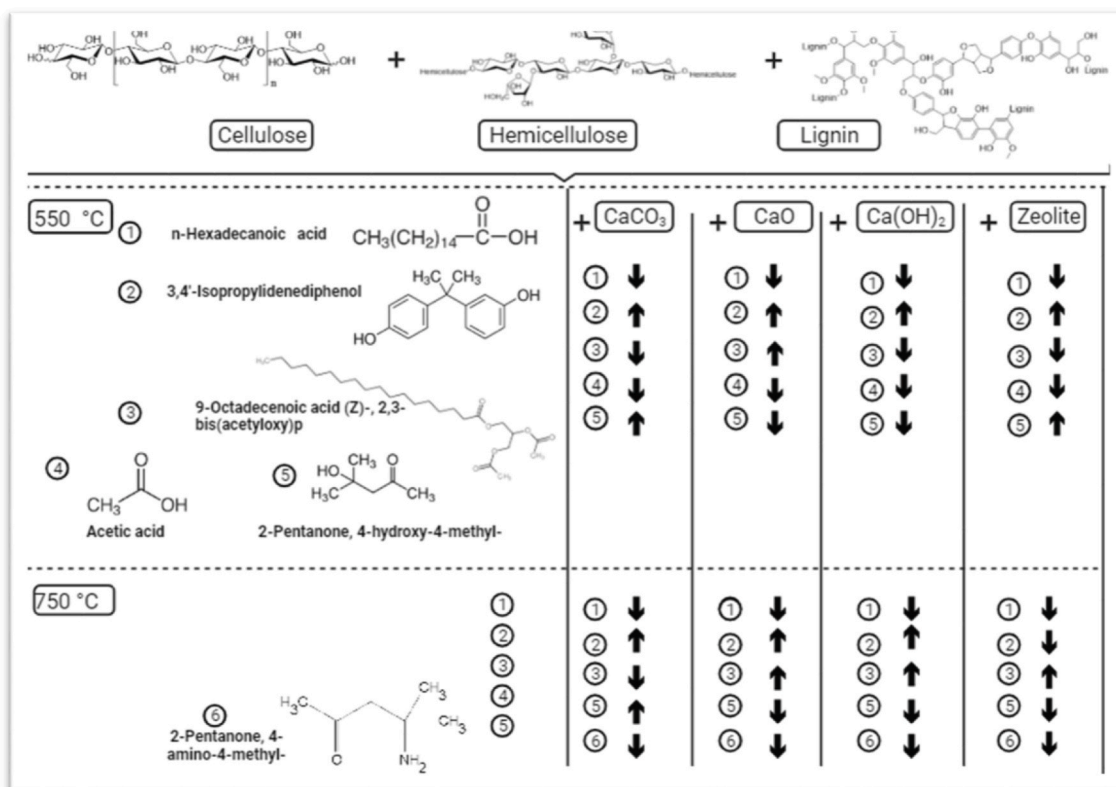


Fig. 4. Trends of the main compounds detected in the non-catalytic and catalytic bio-oil.

has applications in fine chemicals and pharmaceuticals [67], and 3-Methyl-1,2-cyclopentanedione (2.0 % at 550 °C), serving as a precursor in pharmaceuticals [68,69]. Compounds such as caffeine (up to 8 % in zeolite at 550 °C) and catechol (5.4 % at 550 °C) have diverse applications in food, beverages, and cosmetics [70,71]. The separation and isolation of these compounds from bio-oil typically involve techniques such as distillation, solvent extraction, and chromatography. These methods help separate the bio-oil components based on their boiling points and chemical properties, enabling the recovery of valuable compounds like n-hexadecanoic acid (up to 18 %) and phenol (4.0 % with CaCO₃) for further industrial use [72,73].

The separation and isolation of compounds from bio-oil produced during pyrolysis typically involve several techniques, such as distillation, solvent extraction, and chromatography. For instance, caffeine (up to 8.0 %) using sequencing temperature-raising pyrolysis [74] and phenol (about 4.0 %) from the bio-oil by solvent extraction can effectively isolate phenols using liquid-liquid extraction using chloroform and n-hexane [75], and utilizing precipitation and Soxhlet extraction for retrieving 1,6-anhydro-beta-D-glucopyranose (Levoglucosan) (1.8 %) [76]. Chromatography can further purify compounds like 4-Methylcatechol (2 %) and catechol (5.4 %) based on their chemical properties [76]. Additionally, nanofiltration and membrane separation techniques may be employed to isolate smaller molecules such as acetic acid from larger bio-oil constituents [77]. These methods collectively enable the efficient recovery of valuable compounds, contributing to the development of sustainable materials and chemicals.

3.4. Effect on char characterization

The SEM image (Fig. 5a) shows rough char surfaces at 550 °C for the ternary feed resulting from the decomposition of organic matter and the loss of volatile components during pyrolysis, while only a few rough surfaces are due to the presence of residual minerals or the preservation of specific biomass structures. However, at 750 °C (Fig. 5f), it becomes

smoother due to the ashy nature of the char due to the high decomposition of the char to gas and bio-oil. Furthermore, the structures look distinctly different in the presence of catalysts. However, the rough nature persists for CaCO₃, 750 °C. It still looks rough at 750 °C, unlike the non-catalytic feed. In the presence of CaO, you see a lot more cracks and roughness at both temperatures than CaCO₃, which shows the distinction between the two catalysts because of their respective activity. CaO tends to have more precipitates on its surface at 750 °C, probably the CaCO₃ that forms at higher temperatures in addition to CaO. The images for Ca(OH)₂ (Fig. 5d–i) show some form of residue on the surfaces and relatively small particle sizes – compared to all catalytic chars. Additionally, the zeolite chars are more aggregated, with less precipitation.

The elemental analysis (SEM-EDS) of the catalytic chars resulting from the pyrolysis of non-catalytic (ternary) and catalytic feeds at temperatures of 550 and 750 °C reveals distinct compositional differences among the experimental conditions (Fig. 6). The carbon content exhibits relatively high levels across all conditions, particularly reaching peaks in the non-catalytic conditions at 550 °C (80 %) and 750 °C (82 %), implying the prevalence of carbonaceous compounds.

