Aromatic hydrocarbons rich bio-oil production from Miscanthus pyrolysis by coupling torrefaction and MoO₃/ZSM-5 dual catalysis process

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A B S T R A C T

The valorization of Miscanthus pyrolysis by coupling torrefaction and MoO₃/ZSM-5 dual catalysis process was studied to generate the aromatic hydrocarbons rich bio-oil, biochar, and combustible gas. With the optimal conditions of torrefied Miscanthus at 280 °C, MoO₃/ZSM-5 catalysis process converted 24.17 % bio-oil, 30.27 % biochar, and 45.56 % gas. The coupled system accessed bio-oil phase deoxygenation by reducing the oxygen-containing compound content to 6.27 %. The aromatic yield reached 91.38 %, with an outstanding benzene, toluene and xylene (BTX) selectivity of 52.24 %. Isolating investigations revealed that torrefaction declined the oxygen content of Miscanthus to 5.24 %, increasing their calorific value and promoting subsequent catalytic pyrolysis through deoxygenation. When only using the ZSM-5 catalyst, the increase in torrefaction temperature enhanced aromatic hydrocarbon compounds conversion in the bio-oil, leading to a boost in their content from 55.01 % to 75.97 %. Correspondingly, MoO₃ promoted deoxygenation, decreased the ketone content from 40.4 % to 21.92 %, and inhibited the generation of aldehydes. The combination of MoO₃ and ZSM-5 with torrefaction delivered a superimposed effect on yielding aromatic hydrocarbons and BTX, which allowed a promising product upgrading method for obtaining high-quality bio-oil.

1. Introduction

Biomass is the potential to produce sustainable fuels and chemicals as a renewable resource, making it a promising solution within the increasingly pressing global need for alternative sustainable energy sources (Huber et al., 2006). As an abundant lignocellulosic biomass, Miscanthus has garnered attention as a sustainable energy source due to its rapid growth, capacity to thrive in diverse environmental conditions, high productivity, and high calorific value (Liu et al., 2021; Tian et al., 2020). Numerous research studies have employed Miscanthus as a pyrolytic feedstock in order to directly convert it into liquid fuels via fast pyrolysis, providing evidence of its promise as a viable alternative to fossil fuels. The resulting bio-oil the process comprises a range of compounds, including aliphatic and aromatic hydrocarbons. However, despite the promising prospects of bio-oil, its extensive utilization as a fuel source has been constrained by various drawbacks, including its high acidity, oxygen content, suboptimal low thermal stability, and comparatively lower calorific value (Zhu et al., 2019). Feedstock pretreatment and the employment of catalysts are acknowledged as crucial

factors in improving the feasibility of bio-oil as a renewable energy source, aiming to overcome its inherent limitations (Kan et al., 2020; Zheng et al., 2020). It considers two aspects of bio-oil upgrading: removing oxygen from raw biomass to reduce condensation during pyrolysis and compressing pyrolytic volatile matter through catalytic pyrolysis to produce high-value substances (Khan et al., 2019).

Torrefaction involves subjecting biomass to heat in an oxygen-free environment, typically at temperatures between 200 and 300 °C, to remove moisture and volatile compounds. This thermal treatment results in a more stable and energy-dense material. This process enables removing volatilizable polysaccharide and lignin content to a small percentage for creating an easy handling process followed (Xin et al., 2018). Many researches have reported findings regarding the advantages of pretreating biomass through torrefaction, which confirmed that torrefaction removed oxygen from lignocellulose in the primary forms (Cen et al., 2021; Tian et al., 2022). Wang et al. (2017a) made significant observation that torrefaction led to a substantive drop in the oxygen content of cellulose and hemicellulose as well as O/C ratio. In the sight of the reaction mechanism, biomass torrefaction pretreatment reduces

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oxygenated chemicals (e.g., acids, ketones, aldehydes, furans, etc.) generated from following pyrolysis, leading to an improved quality of bio-oil derived from biomass pyrolysis (Chen et al., 2017). Accordingly, the selectivity of hydrocarbons during pyrolysis elevates during the torrefaction process, which enhances the bio-oil quality. Compared to virgin pine, torrefed pine was found to produce a significantly greater yield of hydrocarbons (Neupane et al., 2015).

In addition to pretreatment, the utilization of catalytic pyrolysis presents a practical approach to boost the stability, quality, and efficiency of bio-oil (Gou et al., 2017). Vapors volatilized by pyrolysis are usually brought into contact with the catalyst before condensation for initiating the catalytic upgrading procedure. Among the reaction reagents, the acid catalyst is one of the most widely used in catalytic pyrolysis. Acid-catalyzed fast pyrolysis upgrades bio-oil by accelerating chemical reactions, producing more hydrocarbons, removing oxygen-containing groups, and creating higher quality, stable products. For both bioenergy and chemical industries, the promising application of biomass lies in its conversion into valuable fuels and chemicals. The highly acidic sites in catalysts, such as ZSM-5, could significantly enhance the reaction efficiency (Wang et al., 2016; Nishu et al., 2020). While ZSM-5 possesses a uniform pore size and shape, making it efficient in generating aromatic hydrocarbons and olefins (Zhang et al., 2013), its microporous characteristics pose constraints on the diffusion of larger intermediate reactants (Popescu et al., 2013). A multifunctional catalytic fast pyrolysis system would be required to convert oxygenates into smaller oxygenate molecules for enhancing pyrolysis over ZSM-5 to increase the availability of reactants in the channel and yield more aromatics (Yang et al., 2018).

Metal oxide is another group of catalysts with the capacity and easy accessibility to promote pyrolysis, producing valuable bio-oil by removing oxygen-containing groups, thus reducing the molecular size (Ahmed et al., 2020; Fan et al., 2017; Stefanidis et al., 2016). Stefanidis et al. (2016) demonstrated the high efficacy of MgO as a catalyst in reducing the oxygen content in bio-oil, exhibiting catalytic performance comparable to or surpassing that of acidic ZSM-5. In their Py-GC/MS analysis study, Zhang et al. (2022) discovered that incorporating CaO or MgO into ZSM-5 resulted in a notable enhancement of aromatic hydrocarbon conversion.

