UNIVERSITY OF LEEDS

This is a repository copy of *Catalytic vapor phase upgrading of sawdust pyrolysis using metal oxide catalysts: The support effect*.

White Rose Research Online URL for this paper:
https://eprints.whiterose.ac.uk/id/eprint/223040/

Version: Accepted Version

Article:

Singh, R., Anand, V., Chakinala, N. orcid.org/0000-0003-1835-3464 et al. (2 more authors) (2025) Catalytic vapor phase upgrading of sawdust pyrolysis using metal oxide catalysts: The support effect. Journal of Analytical and Applied Pyrolysis, 185. 106864. ISSN: 0165-2370

https://doi.org/10.1016/j.jaap.2024.106864

This is an author produced version of an article published in the Journal of Analytical and Applied Pyrolysis made available under the terms of the Creative Commons Attribution License (CC-BY), which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited.

Reuse
This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here: https://creativecommons.org/licenses/

Takedown
If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

White Rose
university consortium
Universities of Leeds, Sheffield & York

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk/

Catalytic Vapor Phase Upgrading of Sawdust Pyrolysis using Metal Oxide Catalysts: The Support Effect

Ranjita Singh[1, 2], Vaibhav Anand[1], Nandana Chakinala[1, 3], Kaustubha Mohanty[4], Anand G. Chakinala[1*]

[1]Chemical Reaction Engineering Laboratory, Department of Biotechnology & Chemical Engineering, Manipal University Jaipur, Jaipur 303007, Rajasthan, India

[2]Department of Biosciences, Manipal University Jaipur, Jaipur 303007, Rajasthan, India

[3]School of Chemistry, University of Leeds, Leeds, LS2 9JT, United Kingdom

[4]Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781039, India

*E-mail: Dr. Anand G. Chakinala, anandgupta.chakinala@jaipur.manipal.edu,

ABSTRACT

Biocrude derived from biomass is unstable and has limited applications and vapor-phase upgrading of biomass pyrolysis over a catalyst can enhance bio-oil quality and yield, yet catalyst deactivation due to coke formation remains a major challenge. This study explores the effects of different magnesium oxide (MgO) catalysts supported on ZSM-5, Al_2O_3, ZrO_2, TiO_2 on the pyrolysis product yield, composition, and the extent of coke formation. Studies were conducted in a fixed-bed reactor at 550 °C at two different catalyst to biomass loadings (C/B) of 1:6, and 1:1. Non catalytic pyrolysis of sawdust resulted in the biocrude, gas, and char yields of ~32 wt%, ~29 wt%, and ~39 wt% respectively. At a low C/B ratio, pyrolysis product yields were approximately comparable to those under non-catalytic conditions. However, at a high C/B ratio, biocrude yield decreased significantly - ~50 % with ZSM-5, ~35 % with Al_2O_3, ~20 % with TiO_2, and ~16 % with ZrO_2 support catalysts. This shift was accompanied by an 18% increase in gas yield, while char yield showed only minor changes. Using ZSM-5 and Al_2O_3 supported catalysts, low C/B ratios significantly increased phenolic content in the biocrude

(~58%). In contrast, higher C/B ratios enhanced the hydrocarbons (~10%) and aromatics (~32%) content, reducing phenolics and thereby lowering the biocrude's overall oxygen content, enhancing its stability. TiO_2 and ZrO_2 supports produced higher proportions of lower carbon chain length compounds, though with reduced hydrocarbon content compared to ZSM-5. Both ZSM-5 and ZrO_2 supports demonstrated sufficient thermal stability as compared to other supports. Overall, this study highlights the influence of different catalyst supports in catalytic vapor phase upgrading of sawdust derived biocrude to selectively optimize bio-oil composition, increasing fuel or chemical potential while addressing coke formation.

***Keywords*:** Catalytic pyrolysis; magnesium oxide; supports, phenolics; hydrocarbons

1 Introduction

The environmental impact of fossil fuels for energy applications has led to an increased awareness in terms of decarbonizing society with an increase in the usage of more sustainable alternatives[1]. Conversion of lignocellulosic biomass into liquid chemicals and fuels offers several benefits in terms of sustainability and reduced emissions[2,3]. There are several thermochemical approaches (e.g., pyrolysis, gasification, liquefaction) for converting biomass into chemicals/fuels. However, the properties of the bioliquids derived from the biomass pyrolysis process are relatively unstable with different characteristics that are due to the biomass heterogeneity and processing conditions. Thus, it is essential to improve the produced biocrude properties in terms of viscosity reduction, less acidity, reduced oxygenates, and better stability[4,5].