The lowest carbon content was at 550 °C in the presence of CaO but with a high oxygen content. Interestingly, in the case of Ca(OH)₂, the oxygen content is almost as much as the carbon content, which is also reflected in the lowest acids (oxygenated compound) content in the bio-oil with 12–14 %; the high oxygenated compounds embedded within the char particles reflect probable precipitation of compounds due to the interaction with acids. The SEM images also attest to the same effect (Fig. 6). Additionally, the total bio-oil and char yields were lowest (32, 43 %), respectively, in the presence of Ca(OH)₂. Fig. 7 shows the inverse trend between the acid content in bio-oil and the oxygen content in the char; this finding should be studied in further depth in the future by applying statistical tests, such as correlation and regression analyses, to verify whether the observed inverse relationship holds across various experimental conditions. Ca(OH)₂-based chars also seem to have higher

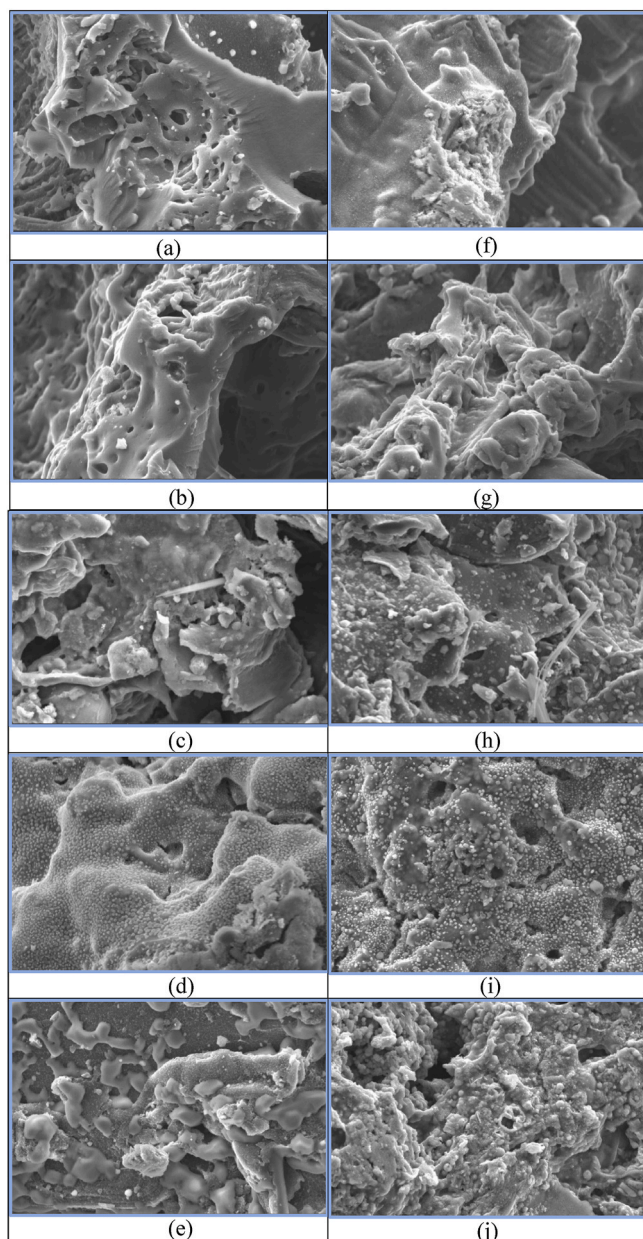


Fig. 5. SEM images of the chars at 550 °C, and 750 °C using non-catalytic feed (a, f), catalytic CaCO_3 (b, g), CaO (c, h), Ca(OH)_2 (d, i), and zeolite (e,j).

calcium content than the other catalysts. The calcium content also increased from ~4 % to ~11 % with increasing temperature in the presence of zeolites, but this is at the expense of a higher oxygen content and lower carbon content; with increasing temperature, the lowering of carbon could alter the relative ratios of the other elements present in the sample.

Similarly, the lower oxygen content in CaO -based chars could have relatively increased the nitrogen content. Also, the nitrogen content remains zero in all samples, except for CaO at 550 °C, where nitrogen content rises to 2.2 %. The nitrogen-containing compounds in the bio-oil in the form of amides at 750 °C, respectively, lead us to believe that certain compound reaction pathways interact with the nitrogen-containing compounds in the char cracking to give off amides at higher temperatures.

All other elements are in small quantities, so any variation is not significant for discussion. However, the following section mentions a few variations amongst the chars. Among the various elements studied,

sodium (Na) and magnesium (Mg) exhibit consistently low levels across all conditions. Potassium (K) content is highest in zeolite at 550 °C and subsequently declines. Also, the iron (Fe) content is undetected in all feeds except zeolite chars. The pore sizes of zeolite perhaps allow certain elements to be trapped, while the catalytic behaviour of calcium-based catalysts is natural. Silicon (Si) and phosphorus (P) are present in minor quantities, while sulfur (S) and chlorine (Cl) content remains relatively modest, implying a limited presence of such corresponding compounds.

The detected variations in elemental composition underscore the discernible impacts of catalysts on the pyrolysis process and the resulting char composition. Carbon and oxygen levels are generally consistent, highlighting the dominance of carbonaceous compounds with varying degrees of oxidation. Nitrogen content appears to be minimally affected by the presence of catalysts. Mainly, the distribution of other elements such as sodium, magnesium, calcium, and iron exhibits discernible patterns across the different conditions; however, they are in minimal amounts in the chars.

In this study, the separation of char from the catalyst poses some challenges, as it remained mixed with the char (Fig. 6). Given that the catalyst constitutes a relatively small fraction of the overall feedstock, it is essential to consider its potential impact on the physical characteristics of the char without overstating its influence on the overall yield. The prolonged vapor residence time within the catalyst pores during in situ catalytic fast pyrolysis (>10 s) facilitates significant conversion to secondary products, such as aromatics and coke, which complicates the precise quantification of char constituents [78]. However, future studies will implement more rigorous separation methods, such as increasing the particle size of the catalysts to better remove the catalysts or to better isolate the catalyst from the char [79]. This would allow for a clearer assessment of the char's intrinsic properties, free from potential catalytic residues. While the presence of the catalyst complicates yield analysis, it could also offer potential benefits in enhancing the char's functionality in various applications. Further research into the interactions between the char and the catalyst will be crucial to optimize the pyrolysis process and fully realize the potential of the resultant char as a gasifying agent.

3.5. Reaction pathways

Reaction pathways are simplifications of the complex chemical reactions occurring during biomass pyrolysis because of the presence of catalysts. The following is a summary of the reaction pathways that could probably have occurred in the presence of the studied catalysts to yield different products and compositions.

- i. Reactions increasing ketones: The thermal decomposition of acids and carbonyl compounds present in the biomass can lead to the formation of ketones, aldehydes, and alkenes. The increase in aromatic compounds (38 % increases significantly with temperature, even without a catalyst, due to the decarboxylation of acids and alcohols, yielding high CO and CO_2 levels [16]. As documented in the literature, aromatics have increased at elevated temperatures (>700 °C) [2]. Furthermore, catalysts like CaO enhance decarboxylation and decarbonylation reactions, increasing yields of specific compounds. Ketone compounds such as 2-heptadecanone and 2-nonadecanone exhibited a notable increase in synthesis with the addition of CaO . CaCO_3 and CaO catalysts boosted ketones to 22 % and 14 %, respectively. This indicates that these catalysts might facilitate ketone-forming reactions, such as decarbonylation. Ding and colleagues also confirmed that the utilization of CaO as the catalyst medium effectively converts acids into ketones and hydrocarbons due to neutralization reactions, thermal cracking, and catalytic cracking [48,80].
- ii. Increasing alcohols: Dehydration reactions involving hydroxyl groups can lead to the formation of alkenes and water molecules.