Both catalytic pyrolysis and biomass torrefaction pretreatment significantly promoted bio-oil upgrading from the evidence offered by earlier research. However, research on synergistic affecting bio-oil upgrading is still rare. Since these approaches underwent distinct mechanisms, cooperating may boost aromatic hydrocarbon conversion by uptaking both advantages. In our previous studies, within a pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) analysis platform, the integration of MoO₃/ZSM-5 dual catalyst and torrefaction pretreatment were examined to pursue boosting hydrocarbon in bio-oil (Tian et al., 2022). Results indicate that torrefaction pretreatment integrated with catalytic pyrolysis boosted aromatic hydrocarbon products remarkably. According to the hypothesis confirmed, this work further elucidates the impacts of varying torrefaction temperatures and dual-catalyst systems in the process of catalytic pyrolysis to generate aromatic from Miscanthus. Catalytic or non-catalytic pyrolysis investigations were undertaken at various temperatures to optimize the pyrolysis temperature, with the focus on examining the impacts of various torrefaction temperatures and catalysts, including ZSM-5, MoO₃, and MoO₃/ZSM-5, on the phase products, the composition and output of bio-oil. The results of this research offer vital perspectives on advancing biomass pyrolysis industry in a sustainable and efficient manner.

2. Materials and methods

2.1. Materials

The study employed Miscanthus sourced from a farm in Changsha,

Hunan Province, China, which underwent pretreatment involving air-drying and crushing to particles of 75 μm in size applying a 200-screen mesh sieve prior to experimentation. The study investigated catalyzed pyrolysis using two catalysts, ZSM-5 and MoO₃. The ZSM-5 catalyst, a zeolite with a large surface area of 394.5 m²/g, a silica to alumina ratio of 30, a pore capacity of 0.28 nm and a pore size of 2.8 nm, was employed during the pyrolysis process. The MoO₃ was purchased from Sigma Aldrich and crushed into particles less than 75 μm in size before calcination and drying. Both catalysts were subjected to a calcination process in a muffle furnace to eliminate any residual template materials or humidity in the channels. To ensure that the ZSM-5 and MoO₃ catalysts were completely dry and free of any moisture, they were placed in a furnace at 105 °C overnight before conducting the catalytic pyrolysis experiments.

2.2. Torrefaction pretreatment

Before the Miscanthus torrefaction was processed in a horizontal tubular furnace, an inert environment was established by purging nitrogen at a rate of 300 mL/min lasting 30 min. Subsequently, the horizontal tube furnace was raised to a predetermined temperature (220, 250, or 280 °C). Once it was in a stable temperature range, 10 g Miscanthus were delivered into the heating zone through a quartz boat to undertake a 30-minute torrefaction process. The samples used in the study were identified as RM (raw Miscanthus) and TM-220, TM-250, and TM-280 (torrefed Miscanthus samples at different temperatures).

2.3. Pyrolysis experiments

This study conducted catalytic pyrolysis experiments on Miscanthus employing a fixed bed reactor. The system included carrier gas supply, pyrolysis, condensation, liquid collection, and gas analysis components. The condensation unit consisted of a U-shaped chilling tube immersed in liquid nitrogen as a cooling medium. A following portable infrared gas analyzer (Photon) conducted the obtained gas compositions.

In a running, the system was purged by nitrogen gas with a 200 mL/min flow rate for 30 min before each experiment to create an inert situation. The catalyst arrangement and blending ratio followed the previous work (Tian et al., 2022). Each experiment kept the weight of the pyrolyzed Miscanthus at constant 3 g. For ZSM-5 catalytic fast pyrolysis exclusively, the ZSM-5/Miscanthus mass ratio was 3:1, and the separation was achieved through a silica wool layer. When only with MoO₃ pyrolysis, the MoO₃/Miscanthus mass ratio was 2:1 and mixed biomass and MoO₃. During the dual catalyst pyrolysis process, the ZSM-5/Miscanthus/MoO₃ mass ratio was 3:1:2, the Miscanthus sample are mixed with MoO₃, and the ZSM-5 catalyst is placed separately, separated by an asbestos layer. The process of pyrolysis involved heating the fixed bed to a predetermined temperature, delivering the quartz crucible containing the sample to the reactor, and then carrying it out for 15 min.

2.4. Analysis and test methods

The composition of ash, volatile matter (VM), and fixed carbon (FC) in Miscanthus was determined using proximate analysis and industrial analysis conducted with the Changsha China Electric Furnace Factory SX-4–10, following the GB/T28731–2012 standard method. The calorific value of the Miscanthus samples was calculated utilizing the Dulong formula, as demonstrated in Eq. (1).

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \qquad (1)$$

The FTIR method was employed to examine the surface functional groups of Miscanthus samples. The sample discs were made by mixing Miscanthus samples with KBr at a ratio of 1:100, covering the wavelength range of 650–4000 cm^{-1} with a resolution of 4 cm^{-1}. The chemical components of the resulting bio-oil were assessed utilizing an Agilent 7890B-5977A GC-MS instrument. The GC-MS injector

temperature was adjusted to 275 °C, with a carrier gas spill rate of 1:50, using high-purity helium. The GC column oven was programmed to undergo a starting from 40 °C and gradually reaching 270 °C within 5 min. All compounds in the samples were accurately characterized using the NIST library, and their concentrations were determined by measuring the peak areas in the chromatographic analysis. The relative selectivity of the benzene, toluene, and xylene (BTX) compounds was calculated using the specific equation Eq. (2).

$$\text{Selectivity of BTX} = \frac{P\text{eak area of BTX}}{\text{Total peak area of aromatic hydrocarbon}} \times 100\%$$

(2)