Catalytic pyrolysis is a way to produce improved biocrude and several catalysts were tested with different biomass feeds on the biocrude yields and composition. Magnesium oxide (MgO) impregnated biochar has been thoroughly studied in the literature as CO_2 adsorbents and has excellent efficiency in removing phosphate and nitrate from water[6,7]. However, bio-oil characteristics from catalytic pyrolysis of Magnesium-loaded biomass received little attention in the literature. MgO is an inexpensive alkaline earth element that can reduce the acidic nature of bio-oil by converting acid components into ketones through a Ketonization reaction. Additionally, it was suggested in literature that MgO-ZSM-5 and MgO-Beta, also enhance the deoxygenation efficiency due to the acidic and basic sites of these catalysts as well as while increasing Mg doping in zeolite and Al-MCM-41 enhance the yields of aromatic hydrocarbons in the bio-oil[8]. It has also been reported that when eucalyptus woodchips are converted into bio-oil, MgO/HZSM-5, which contains Lewis acidic and basic sites, improves deoxygenation efficiency. Similarly, MgO/Al_2O_3 and MgO/ ZrO_2 with the highest acidity and basicity showed enhanced pyrolytic oil content selectivity toward ketones, furans, and hydrocarbons, respectively, indicating that the properties of these active sites in the catalytic pyrolysis reaction may have distinct functions[9].

It has been demonstrated that in-situ catalytic pyrolysis increases the output of organic liquids with less oxygenated chemicals and maximizes hydrocarbons with ZSM-5[10]. Alumina, zirconia, and titanium oxides (anatase and rutile), catalysts were reportedly used in Jatropha wastes bio-oil refining the results show that TiO_2 (anatase) and Al_2O_3 were the best metal oxide catalysts for enhancing aliphatic and aromatic hydrocarbon components and reducing oxygen-rich components[11]. In addition, Levoglucosenone or phenol compounds were produced exclusively through catalytic pyrolysis utilizing carbon-based catalysts in bio-oil[12,13]. In our earlier work, vapor phase upgradation of sawdust biomass pyrolysis was reported with different metal oxides (MgO, CuO, ZnO, NiO, and Bi_2O_3) supported on alumina was studied, where MgO and CuO supported catalysts led to enhanced aromatics and hydrocarbons with low phenolic content in the obtained biocrude[14].

Previous research has mainly focused on MgO with a single support like alumina for biocrude upgradation. However, this study explores magnesium oxide with different support catalysts in both low and high C/B ratios. This work is primarily composed of one main objective: to understand the impact of MgO on different supports (ZSM-5, Al_2O_3, ZrO_2, TiO_2) and different feed ratios on the biocrude yield and composition.

2 Material and Methods

2.1 Materials

The sawdust (SD) biomass pellets used in this study are discussed in detail and reported elsewhere[14]. The proximate analysis of the sawdust biomass used in this study typically consists of ~11% moisture, ~76% volatiles, 6% ash, and 7% fixed carbon. The elemental composition analysis indicates ~44% carbon, ~5% hydrogen, ~1% nitrogen, and ~50% oxygen. Additionally, the biomass mainly comprised of ~35% cellulose, ~27% hemicellulose, and ~25% lignin content. The biomass feed was dried at ~ 100 °C for 1 h before the experiments Magnesium nitrate hexahydrate (A.R. grade with purity 98%), Zirconium dioxide (> 97 %), Titanium oxide (> 98.5 %), ZSM-5, and Methanol (> 99.8 %), required for catalyst preparation, were purchased from Loba Chemie Pvt. Ltd. Commercial ~4 mm Al_2O_3 pellets used in this study were procured from Gujarat Multi Gas Base Chemicals, Gujarat, India.

2.2 Catalyst preparation

The wet impregnation method was adapted for the preparation of 10 wt% of MgO deposited on different supports. Typical procedure involves preparation of solution of calculated amount of magnesium precursor dissolved in methanol with continuous stirring. Followed by addition of calculated amounts of the support material ($ZSM\text{-}5/Al_2O_3/ZrO_2/TiO_2$) in the solution prepared earlier which is further mixed (1h) and sonicated (1 h). The solution was filtered and allowed to dry at 100 °C in an oven which is then further calcined at 600 °C for 3 h. Catalysts synthesized with this procedure (MgO/ZSM-5, MgO/Al_2O_3, MgO/ZrO_2, and MgO/TiO_2) were directly used in the studies.

2.3 Pyrolysis experiment set-up

SD was catalytically pyrolyzed in a custom-built fixed-bed reactor that is described in detail in our earlier work[14,15] and the schematic of the set-up is given in the supplementary information. The reactor is a hollow cylinder made up of stainless-steel with a 4 cm ID and a 50 cm heating zone. The heating rate of biomass pyrolysis inside the reactor was estimated to be 35 °C min^{-1}. The tests were conducted with different MgO supported catalysts at an optimized temperature of 550 °C and at different C/B ratio (1:1) and (1:6) to check the role of catalysts on biocrude upgradation. The C/B ratio of 1:1 typically corresponds to a weight hourly space velocity of 3.2 $\mathrm{g/h/g_{cat}}$ and this value is typically in the range of industrial scale operations. These C/B ratios were selected to investigate the effects of low and high catalyst loadings on product yield, composition, and coke formation, based on prior studies that employed varied ratios[14]. A lower C/B ratio corresponds to a shorter contact time over the catalyst bed while a higher C/B ratio favors high contact time in the catalyst bed and thus two extremes are studied to understand the support effect. All catalytic experiments were conducted with the catalyst placed directly over the biomass bed, so that the vapors can more effectively contact the catalyst, promoting the production of deoxygenated compounds and improving bio-oil quality. The biocrude, char yields were calculated using Eq. (1), Eq. (2) respectively and gas yield was calculated from the difference using Eq.(3).