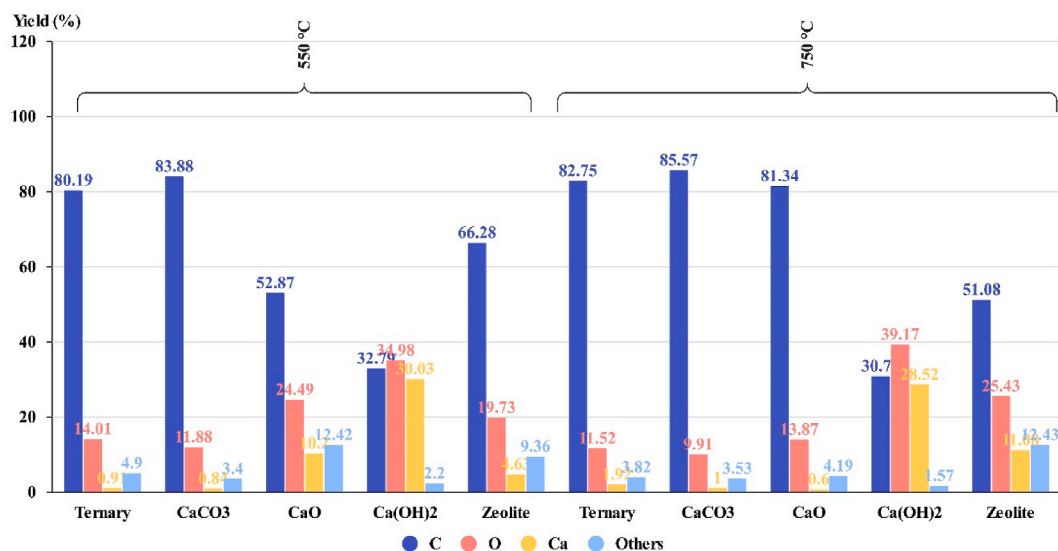


Fig. 6. EDS results of the at 550 °C and 750 °C for ternary feed char.

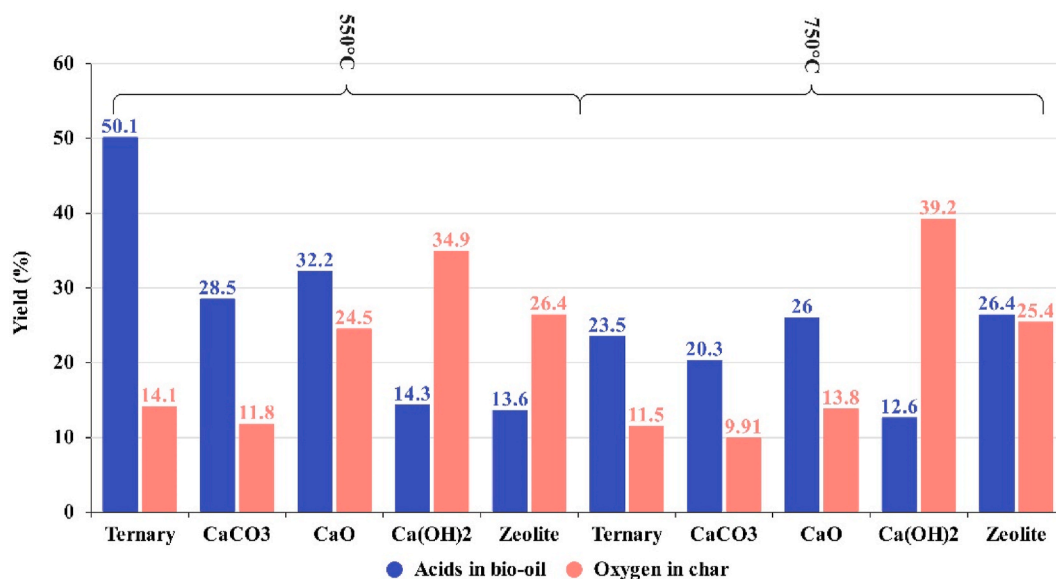


Fig. 7. Comparing the acids and oxygen content in the bio-oil and char with and without catalyst.

CaO or CaCO₃ could catalyze these reactions, influencing the production of alkenes and alcohols. At 550 °C, carbohydrate compounds such as. beta-D-glucopyranose, 1,6-anhydro- show enhanced yields in the presence of Ca(OH)₂, while at 750 °C, the same compound exhibits an increase in yield when pyrolyzed without catalysts and a catalyst except Ca(OH)₂. The transformations of individual glucose monomers involving the rupture and subsequent reconstruction of the ring structure due to dehydration reactions lead to an increase glucopyranose [50].

- iii. Increasing gases and aromatics due to cracking and fragmentation: Large organic molecules in biomass can undergo cracking and fragmentation reactions at high temperatures, resulting in the formation of smaller volatile compounds and aromatics. The presence of catalysts might promote these reactions by providing suitable surfaces for bond cleavage. The intriguing potential for the generation of methane-rich gas arises from the substantial enhancement in CH₄ production facilitated by Ca(OH)₂ at 550 °C, attributed to the cracking of methyl groups and the breaking of C–C bonds. Similarly, Zhang et al. (2014) obtained comparable

outcomes when examining various calcium-based catalysts. CaO's influence on hydrogen generation involved processes like carbonation, water shift, Boudouard reactions, and thermal cracking, boosting CH₄, light hydrocarbons, and hydrogen [34].

Catalysts like CaO or CaCO₃ could act as catalysts for reforming reactions, where larger molecules are broken down into smaller ones through processes like hydrogen transfer, dehydrogenation, and isomerization. The presence of oil shale during the fast pyrolysis maximized the aromatics yields to 35 %, with only 3.0 % of OS enabled by catalytic cracking and reforming [81]. Some compounds might undergo hydrogenation or dehydrogenation reactions in the presence of catalysts. These reactions can influence the distribution of products, such as alkanes and alkenes. The most striking trend emerges with compounds like 3,4'-isopropylidenediphenol and p-cresol, which substantially increase their formation under the influence of Ca(OH)₂ and zeolite at 550 °C. The process of dehydrogenation and transalkylation reactions within the context of the pyrolysis of tyres could lead to p-cresol in the presence of zeolites [52]. This suggests that these

catalysts play a pivotal role in promoting the conversion of precursor molecules into these aromatic compounds.