3. Results and discussion

3.1. Effect of the torrefaction on non-catalytic pyrolysis

Fig. 1(a) displays the experimental outcomes obtained from the pyrolysis of the TM-280 sample at a range of temperatures 450–650 °C (450, 500, 550, 600, or 650 °C). The experimental results revealed a positive association between the pyrolysis temperature and gas yield, with a simultaneous inverse correlation observed in biochar yield. Furthermore, with respect to non-catalytic fast pyrolysis, the oil phase exhibited an initial increase within the temperature span of 450–550 °C. The selection of 550 °C as the optimal pyrolysis temperature was based on the highest bio-oil yield achieved, which reached 29.23 %. This notable yield was attributed to the secondary decomposition of volatiles at higher temperatures, resulting in increased gas yield but reduced bio-oil output. Thus, 550 °C was established as the preferred temperature for maximizing the oil phase with the high yield and quality of on large-scale. Fig. 1(b) illustrates the impacts of distinct torrefaction temperatures on the pyrolysis products of Miscanthus samples. The bio-oil yield exhibited a significant reduction from 44.97 % to 29.23 %. Among the lignocellulosic compositions, lignin and cellulose underwent different pathways during the pyrolysis, which favored the yield of liquid and biochar, respectively (Chutia et al., 2014; Tian et al., 2021). The high thermal stability of lignin prevented its decomposition during the torrefaction of Miscanthus, resulting in lignin residue remaining in the biomass. Furthermore, a temperature rise may have caused further cross-linking of biomass components, resulting in an intensified carbonization of the torrefied Miscanthus, which may even boost producing biochar (Kaveh et al., 2020). Apart from it, the volatiles lost through torrefaction caused a decline in the collectability of the pyrolyzed compositions, which led to the subsequent pyrolysis process reducing volatilizable matter, thus lowering the content of bio-oil (Chen et al., 2014).

Apart from the pyrolysis mechanism, the tendency of changes in the three-phase products with torrefaction temperature change was also related to the feedstock composition. As shown in the previous work, the torrefaction temperature exerted a noticeable influence on the nature of Miscanthus, as higher temperatures triggered a decline in the amount of volatile matter and an elevation in the levels of ash and fixed carbon. It explains the growth of biochar and the reduction of bio-oil. The conventional bio-oil was predominantly composed of a significant quantity of volatile matter. Torrefaction enabled light matter removal and ash and fix-carbon accumulation in the biomass, resulting in a reduced the oil phase ratio and elevated the biochar. The previous work observed the oxygen decrease in the feedstock with the growth torrefaction temperature. But the gas content showed an inapparent trend with the pyrolysis temperature. It was confirmed that oxygen-containing functional group decomposition leads to converting water and carbon dioxide. The stable gas trend indicated gaseous compositions mainly came from the non-volatile matter decomposition rather than the torrefaction removed parts.

Fig. 2(a) illustrates the bio-oil composition resulting from Miscanthus non-catalytic pyrolysis at different torrefaction temperatures. The product distribution of bio-oil underwent a significant change as the torrefaction temperature rose, leading to a considerable decline in the presence of oxygenates. The relative content of aliphatic and phenolic compounds was observed to increase, while oxygenated compounds such as acids, ketones, and furans decreased, in torrefied Miscanthus pyrolysis compared to the original Miscanthus pyrolysis. The relative content of acid steadily declined with the torrefaction, which dropped significantly from 10.31 % of RM to 5.24 % of TM-280, consistent with previous Py-GC/MS findings and similar investigations (Chen et al., 2015). Enhancing torrefaction temperature decreased ketones and aldehydes from 29.67 % and 13.07 % of RM to 18.99 % and 2.21 % of TM-280, respectively. It is might because the torrefaction sponsored the removal of unstable carbon and reduced the yield of ketones and aldehydes during subsequent pyrolysis. It was suggested that the breakdown of hemicellulose during pyrolysis was the reason for the low concentration of furans in bio-oil gained from torrefied Miscanthus without a catalyst (Haji Morni et al., 2021). As a target product in the bio-oil, the phenol amount boosted progressively with the raised terrifying temperature, going from 24.83 % (in RM) to 33.39 % (in TM-280). This reduction could be explained as the phenolics conversion was mainly from the ether bonds broken and demethoxylation within the structural changes of the lignin. The concentration of aliphatic compounds increased significantly with increasing torrefaction temperature from 3.15 % of RM to 21.54 % of TM-280.
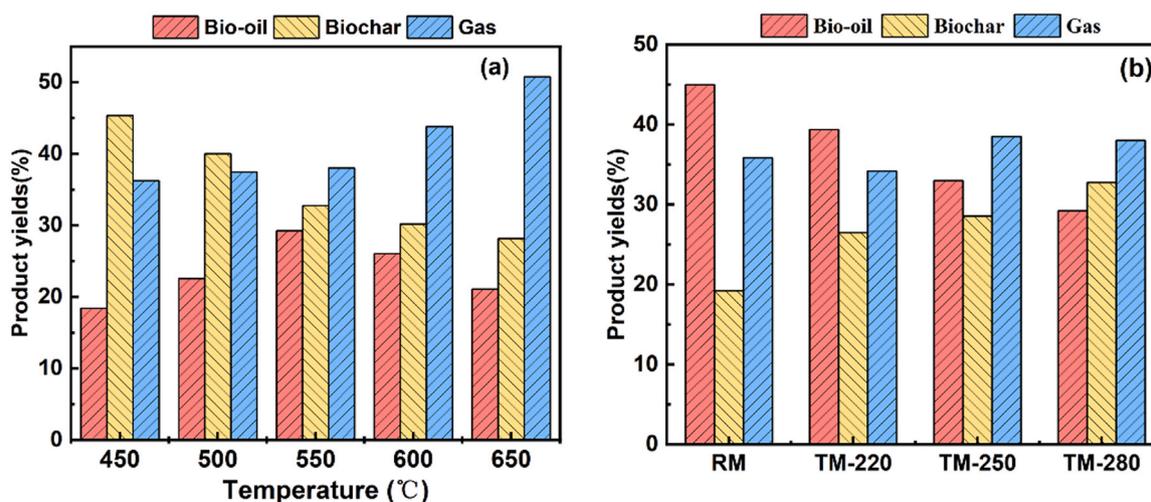
Fig. 1. Three-phase product yields within different pyrolysis temperatures (a) and torrefaction temperatures (b).
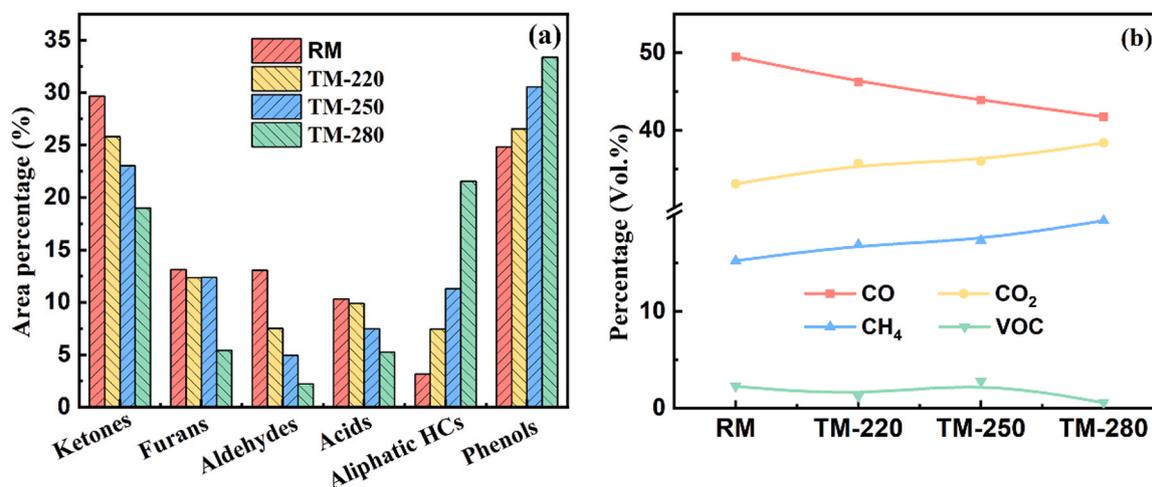
Fig. 2. Non-catalytic pyrolysis produced bio-oil components (a) and gas components (b) with different torrefaction temperatures.

Previous FT-IR spectral research cross-validated the above observation by qualitatively analyzing functional groups and structures (Tian et al., 2022). With the raised torrefaction temperature, the intensity of peaks associated with hydroxyl functional groups in the infrared spectrum of the sample decreased, indicating that dehydration reactions occurred during the torrefaction process. It proven the release of water and other volatile compounds in the biomass at higher temperatures. Similarly, the intensity of peaks regarding the stretching vibrations of carboxyl and carbonyl groups in the IR spectra of the samples decreased with the boosting torrefaction. This trend elucidated that torrefaction causes the breakdown of functional groups containing oxygen through thermal degradation, and the samples underwent decarboxylation and decarbonylation processes. The C-O-C vibration peak in torrefed Miscanthus samples decreased until undetectable at 280 °C with the boost in torrefaction temperature. This phenomenon came from polymer depolymerization, ring cleavage, fragmentation, and polycondensation reactions (Zheng et al., 2015). Furthermore, the bending vibration intensity of methoxyl C-O esters and lignin β-O-4 linkages decreased with rising temperature implying the gradual breakdown of carbohydrates during torrefaction.

3.2. Effect of torrefaction and dual catalysis process on the three-phase product composition

From Fig. 3, it was observable that the yields of the three-phase products of Miscanthus catalytic pyrolysis within various torrefaction temperatures by going through different catalysts. In the comparison of Figs. 3(a) and 1(b), introducing a catalyst during torrefaction at 280 °C triggered a notable decline in the yield of bio-oil to 27.18 % but a considerable increase in gas yield to 41.06 %. This observation provides further evidence that catalysis exerts on the pyrolysis procedure (Chen et al., 2018). The ZSM-5 catalyst initially boosted the generation of pyrolysis gas, and subsequent deoxygenation reactions within the zeolite channels facilitated the generation of aromatic hydrocarbons. Simultaneously, further cracking of primary pyrolysis gases also occurred with the lighter molecules generated. As well as the single catalyst, Fig. 3(c) illustrates the distribution of three-phase pyrolysis products obtained from torrefed Miscanthus using MoO3/ZSM-5 catalytic pyrolysis. The results demonstrate that the synergies of MoO3 and ZSM-5 catalysts decreased bio-oil yield, enhanced gas yield, and leveled off the amount of biochar formed, as seen in Fig. 3(a) and (b) with the use of only ZSM-5 and MoO3 respectively. By using synergetic catalysts, 280 °C torrefed Miscanthus outputted 24.17 % oil and 45.56 % gas, the synergistic effect of MoO3 and ZSM-5 was found to enhance the catalytic cracking of primary pyrolysis volatiles, leading to boosted gas
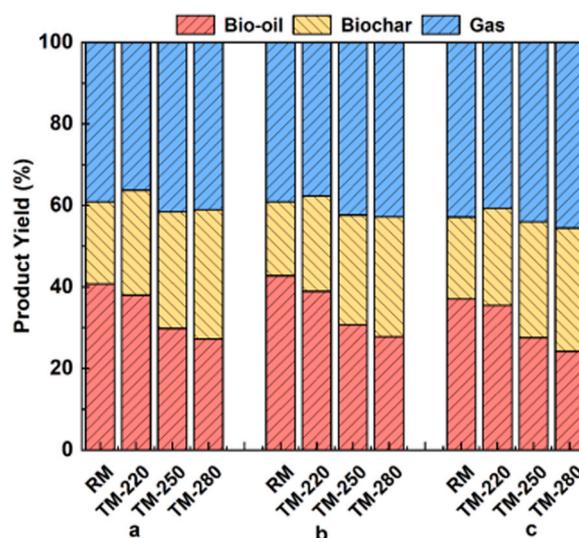
Fig. 3. The yield of three-phase products of torrefed samples within different catalysts: (a) ZSM-5 catalytic pyrolysis, (b) MoO3 catalytic pyrolysis, (c) MoO3/ZSM-5 catalytic pyrolysis.

formation.MoO3 would benefit the reactions of the initial pyrolysis vapors, including ketonization, decarboxylation, aldol condensation, demethylation, and demethoxylation, resulting in the conversion of light intermediate volatiles; the intermediates then went through the porosity of the ZSM-5 catalyst for secondary catalysis to produce CO, CO2, H2O, alkanes, olefins and aromatic hydrocarbons (Zhang et al., 2018a).