- iv. **Aromatization:** Ding and colleagues confirmed that using CaO as the catalyst medium effectively converts acids into ketones and hydrocarbons due to neutralization reactions, thermal cracking, and catalytic cracking [48,80]. Incorporating zeolite notably enhances aliphatic compounds' presence at both temperatures, underscoring its catalytic function in bolstering hydrocarbon creation through effective acid removal and enhanced aromatics and olefins formation via catalytic cracking, neutralization and thermal cracking due to its exceptional porosity [45,46]. [82] Chaerusan et al. describes the increased aromatization process in the presence of zeolites due to the hydrocarbon pool species possessing the capacity for subsequent reactions like cyclization and aromatization, which culminate in the production of monocyclic aromatic hydrocarbons. Conversely, lignin is known to decompose into phenolic compounds through processes like cracking, dehydration, and depolymerization. The active sites found on zeolites expedite the conversion of phenols by catalyzing reactions like oligomerization, decarboxylation, decarbonylation, and dehydroxylation, ultimately resulting in the genesis of monocyclic aromatics. These monocyclic aromatics can further transform into polycyclic aromatics through polymerization reactions. In our case, the phenols have reduced to 750 °C. The aromatics also reduce with increasing temperature, probably due to the coke formation that clogs the zeolite sites. The polycondensation of polycyclic aromatics has previously been reported to lead to coke formation, obstructing the zeolite pores and consequently inducing catalyst deactivation [82]. Some compounds might undergo polymerization reactions, forming larger, aromatic compounds. Catalysts can influence the extent of these reactions, affecting the production of aromatic hydrocarbons. A co-pyrolysis study of MSW and corn stalk with ZSM-5 converted feedstock into aromatics via olefin cyclization and aromatization, yielding up to 58 % [8]. In our case, the aromatics were highest in the presence of zeolite at 550 °C, reaching up to ~49 %. Also, the high Lewis acid sites induced the Diels–Alder reaction, forming more furans; in our study, the highest compound furan, tetrahydro-2-methyl- formed at 750 °C.
- v. **Secondary Reactions:** The interaction of pyrolysis products with catalyst surfaces can lead to secondary reactions, altering the composition of products and influencing pathways such as cracking and isomerization. Catalysts based on calcium have also been documented to substantially enhance the secondary reactions of tar, leading to a rise in the production of gases and char [4]. Their selectivity toward certain pathways can change with temperature due to shifts in reaction energetics. Secondary reactions like cracking and isomerization might become more prominent at higher temperatures. The presence of catalysts could influence these reactions differently at distinct temperatures.
- vi. **Specific product formation:** Catalysts like zeolites might have acidic properties that facilitate reactions like dehydration and isomerization, leading to the production of specific compounds, such as heptane, 4-methyl-, hexadecane, 1-(ethenyloxy)-, and heptadecanenitrile. Ca(OH)₂'s catalytic effect triggers the rearrangement of the precursor's functional groups, possibly involving bond cleavage, isomerization, or other changes. This rearrangement, facilitated by Ca(OH)₂, transforms the precursor into furan-2-carbohydrazide, particularly N₂-(1-methylhexylideno), increasing concentration.

4. Conclusion

The use of catalysts in pyrolysis processes offers a range of advantages that influence product yields and compositions. Analyzing the

impact of catalysts on the pyrolysis of the ternary biomass at different temperatures (550 °C and 750 °C) reveals several significant benefits. Secondary decomposition becomes prevalent at higher temperatures, increasing gas yields and reducing char and liquid oil yields. The introduction of catalysts generally enhances char yields at both temperatures. The bio-oil yield was highest and lowest in the presence of CaCO₃ and Ca(OH)₂, respectively, while the same trends were opposed in the case of gas yields.

Furthermore, the behaviour of gases like CO and CO₂ is influenced by catalysts. Ca(OH)₂ and zeolite considerably increase CH₄ and CO₂ concentrations at 750 °C. The specific effects of each catalyst on gas production and composition depend on catalyst type and temperature, highlighting the intricate interplay between catalysts and reaction pathways. The utilization of various catalysts brought about distinct advantages in altering the composition of the resulting bio-oil. At 550 °C, the initial feed contains acids, alcohols, aldehydes, alkaloids, and aromatics, each indicating specific chemical reactions. All the calcium-based catalysts reduce the acid content and increase the aromatics considerably at both temperatures. Although zeolites accomplish the same at 550 °C, both compound families show opposite trends at 750 °C. This underscores the importance of considering temperature-dependent dynamics within zeolite-mediated reactions. Additionally, CaCO₃ enhances alcohol content, which could promote alcohol formation. Ca(OH)₂ reduces aldehyde content and produces the highest aromatics at 550 °C and 750 °C.

There are specific compounds that could prove beneficial for upgrading purposes and use. For example, 3,4'-isopropylidenediphenol, or bisphenol A, is a significant component in polycarbonate plastics and epoxy resins. Also, beta-D-glucopyranose, 1,6-anhydro- (levoglucosan) has the potential for biofuels and high-value chemicals. Phenol, 4-(1-methyl-1-phenylethyl)- and 4-ethyl- phenols contribute to resins, surfactants, and antioxidants. P-cresol finds use in solvents, synthetic resins, disinfectants, and more, while other compounds contribute to diverse applications in multiple industries.

Therefore, catalysts offer the potential to enhance specific compound yields, reduce corrosiveness, and optimize bio-oil composition for various applications, warranting further research into synergistic effects when combining different catalysts. Future research into understanding intricate reaction mechanisms within complex systems like pyrolysis or catalytic processes should adopt a comprehensive strategy. Mechanistic analyses involving situ spectroscopy, isotopic labelling, and computational modelling can unveil intermediate species and transition states. Essential kinetic investigations can establish rate constants and activation energies, illuminating reaction pathways (necessary for all studied catalysts). Isotope tracing can follow specific functional groups, revealing diverse reaction trajectories. Employing transient techniques like pulse radiolysis and time-resolved spectroscopy can capture and analyze transient intermediates. Also, the effect of catalysts on the physical properties, including viscosity, drop point, acidity, etc., needs to be investigated in the future. The development of catalysts on specific compounds is complicated; the best we can do is to characterize the bio-oil for its physical properties and ensure the acidity and corrosive nature are eliminated as much as possible. At the same time, we look for target compounds that can be useful in the future for upgrading purposes.

CRedit authorship contribution statement

Sabah Mariyam: Writing – original draft, Investigation, Formal analysis, Data curation. **Mohammad Al-Herbawi:** Writing – review & editing, Methodology, Formal analysis, Conceptualization. **Tareq Al-Ansari:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Gordon McKay:** Writing – review & editing, Supervision, Resources, Funding acquisition.

Funding

The authors would like to thank Qatar National Research Fund for supporting this research under the National Priorities Research Program Award Number NPRP11S-0117–18032.

Acknowledgements

The authors express their gratitude for the assistance from Qatar National Research Fund and Hamad Bin Khalifa University. They declare that any opinions, findings, conclusions, or recommendations presented in this material are their own and do not necessarily represent the views of any of the parties mentioned. The authors also extend their appreciation to Qatar National Library for providing access to articles.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biombioe.2024.107471>.