3.3. Effect of torrefaction and dual catalysis process on the bio-oil composition

From Fig. 4, it was observable that the compositions of bio-oil within various treatments were analyzed. The highest yields of ketones and aldehydes emerged when using the raw Miscanthus (RM) without a catalyst, with a total of 28.55 %. The increasing torrefaction temperature decreased the content of ketones and aldehydes. The categories with similar trends also contained furan, acids, and esters. Contrarily, the non-catalysis of TM-280 facilitated the highest amount of phenolics at 34.84 %. No hydrocarbon was detected in non-catalytic pyrolysis. The torrefaction of Miscanthus led to partial carbon oxidizing to carbon dioxide and water, while the rest forms carbonized solids. These highly

Selective (wt%)   0 [gradient] 95

	Ketone & Aldehyde					Phenolics						Furans			Acids		Ester			Hydrocarbon		Sum
	Butyraldehyde	Hydroxyacetone	1-Hydroxy-2-butanone	1,2-Cyclopentanedione	Methylcyclopentenone	phenol	O-cresol	P-methylphenol	3-methylphthalic phenol	4-Methylcatechol	Catechol	2-Hydroxytetrahydrofuran	2,4-Dimethylfuran	2,3-dihydrobenzofuran-	propionic acid	butyrate	methyl glycolate	γ-Butyrolactone	Ethylene glycol diacetate	Aromatic hydrocarbon	Aliphatic hydrocarbon	
R	2.29	6.97	7.59	5.7	6	3.37	1.55	2.25			8.47	4.27	2.4	4.98	4.46	6.45		2.45				69.2
T-220	2.1	1.4	5.03	5.54	4.36	3.51	2.03	2.58	2.18	2.25	11.78	2.58	2.94	3.63	3.45	4.45		3.485				63.3
T-250	1.77	1.72	4.02	5.54	4.56	4.05	2.16	3.17	2.82	4	14.19	4.25	2.75	1.49	2.47	3.87	0.45	4.048				67.33
T-280	1.1	1.06	3.18	3.76	3.95	6.03	2.25	2.96	2.82	4	16.78	5.4	1.45		1.92	3.49	1.19	4.29				65.63
R-M		4.06	4.18	5.45	3.41	6.49	3.35	3.24	1.26		1.38	4.48	2.35	6.18	2.56	5.6	2.44		3.13		2.4	61.96
T-220-M		2.4	2.36	5.06	2.49	7.55	3.25	5.45	2.34	0.52	2.75	3.6		4.72	3.66	3.05	3.77	2.75	3.18		5	63.9
T-250-M		1.14	2.06	5.79	2.49	6.87	2.22	4.83	3.48	0.87	3.57	3.85		2.38	1.5	1.94	4.09	1.28	3.28		9.73	61.37
T-280-M		1.04		4.36	1.39	6.32	3.54	5.26	3.65	1.36	2.62	3.84		1.26	2.71	2.33	4.68	2.34	3.34		15.94	65.98
R-Z		1.35	1.91	5.17		3.37	1.83					2.74			1.73			1.79		45.65	9.36	74.9
T-220-Z		1.15				3.9	2.16					1.48			0.3			1.07		48.75	12.89	71.7
T-250-Z				1.09		1.28	1.45					1.04			0.89			0.45		51.91	18.84	76.95
T-280-Z						1.42	1.92					1.02			0.41					54.65	24.92	84.34
R+Z/M		0.54			1.23	3.24	2.45					2.11			0.56					69.66	9.68	89.47
T-220-Z/M						2.45	1.14					1.45								70.98	12.74	88.76
T-250-Z/M						1.454														88.59	2	92.04
T-280-Z/M						1.11														91.38	2.36	94.85

Fig. 4. Bio-oil-composition analysis within different conditions treated. (Raw Miscanthus was abbreviated as R, MoO_3 was M, ZSM-5 was Z, and TM-220, 250, and 280 were the torrefaction temperature).

carbonated solids have excellent chemical stability and acid resistance. Additionally, ketones and aldehydes, with high reactivity properties, can result in the instability of the pyrolysis oil through polymerization and cross-linking reactions (Kethobile et al., 2020). Torrefaction pre-treatment, therefore, facilitated lignocellulose de-carbonylation reactions, thus reducing the output of ketones and aldehydes.

In opposite to non-catalytic pyrolysis, MoO_3 catalytic pyrolysis significantly reduced the relative phenol content and less changed with the torrefaction temperature. For the Miscanthus torrefied at 280 °C, catalytic pyrolysis with MoO_3 produced 6.44 % phenolics. However, a significant decline of 26.95 % in the conversion of the oil phase was observed as a result of this process. The phenolic reduction in catalytic pyrolysis with MoO_3 is believed to be due to its ability to catalyze the depolymerization of lignin and remove its methoxy and unsaturated branches, resulting in a modified molecular structure (Zhang et al., 2018b). The integration of MoO_3 in the catalytic pyrolysis process increases the proportion of light ketone and furan molecules in the oil phase. Specifically, MoO_3 facilitates ketonization and aldol condensation by promoting C-C coupling and dehydration (Zhang et al., 2023). The increased torrefaction temperature boosted these reactions, reducing the aldehyde content from 12.08 % in R-M to 6.44 % in TM-280-M. This change indicates that MoO_3 contributes significantly to improving small groups in the volatiles. With utilizing the catalyst, the formation of aldehydes was inhibited, thus resulting in a more stable bio-oil (Zhang et al., 2018c).