Data availability

Data will be made available on request.

References

- W.A. Wan Mahari, E. Azwar, S.Y. Foong, A. Ahmed, W. Peng, M. Tabatabaei, M. Aghbashlo, Y.-K. Park, C. Sonne, S.S. Lam, Valorization of municipal wastes using co-pyrolysis for green energy production, energy security, and environmental sustainability: a review, *Chem. Eng. J.* 421 (2021) 129749, <https://doi.org/10.1016/j.cej.2021.129749>.
- T. Shan Ahamed, S. Anto, T. Mathimani, K. Brindhadevi, A. Pugazhendhi, Upgrading of bio-oil from thermochemical conversion of various biomass – mechanism, challenges and opportunities, *Fuel* 287 (2021) 119329, <https://doi.org/10.1016/j.fuel.2020.119329>.
- M. Raza, A. Inayat, A. Ahmed, F. Jamil, C. Ghenai, S.R. Naqvi, A. Shanableh, M. Ayoub, A. Waris, Y.-K. Park, Progress of the pyrolyzer reactors and advanced technologies for biomass pyrolysis processing, *Sustainability* 13 (2021), <https://doi.org/10.3390/su131911061>.
- S. Mariyam, T. Al-Ansari, G. McKay, Multibiomass and Natural Marine Waste Catalyst Copyrolysis : Exploring Synergy , Isoconversional Kinetics , Thermodynamics , and Mechanism, 2023, p. 2023.
- T.K. Dada, M. Sheehan, S. Murugavelh, E. Antunes, A review on catalytic pyrolysis for high-quality bio-oil production from biomass (2023) 2595–2614.
- G. Kabir, B.H. Hameed, Recent progress on catalytic pyrolysis of lignocellulosic biomass to high-grade bio-oil and bio-chemicals, *Renew. Sustain. Energy Rev.* 70 (2017) 945–967, <https://doi.org/10.1016/j.rser.2016.12.001>.
- Y. Zhao, X. Yang, Z. Fu, R. Li, Y. Wu, Synergistic effect of catalytic co-pyrolysis of cellulose and polyethylene over HZSM-5, *J. Therm. Anal. Calorim.* 140 (2020) 363–371, <https://doi.org/10.1007/s10973-019-08633-7>.
- H. He, X. Ma, Z. Yu, L. Chen, X. Chen, A study on the deoxidation effect of different acidic zeolites during the co-pyrolysis of aged municipal solid waste and corn stalk, *J. Anal. Appl. Pyrolysis* 159 (2021) 105319, <https://doi.org/10.1016/j.jaap.2021.105319>.
- Y.M. Kim, T.U. Han, S. Kim, J. Jae, J.K. Jeon, S.C. Jung, Y.K. Park, Catalytic co-pyrolysis of epoxy-printed circuit board and plastics over HZSM-5 and HY, *J. Clean. Prod.* 168 (2017) 366–374, <https://doi.org/10.1016/j.jclepro.2017.08.224>.
- S. Mariyam, S. Zuhara, P. Parthasarathy, G. McKay, A review on catalytic fast Co-pyrolysis using analytical py-GC/MS, *Molecules* 28 (2023), <https://doi.org/10.3390/molecules28052313>.
- R. Mahadevan, S. Adhikari, R. Shakya, K. Wang, D. Dayton, M. Lehigh, S.E. Taylor, Effect of alkali and alkaline earth metals on in-situ catalytic fast pyrolysis of lignocellulosic biomass: a microreactor study, *Energy Fuel* 30 (2016) 3045–3056, <https://doi.org/10.1021/acs.energyfuels.5b02984>.
- H. Li, Y. Wang, N. Zhou, L. Dai, W. Deng, C. Liu, Y. Cheng, Y. Liu, K. Cobb, P. Chen, R. Ruan, Applications of calcium oxide-based catalysts in biomass pyrolysis/gasification – a review, *J. Clean. Prod.* 291 (2021) 125826, <https://doi.org/10.1016/j.jclepro.2021.125826>.
- A. Imran, E.A. Bramer, K. Seshan, G. Brem, An overview of catalysts in biomass pyrolysis for production of biofuels, *Biofuel Res. J.* 5 (2018) 872–885, <https://doi.org/10.18331/BRJ2018.5.4.2>.
- L. Fan, P. Chen, N. Zhou, S. Liu, Y. Zhang, Y. Liu, Y. Wang, M.M. Omar, P. Peng, M. Addy, Y. Cheng, R. Ruan, In-situ and ex-situ catalytic upgrading of vapors from microwave-assisted pyrolysis of lignin, *Bioresour. Technol.* 247 (2018) 851–858, <https://doi.org/10.1016/j.biortech.2017.09.200>.
- S. Mariyam, T. Al-Ansari, G. McKay, Particle size impact on pyrolysis of multi-biomass: a solid-state reaction modeling study, *Energy Sources, Part A Recover. Util. Environ. Eff.* (n.d.), <https://doi.org/10.1080/15567036.2023.2196945>.
- S. Mariyam, M. Alherbawi, N. Rashid, T. Al-Ansari, G. McKay, Bio-oil production from multi-waste biomass Co-pyrolysis using analytical py–GC/MS, *Energies* 15 (2022), <https://doi.org/10.3390/en15197409>.
- S. Mariyam, M. Alherbawi, S. Pradhan, T. Al-Ansari, G. McKay, Biochar yield prediction using response surface methodology : effect of fixed carbon and pyrolysis operating conditions, *Biomass Convers. Biorefinery* (2023), <https://doi.org/10.1007/s13399-023-03825-6>.
- S. Yin, R. Dolan, M. Harris, Z. Tan, Subcritical hydrothermal liquefaction of cattle manure to bio-oil: effects of conversion parameters on bio-oil yield and characterization of bio-oil, *Bioresour. Technol.* 101 (2010) 3657–3664, <https://doi.org/10.1016/j.biortech.2009.12.058>.
- D.R. Vardon, B.R. Moser, W. Zheng, K. Witkin, R.L. Evangelista, T.J. Strathmann, K. Rajagopalan, B.K. Sharma, Complete utilization of spent coffee grounds to produce biodiesel, bio-oil, and biochar, *ACS Sustain. Chem. Eng.* 1 (2013) 1286–1294, <https://doi.org/10.1021/sc400145w>.
- H. Ahmed, R.S. Abolore, S. Jaiswal, A.K. Jaiswal, Toward circular economy: potentials of spent coffee grounds in bioproducts and chemical production, *Biomass* 4 (2024) 286–312.
- N. Zhong, X. Ren, L. Cheng, M. Yamamoto, T. Leskinen, J. Lommi, H. Zhu, T. Granstrom, J. Saddler, X. Bi, Microwave-assisted catalytic pyrolysis of commercial residual lignin with in-situ catalysts to produce homogenous bio-oil and high-yield biochar with enriched pores, *Energy Convers. Manag.* 295 (2023) 117620, <https://doi.org/10.1016/j.enconman.2023.117620>.
- S. Mariyam, G. McKay, T. Al-Ansari, Waste catalyst potential for co-pyrolysis of biomass and single-use plastics: model-free isoconversional kinetics and thermodynamics, *Environ. Dev. Sustain.* (2023), <https://doi.org/10.1007/s10668-023-03981-9>.
- S. Wongsakulphasatch, K. Sukchoknamchai, N. Suthapot, W. Praikaw, C. Chaisuk, W. Kiatkittipong, N. Laosiripojana, S. Assabumrungrat, Effect of calcium precursors on pelletized property and cyclic CO₂ capture performance, *MATEC Web Conf.* 192 (2018) 7–10, <https://doi.org/10.1051/mateconf/201819203057>.
- J. Akhtar, N. Saidina Amin, A review on operating parameters for optimum liquid oil yield in biomass pyrolysis, *Renew. Sustain. Energy Rev.* 16 (2012) 5101–5109, <https://doi.org/10.1016/j.rser.2012.05.033>.
- S. Mariyam, M. Shabbaz, T. Al-Ansari, H.R. Mackey, G. McKay, A critical review on co-gasification and co-pyrolysis for gas production, *Renew. Sustain. Energy Rev.* 161 (2022) 112349, <https://doi.org/10.1016/j.rser.2022.112349>.
- W. Li, H. Huang, Q. Wang, Z. Zhang, Protection of pyrolysis gases combustion against charring materials' surface ablation, *Int. J. Heat Mass Tran.* 102 (2016) 10–17, <https://doi.org/10.1016/j.ijheatmasstransfer.2016.05.143>.
- D. Hong, Z. Cao, X. Guo, Effect of calcium on the secondary reactions of tar from Zhundong coal pyrolysis: a molecular dynamics simulation using ReaxFF, *J. Anal. Appl. Pyrolysis* 137 (2019) 246–252, <https://doi.org/10.1016/j.jaap.2018.11.033>.
- H.J. Park, H.S. Heo, Y.K. Park, J.H. Yim, J.K. Jeon, J. Park, C. Ryu, S.S. Kim, Clean bio-oil production from fast pyrolysis of sewage sludge: effects of reaction conditions and metal oxide catalysts, *Bioresour. Technol.* 101 (2010) S83–S85, <https://doi.org/10.1016/j.biortech.2009.06.103>.
- E.E. Kwon, T. Lee, Y.S. Ok, D.C.W. Tsang, C. Park, J. Lee, Effects of calcium carbonate on pyrolysis of sewage sludge, *Energy* 153 (2018) 726–731, <https://doi.org/10.1016/j.energy.2018.04.100>.
- L. Ding, Z. Zhou, Q. Guo, W. Huo, G. Yu, Catalytic effects of Na₂CO₃ additive on coal pyrolysis and gasification, *Fuel* 142 (2015) 134–144, <https://doi.org/10.1016/j.fuel.2014.11.010>.
- Z. Wang, J. Tan, Y. He, Y. Yuan, L. Liu, Y. Zhu, K. Cen, Catalytic effect of metal chloride additives on the volatile gas release characteristics for high-temperature lignite pyrolysis, *Energy Fuels* 33 (2019) 9437–9445, <https://doi.org/10.1021/acs.energyfuels.9b01342>.
- J. Yongbin, H. Jiejie, W. Yang, Effects of calcium oxide on the cracking of coal tar in the freeboard of a fluidized bed, *Energy Fuels* 18 (2004) 1625–1632, <https://doi.org/10.1021/ef034077v>.
- L. Liu, S. Kumar, Z. Wang, Y. He, J. Liu, K. Cen, Catalytic effect of metal chlorides on coal pyrolysis and gasification part I. Combined TG-FTIR study for coal pyrolysis, *Thermochim. Acta* 655 (2017) 331–336, <https://doi.org/10.1016/j.tca.2017.07.007>.
- L. Zhang, B. Zhang, Z. Yang, Y. Yan, Pyrolysis behavior of biomass with different Ca-based additives, *RSC Adv.* 4 (2014) 39145–39155, <https://doi.org/10.1039/c4ra04865b>.
- X. Chen, Y. Chen, H. Yang, W. Chen, X. Wang, H. Chen, Fast pyrolysis of cotton stalk biomass using calcium oxide, *Bioresour. Technol.* 233 (2017) 15–20, <https://doi.org/10.1016/j.biortech.2017.02.070>.
- Z. Wang, F. Wang, J. Cao, J. Wang, Pyrolysis of pine wood in a slowly heating fixed-bed reactor: potassium carbonate versus calcium hydroxide as a catalyst, *Fuel Process. Technol.* 91 (2010) 942–950, <https://doi.org/10.1016/j.fuproc.2009.09.015>.
- M. Auta, L.M. Ern, B.H. Hameed, Fixed-bed catalytic and non-catalytic empty fruit bunch biomass pyrolysis, *J. Anal. Appl. Pyrolysis* 107 (2014) 67–72, <https://doi.org/10.1016/j.jaap.2014.02.004>.
- Q. Li, A. Faramarzi, S. Zhang, Y. Wang, X. Hu, M. Gholizadeh, Progress in catalytic pyrolysis of municipal solid waste, *Energy Convers. Manag.* 226 (2020) 113525, <https://doi.org/10.1016/j.enconman.2020.113525>.
- S. Kumar, R. Srivastava, J. Koh, Utilization of zeolites as CO₂ capturing agents: advances and future perspectives, *J. CO₂ Util.* 41 (2020) 101251, <https://doi.org/10.1016/j.jcou.2020.101251>.
- I. Soltani, E. Berrich, M. Romdhane, A. Fethi, Heating rate and ZSM-5 catalyst effects on date palm (*Phoenix dactylifera* L.) stones pyrolysis: thermogravimetric