In Fig. 4, the influence of torrefaction temperatures on the product distribution in ZSM-5 was depicted. The integration of ZSM-5 caused a change the bio-oil composition. Combining ZSM-5 and MoO_3 upgraded bio-oil composition by reducing oxygenated components, such as ketones, furans, aldehydes, and acids. The acid content, notably, exhibited a relatively low content of 0.56 % in the bio-oil. It could be attributed to the deoxidation and decarboxylation processes occurring within the catalyst's pores and channels. Deoxidation led carboxylic acid to lose oxygen, formatting H_2O and ketones, and decarboxylation removed the carboxyl group of the carboxylic acid (Cueto et al., 2022). The predominant constituents of the bio-oil shifted from oxygenated compounds to aromatic hydrocarbons, with the highest proportion recorded at 52.65 % (Li et al., 2022). With the boost in torrefaction temperature, the aromatic hydrocarbons content increased from 9.36 % for the original Miscanthus to 24.93 % for the TM-280 sample. The integration

of ZSM-5 catalytic pyrolysis and torrefaction led to more hydrocarbons from cellulose than other components. This phenomenon has been demonstrated by Tian et al. (2022) and Ma et al. (2019). Torrefaction could increase cellulose content by decomposing hemicellulose and partial lignin (Murugappan et al., 2016). This process eliminated active intermediates and provided more furan derivatives generated from cellulose degradation and olefins for Diels–Alder reaction, which resulted in higher aromatic content (Gao et al., 2023).

The dual catalysis system incorporated with torrefaction combined the advantages of these processes. The product qualitative compositions performed similarly in ZSM-5 catalysis and dual catalysis; incorporating MoO_3, however, enforced the relative proportion of aromatics in the pyrolysis bio-oil and inhibited the production of phenols compared to the bio-oil using only a single ZSM-5 catalyst. The torrefied Miscanthus catalytic pyrolysis with dual MoO_3/ZSM-5 reached 91.38 % aromatic hydrocarbon in TM-280, confirming the dehydration and methoxy group removal reactions facilitated phenols formation (Che et al., 2019). It is 38.37 % higher than the results obtained by ZSM-5 catalytic reaction alone; meanwhile, the content of oxygen-containing compounds is also lower than that of single ZSM-5 catalytic or non-catalytic reactions. ZSM-5 and MoO_3 catalysts added during Miscanthus awn pyrolysis can decrease bio-oil yield but increase aromatic hydrocarbon content. Torrefaction further increases the proportion of aromatic hydrocarbons from 61.71 % to 91.38 %. These processes affected biomass pyrolysis aromatization (Green et al., 2016).

Fig. 5 presents the impact of various torrefaction temperatures on the product distribution and BTX selectivity in the bio-oil derived from Miscanthus catalytic pyrolysis using dual MoO_3/ZSM-5. Dual catalysts allowed the torrefied Miscanthus pyrolysis conversing towards aromatic hydrocarbons. The MoO_3 deoxygenation could first reduce the size of pyrolytic oxygenated compounds into smaller hydrocarbon precursors, thus facilitating the diffusion and aromatization in the ZSM-5 pore channel (Lu et al., 2018). The oxygenates decreased with the enhancement of the torrefaction. Aliphatic HCs trend showed irregularly within the temperature control. With the increasing torrefaction temperature, the selectivity for monocyclic aromatic hydrocarbons boosted to 52.24 %, and the selectivity of 23.32 % of toluene, 17.68 % of xylene, and 11.24 % of benzene. The lower benzene yield might be because of the different deoxygenation pathways of the oxygenated precursors. During the catalytic pyrolysis, the oxygenated precursors underwent
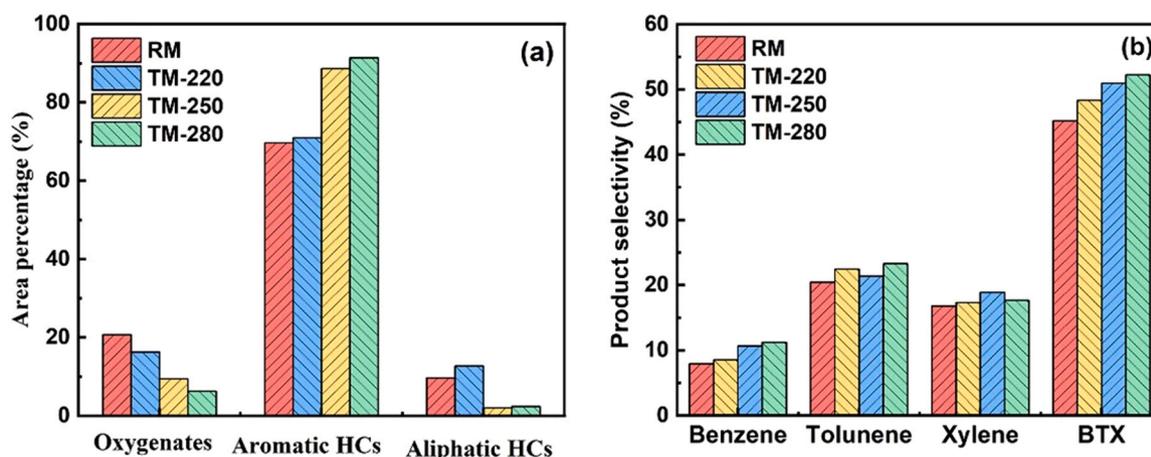
Fig. 5. Distribution of oil compositions (a) and BTX selectivity (b) from Miscanthus catalytic pyrolysis through dual MoO$_3$/ZSM-5.

demethoxylation and dehydration to form toluene and xylenes (Jae et al., 2011).

3.4. Effect of torrefaction and dual catalysis process on the composition of gaseous products

Fig. 6 illustrates the distribution of gases produced during catalytic pyrolysis using ZSM-5 (a), MoO$_3$ (b), and MoO$_3$/ZSM-5 (c) catalysts that are affected by different torrefaction temperatures. The volume fraction of CO produced by catalytic pyrolysis decreased by 6.45 %, 5.62 %, and

10.59 % with rising torrefaction temperature to 280 °C for the three catalyst modes. Besides, ZSM-5, MoO$_3$, and dual MoO$_3$/ZSM-5 catalytic pyrolysis showed an increase in the volume percentage of CO$_2$ by 4.49 %, 3.22 %, and 4.66 %, respectively, indicating the occurrence of secondary decomposition reactions. The reason might be that when the torrefaction enhanced, hemicellulose was easier to decompose, thus making deoxidation and decarboxylation reactions occur to generate stable gas during the catalytic pyrolysis process. It observed no significant distinction between the dual catalysts and the single catalyst system in terms of the trend of pyrolysis gas phase products.
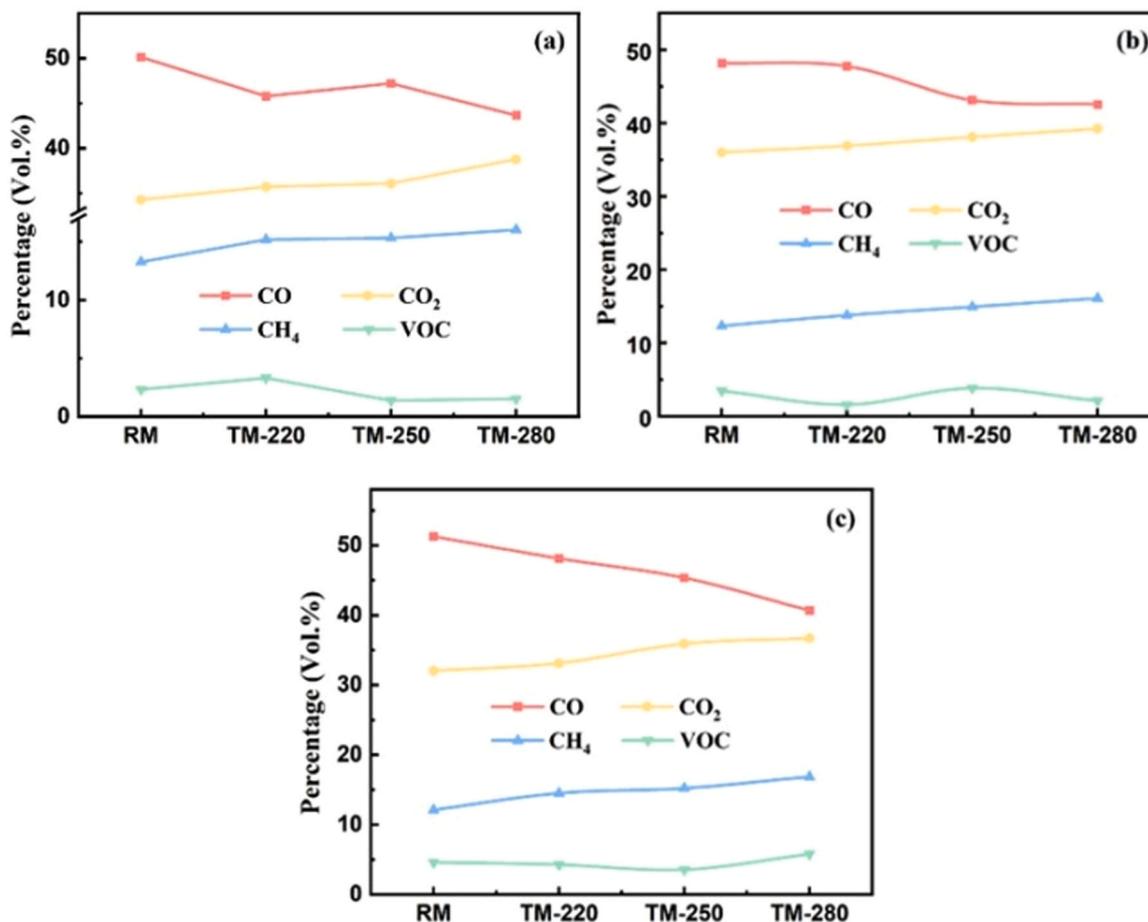
Fig. 6. Distribution of gas products under torrefaction and catalytic pyrolysis with different catalysts (a) ZSM-5 catalytic pyrolysis (b) MoO$_3$ catalytic pyrolysis (c) MoO$_3$/ZSM-5 catalytic pyrolysis.

3.5. Mass balance of torrefaction and dual catalytic process

Fig. 7 shows the process mass balance of Miscanthus to aromatic products through torrefaction and dual catalytic conversion within optimal conditions. When subjected to torrefaction at 280 °C, the tor-refied sample retained 64.5 % of its initial mass. During pyrolysis, due to high temperature, the glycosidic bond in lignin is broken, and the side chain acetyl and methylene groups are desorbed to form oxygen containing gas products, thus separating some hemicellulose and cellulose with poor thermal stability. The torrefaction process causes the disruption of glycosidic linkages and the desorption of side chain acetyl and methylene groups to form oxygen-containing gaseous products, which isolated partial hemicellulose and cellulose with poor thermal stability (Wang et al., 2017b; Yang et al., 2007). The proportions of bio-oil, biochar, and gas in the non-catalytic pyrolysis process of torre-fied Miscanthus were 29.23 %, 32.75 %, and 38.02 %, respectively. The participation of dual MoO_3/ZSM-5 improved the catalytic cracking of primary pyrolysis volatiles. The addition of MoO_3 as a catalyst facili-tated a range of chemical transformations, such as the conversion of carboxylic acids to ketones, the elimination of carboxyl groups from organic compounds, the condensation of aldehydes, the elimination of methyl groups, and the elimination of methoxy groups. These generated intermediate species then traversed the channels of the ZSM-5 catalyst, undergoing subsequent catalytic reactions to generate CO, CO_2, H_2O, alkanes, olefins, and aromatic hydrocarbons (Lazaridis et al., 2018). Due to these catalytic cracking, the final yield of bio-oil decreased from 29.23 % in non-catalytic pyrolysis to 24.17 %; the content of oxygenated compounds, however, sharply fell to 6.27 %, achieving the goal of deoxidation in bio-oil more efficiently (Carlson et al., 2009).