- analysis, production and characterization of syngases and bio-oils, *J. Energy Inst.* 110 (2023) 101295, <https://doi.org/10.1016/j.joei.2023.101295>.
- [41] C. Liu, H. Wang, A.M. Karim, J. Sun, Y. Wang, Catalytic fast pyrolysis of lignocellulosic biomass, *Chem. Soc. Rev.* 43 (2014) 7594–7623, <https://doi.org/10.1039/C3CS60414D>.
- [42] J. McNutt, Q. Sophia He, Spent coffee grounds: a review on current utilization, *J. Ind. Eng. Chem.* 71 (2019) 78–88, <https://doi.org/10.1016/j.jiec.2018.11.054>.
- [43] L. Chen, Z. Yu, J. Liang, Y. Liao, X. Ma, Co-pyrolysis of *Chlorella vulgaris* and kitchen waste with different additives using TG-FTIR and Py-GC/MS, *Energy Convers. Manag.* 177 (2018) 582–591, <https://doi.org/10.1016/j.enconman.2018.10.010>.
- [44] K. Ding, Z. Zhong, J. Wang, B. Zhang, L. Fan, S. Liu, Y. Wang, Y. Liu, D. Zhong, P. Chen, R. Ruan, Improving hydrocarbon yield from catalytic fast co-pyrolysis of hemicellulose and plastic in the dual-catalyst bed of CaO and HZSM-5, *Bioresour. Technol.* 261 (2018) 86–92, <https://doi.org/10.1016/j.biortech.2018.03.138>.
- [45] J. Wang, Z. Zhong, K. Ding, B. Zhang, A. Deng, M. Min, P. Chen, R. Ruan, Co-pyrolysis of bamboo residual with waste tire over dual catalytic stage of CaO and co-modified HZSM-5, *Energy* 133 (2017) 90–98, <https://doi.org/10.1016/j.energy.2017.05.146>.
- [46] S. Zhang, H. Zhang, X. Liu, S. Zhu, L. Hu, Q. Zhang, Upgrading of bio-oil from catalytic pyrolysis of pretreated rice husk over Fe-modified ZSM-5 zeolite catalyst, *Fuel Process. Technol.* 175 (2018) 17–25, <https://doi.org/10.1016/j.fuproc.2018.03.002>.
- [47] Nishu, R. Liu, M.M. Rahman, M. Sarker, M. Chai, C. Li, J. Cai, A review on the catalytic pyrolysis of biomass for the bio-oil production with ZSM-5: focus on structure, *Fuel Process. Technol.* 199 (2020) 106301, <https://doi.org/10.1016/j.fuproc.2019.106301>.
- [48] T. Deng, Z. Yu, X. Zhang, Y. Zhang, L. Chen, X. Ma, Catalytic co-pyrolysis behaviors and kinetics of camellia shell and take-out solid waste using pyrolyzer – gas chromatography/mass spectrometry and thermogravimetric analyzer, *Bioresour. Technol.* 297 (2020) 122419, <https://doi.org/10.1016/j.biortech.2019.122419>.
- [49] L.-Y. Zhang, J.-P. Cao, X.-Y. Ren, X.-B. Feng, J.-X. Wang, Z.-M. He, T.-L. Liu, Z. Yang, X.-Y. Zhao, H.-C. Bai, Catalytic upgrading of cellulose pyrolysis volatiles over Ce modified hierarchical ZSM-5 zeolite: insight into the effect of acid properties on light aromatics and catalyst stability, *Ind. Eng. Chem. Res.* 61 (2022) 287–298, <https://doi.org/10.1021/acs.iecr.1c04081>.
- [50] M.-Y. Hua, B.-X. Li, Co-pyrolysis characteristics of the sugarcane bagasse and *Enteromorpha prolifera*, *Energy Convers. Manag.* 120 (2016) 238–246, <https://doi.org/10.1016/j.enconman.2016.04.072>.
- [51] W. Chen, M. Ye, M. Li, B. Xi, J. Hou, X. Qi, J. Zhang, Y. Wei, F. Meng, Characteristics, kinetics and product distribution on pyrolysis process for waste wind turbine blades, *J. Anal. Appl. Pyrolysis* 169 (2023) 105859, <https://doi.org/10.1016/j.jaap.2023.105859>.
- [52] M.A. Charitopoulou, S.D. Stefanidis, A.A. Lappas, D.S. Achilias, Catalytic pyrolysis of polymers with brominated flame-retardants originating in waste electric and electronic equipment (WEEE) using various catalysts, *Sustain. Chem. Pharm.* 26 (2022) 100612, <https://doi.org/10.1016/j.scp.2022.100612>.
- [53] J.I. Osayi, P. Osifo, Utilization of synthesized zeolite for improved properties of pyrolytic oil derived from used tire, *Int. J. Chem. Eng.* 2019 (2019) 6149189, <https://doi.org/10.1155/2019/6149189>.
- [54] M. Chen, S. Zhang, Y. Su, X. Niu, S. Zhu, X. Liu, Catalytic co-pyrolysis of food waste digestate and corn husk with CaO catalyst for upgrading bio-oil, *Renew. Energy* 186 (2022) 105–114, <https://doi.org/10.1016/j.renene.2021.12.139>.
- [55] P.T. Williams, N. Nugranad, Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks, *Energy* 25 (2000) 493–513, [https://doi.org/10.1016/S0360-5442\(00\)00009-8](https://doi.org/10.1016/S0360-5442(00)00009-8).
- [56] F.J. Sánchez-Borrogo, N. García-Criado, J.F. García-Martín, P. Álvarez-Mateos, Determination of the composition of bio-oils from the pyrolysis of orange waste and orange pruning and use of biochars for the removal of sulphur from waste cooking oils, *Agronomy* 12 (2022), <https://doi.org/10.3390/agronomy12020309>.
- [57] M. Arabiourrutia, G. Bensidhom, M. Bolaños, A.B.H. Trabelsi, M. Olazar, Catalytic pyrolysis of date palm seeds on HZSM-5 and dolomite in a pyroprobe reactor in line with GC/MS, *Biomass Convers. Biorefinery* (2022), <https://doi.org/10.1007/s13399-022-02493-2>.
- [58] M.S. Abu Bakar, A. Ahmed, D.M. Jeffery, S. Hidayat, R.S. Sukri, T.M.I. Mahlia, F. Jamil, M.S. Khurruam, A. Inayat, S. Moogi, Y.-K. Park, Pyrolysis of solid waste residues from Lemon Myrtle essential oils extraction for bio-oil production, *Bioresour. Technol.* 318 (2020) 123913, <https://doi.org/10.1016/j.biortech.2020.123913>.
- [59] M.M. Hossain, I.M. Scott, F. Berruti, C. Briens, Application of novel pyrolysis reactor technology to concentrate bio-oil components with antioxidant activity from tobacco, tomato and coffee ground biomass, *Waste and Biomass Valorization* 9 (2018) 1607–1617, <https://doi.org/10.1007/s12649-017-9943-8>.
- [60] J.A. Oyeibanji, O.S.I. Fayomi, O.I. Oyeniyi, P.G. Akor, S.T. Ajayi, Physico-chemical analysis of pyrolyzed bio-oil from *Lophira alata* (ironwood) wood, *J. Environ. Pollut. Manag.* 4 (2022) 101.