More importantly, the process is the potential to provide novel insight to upgrade the current biomass pyrolysis facilities. The torre-faction enables the manufacturing of wood vinegar and stable ligno-cellulosic biomass. Subsequently, the torrefied biomass goes through catalytic pyrolysis to produce biochar, gas, and valuable chemicals. Biochar can be utilized as a carbon material in various fields. The gas produced contains a high amount of combustible gas, allowing balance in the energy cost of the plant. Because of the high selectivity of aromatic hydrocarbons, the oil phase can be refined into sustainable replacements for petroleum-based chemicals.

4. Conclusions

The coupling of torrefaction and dual catalysts pyrolysis of Mis-canthus exhibited the outstanding capability of converting aromatic hydrocarbons. With the optimal conditions, the total aromatic hydro-carbon yield and MAHs selectivity in the oil phase was 91.38 % and 52.24 %, respectively, higher than that of a single catalyst or non-catalytic pyrolysis. Torrefaction enabled the removal of undesirable oxygenates and elevation of hydrocarbon content, while individual catalysis of ZSM-5 converted the pyrolyzed components to aromatic hydrocarbons. The MoO_3 reduced the ketone content and promoted deoxygenation and olefin aromatization. This process effectively inte-grated the intermediates' removal of torrefaction, aromatization of ZSM-5, and deoxygenation of MoO_3, with coordinated effects. This approach has remarkable efficiency and potential for upgrading biomass pyrolysis facilities towards generating valuable fuels and chemicals.

CRediT authorship contribution statement

Hong Tian: Conceptualization, Methodology, Validation, Project administration, Resources. **Rui Zhu:** Validation, Investigation, Writing – original draft. **Lei Chen:** Methodology, Validation, Investigation. **Jia-wei Wang:** Funding acquisition, Writing – review & editing. **Yi Cheng:** Conceptualization, Validation, Project administration, Writing – orig-inal draft, Writing – review & editing.

Declaration of Competing Interest

The authors would like to submit the manuscript to publish in Fuel Processing Technology. No conflict of interests exists in the submission
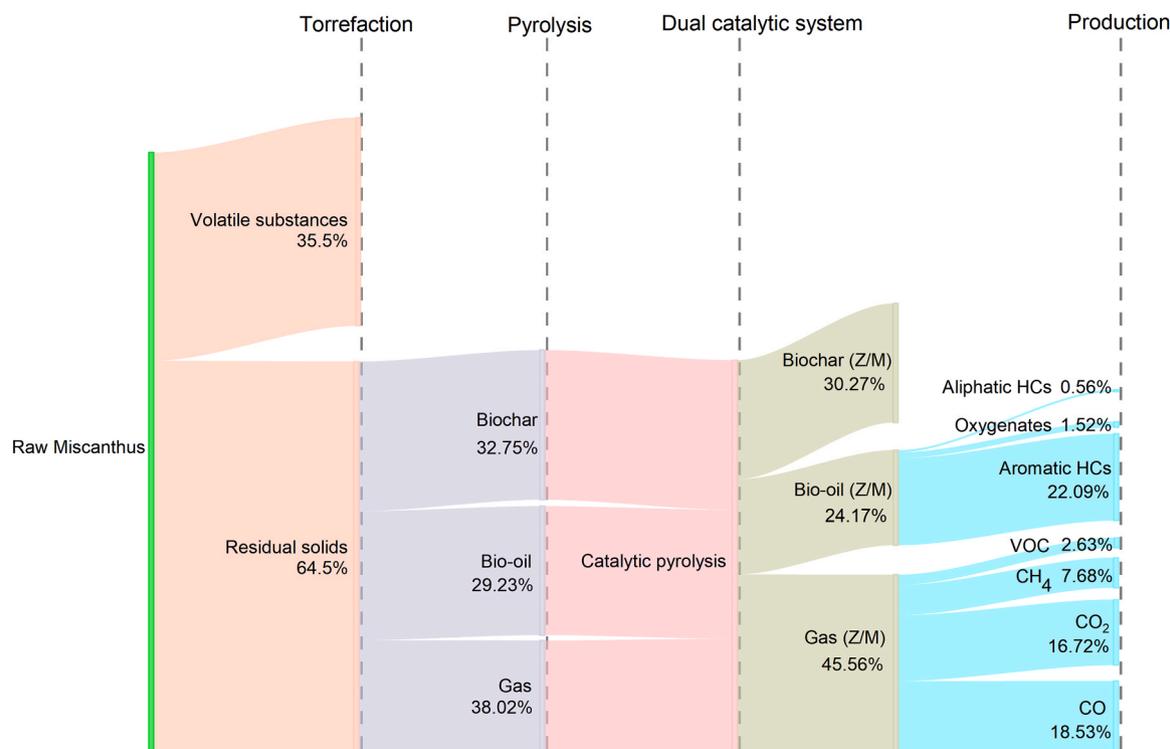
Fig. 7. Process mass balance of Miscanthus to aromatic products through torrefaction pretreatment and dual catalytic conversion. (Optimal conditions: torrefaction at 280 °C, pyrolysis at 550 °C, and with MoO_3/ZSM-5 dual catalysis process).

of this manuscript, and all authors mutually approved the manuscript that is enclosed. The authors declare this work was original research that has not been previously published or under consideration for publication elsewhere, in whole or in part.

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Data Availability

No data was used for the research described in the article.

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