- [61] T.E. Odetoeye, K.R. Onifade, M.S. AbuBakar, J.O. Titiloye, Pyrolysis of Parinari polyandra Benth fruit shell for bio-oil production, *Biofuel Res. J.* 1 (2014) 85–90, <https://doi.org/10.18331/BRJ2015.1.3.5>.
- [62] Y. Zhang, H. Cui, W. Yi, F. Song, P. Zhao, L. Wang, J. Cui, Highly effective decarboxylation of the carboxylic acids in fast pyrolysis oil of rice husk towards ketones using CaCO₃ as a recyclable agent, *Biomass Bioenergy* 102 (2017) 13–22, <https://doi.org/10.1016/j.biombioe.2017.04.004>.
- [63] W. Zuo, B. Jin, Y. Huang, Y. Sun, Thermal decomposition of three kinds of sludge by TG–MS and PY–GC/MS, *J. Therm. Anal. Calorim.* 121 (2015) 1297–1307, <https://doi.org/10.1007/s10973-015-4651-8>.
- [64] H.B.T.-R.M. B.S. Greim, Bisphenol A, Elsevier, 2023, <https://doi.org/10.1016/B978-0-12-824315-2.00461-9>.
- [65] P.R. Patwardhan, J.A. Satrio, R.C. Brown, B.H. Shanks, Product distribution from fast pyrolysis of glucose-based carbohydrates, *J. Anal. Appl. Pyrolysis* 86 (2009) 323–330, <https://doi.org/10.1016/j.jaap.2009.08.007>.
- [66] K. Wu, H. Wu, H. Zhang, B. Zhang, C. Wen, C. Hu, C. Liu, Q. Liu, Enhancing levoglucosan production from waste biomass pyrolysis by Fenton pretreatment, *Waste Manag.* 108 (2020) 70–77, <https://doi.org/10.1016/j.wasman.2020.04.023>.
- [67] X. Hu, Y. Pang, H. Mu, X. Meng, X. Wang, Z. Wang, J. Yan, Synthesis and gas separation performances of intrinsically microporous polyimides based on 4-methylcatechol-derived monomers, *J. Membr. Sci.* 620 (2021) 118825, <https://doi.org/10.1016/j.memsci.2020.118825>.
- [68] X. Liu, R. Cui, J. Shi, Q. Jiang, J. Gao, Z. Wang, X. Li, Separation and microencapsulation of antibacterial compounds from wood vinegar, *Process Biochem.* 110 (2021) 275–281, <https://doi.org/10.1016/j.procbio.2021.08.020>.
- [69] Z. Li, Z. Zhang, L. Wu, H. Zhang, Z. Wang, Characterization of five kinds of wood vinegar obtained from agricultural and forestry wastes and identification of major antioxidants in wood vinegar, *Chem. Res. Chin. Univ.* 35 (2019) 12–20, <https://doi.org/10.1007/s40242-019-8207-5>.
- [70] R. Urrialde, Caffeine, B.B.T.-E. of H.N., in: Fourth E. Caballero (Ed.), Academic Press, 2023, <https://doi.org/10.1016/B978-0-12-821848-8.00062-7>.
- [71] A. Padmanaban, G. Murugadoss, N. Venkatesh, S. Hazra, M. Rajesh Kumar, R. Tamilselvi, P. Sakthivel, Electrochemical determination of harmful catechol and rapid decolorization of textile dyes using ceria and tin doped ZnO nanoparticles, *J. Environ. Chem. Eng.* 9 (2021) 105976, <https://doi.org/10.1016/j.jece.2021.105976>.
- [72] National Center for Biotechnology Information, PubChem compound summary for CID 985, palmitic acid. <https://pubchem.ncbi.nlm.nih.gov/compound/Palmitic-acid>, 2023. (Accessed 22 August 2023).
- [73] M. Ataei, A.S. Maghsoudi, in: B.S. Hassani (Ed.), S.B.T.-R.M., Phenol, Elsevier, 2022, <https://doi.org/10.1016/B978-0-12-824315-2.00168-8>.
- [74] N. Chen, J. Ren, Z. Ye, Q. Xu, J. Liu, S. Sun, Kinetics of coffee industrial residue pyrolysis using distributed activation energy model and components separation of bio-oil by sequencing temperature-raising pyrolysis, *Bioresour. Technol.* 221 (2016) 534–540, <https://doi.org/10.1016/j.biortech.2016.09.062>.
- [75] D.S. Fardhyanti, A. Damayanti, N.A.C. Imani, A. Mulyaningtyas, N. K. Setyawardianingsih, A.L. Andhini, Phenolic compound separation from bio-oil produced from pyrolysis of coffee shell at 700 °C using liquid-liquid extraction, in: *J. Phys. Conf. Ser.*, IOP Publishing, 2020 12002.
- [76] J. Wang, Q. Wei, J. Zheng, M. Zhu, Effect of pyrolysis conditions on levoglucosan yield from cotton straw and optimization of levoglucosan extraction from bio-oil, *J. Anal. Appl. Pyrolysis* 122 (2016) 294–303, <https://doi.org/10.1016/j.jaap.2016.09.013>.
- [77] A. Teella, G.W. Huber, D.M. Ford, Separation of acetic acid from the aqueous fraction of fast pyrolysis bio-oils using nanofiltration and reverse osmosis membranes, *J. Membr. Sci.* 378 (2011) 495–502, <https://doi.org/10.1016/j.memsci.2011.05.036>.
- [78] D.P. Gamliel, S. Du, G.M. Bollas, J.A. Valla, Investigation of in situ and ex situ catalytic pyrolysis of miscanthus × giganteus using a PyGC–MS microsystem and comparison with a bench-scale spouted-bed reactor, *Bioresour. Technol.* 191 (2015) 187–196, <https://doi.org/10.1016/j.biortech.2015.04.129>.
- [79] Y. Zhou, Z. Chen, H. Gong, L. Chen, H. Yu, Study on the feasibility of using monolithic catalyst in the in-situ catalytic biomass pyrolysis for syngas production, *Waste Manag.* 120 (2021) 10–15, <https://doi.org/10.1016/j.wasman.2020.11.016>.
- [80] K. Ding, Z. Zhong, J. Wang, B. Zhang, L. Fan, S. Liu, Y. Wang, Y. Liu, D. Zhong, P. Chen, R. Ruan, Improving hydrocarbon yield from catalytic fast co-pyrolysis of hemicellulose and plastic in the dual-catalyst bed of CaO and HZSM-5, *Bioresour. Technol.* 261 (2018) 86–92, <https://doi.org/10.1016/j.biortech.2018.03.138>.
- [81] Z. Yu, M. Dai, M. Huang, S. Fang, J. Xu, Y. Lin, X. Ma, Catalytic characteristics of the fast pyrolysis of microalgae over oil shale: analytical Py-GC/MS study, *Renew. Energy* 125 (2018) 465–471, <https://doi.org/10.1016/j.renene.2018.02.136>.
- [82] V. Chaerusan, A.C.A. Zahra, A. Anniwaer, P. Zhang, N. Chaihad, J. Rizkiana, K. Kusakabe, Y. Kasai, A. Abudula, G. Guan, Catalytic upgrading of bio-oils derived from terrestrial and marine biomass over various types of zeolites, *J. Anal. Appl. Pyrolysis* 168 (2022) 105735, <https://doi.org/10.1016/j.jaap.2022.105735>.