$$Biocrude\ yield\ (\%) = \left(\frac{Mass\ of\ biocrude}{Mass\ of\ biomass}\right) \times 100 \qquad \text{Eq. (1)}$$

$$Char\ yield\ (\%) = \left(\frac{Mass\ of\ char}{Mass\ of\ biomass}\right) \times 100 \qquad \text{Eq. (2)}$$

$$Gas\ yield\ (\%) = 100 - (Biocrude\ yield + Char\ yield) \qquad \text{Eq. (3)}$$

2.4 Characterization techniques

The Braunauer Emmett Teller (BET) analysis of the catalyst samples was carried out to determine the surface area of both fresh and spent samples using nitrogen adsorption/desorption tests performed on an Autosorb-IQ (Quanta chrome, USA) apparatus. Fourier transform infrared (FTIR) analysis of catalyst samples and biocrudes was performed by Bruker ALPHA with 0.8 cm^{-1} resolution. The catalyst's structure was analyzed *via* a Rigaku X-ray diffractometer (model: SMARTLAB). The catalyst's morphology and compositions were carried out using scanning electron microscopy (SEM), and EDX was performed using a JEOL JSM-7610F Plus field-emission scanning electron microscope[16].

The composition of biocrude was determined using a Shimadzu GCMS-QP2020 and a Rxi-5 MS column. The column (30 m × 0.25 mm, 0.25 μm film thickness) was kept at 50 °C and the injection temperature was 250 °C. Helium was used as the carrier gas at 1.18 mL min^{-1} and a split ratio of 15. The temperature was originally held at 50 °C for 2 min before increasing by 6 °C min^{-1} to 90 °C and then to 120 °C. Before analysis, 200 mg of biocrude was dissolved in 10 mL of hexane, dehydrated with anhydrous sodium sulfate, and then filtered. The composition of the biocrude was determined semi-quantitatively using the chromatographic area percentage. More details of the column specifications are described elsewhere [14].

3 Results and discussion

3.1 Catalyst Characterization

Table 1 lists the physicochemical properties (surface area, total pore volume, and pore diameter) of the fresh catalysts. It is seen from the table that the MgO modified Al_2O_3 has the largest surface area of 164 m^2 g^{-1}, pore volume of 0.2 cm^3 g^{-1}, and smallest pore diameter of 5 nm, whereas MgO modified supports such as ZSM-5, ZrO_2, and TiO_2 have 78 m^2 g^{-1}, 17 m^2 g^{-1} and 15 m^2 g^{-1} surface areas respectively.

Table -1 BET surface area characteristics of fresh catalyst samples.

Catalyst	BET surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Pore diameter (nm)
MgO/ZSM-5	78	0.1	6
MgO/Al_2O_3	164	0.2	5
MgO/TiO_2	17	0.1	31
MgO/ZrO_2	15	0.1	18

The fingerprint regions of the functional groups of these synthesized catalysts were done using FTIR analysis and are displayed in Figure 1. The absorption peak at 3601 cm^{-1} indicates the O-H bonding of the hydroxyl groups. The 2342 cm^{-1} peak represented C-H stretching vibration, while 1703 cm^{-1} indicated the existence of C=O stretching, and 1506 cm^{-1} appeared due to the presence of C=C stretching in samples. The peak at 1036 cm^{-1} was attributed to O-H modes of H–bonded zeolite hydroxyls whereas, 550 cm^{-1} peaks indicate the Mg-O bonding [17] The Si-O-Al peaks in ZSM-5 is observed at 1050 cm^{-1}, Zr-O peaks were identified between 500 and 600 cm^{-1}, and Ti-O-Ti peaks were noted in the range of 400 to 600 cm^{-1}.

<Figure 1>

The XRD analysis of the fresh catalysts is presented in Figure 2 in which the *2θ* values and *hkl* values of MgO modified ZrO_2 catalyst consisted of 30.2°(110), 35.2°(101), 36.9°(111), 42.9°(200), 50.4°(211), 60.3°(220), 62.7°(301) and 75.1°(301) peaks which confirms the presence of MgO and ZrO_2 in crystalline form. MgO modified TiO_2 catalyst also have distinct peaks at 25.3°(101), 36.9°(004), 37.8°(111), 42.9°(200), 48°(211), 53.9°(220), 55.1°(301), 62.3°(311), 70.3°(222) and 75°(302) which indicates the presence of both MgO and TiO_2 in highly crystalline form whereas, MgO supported on Al_2O_3, had peaks at 21°(100), 25.6°(110), 28.7°(111), 43.1°(200) and 52.6°(210) which corresponds to the presence of Al_2O_3 in crystalline form. MgO on ZSM-5, catalyst showed peaks at 15.9°(001), 19°(100), 20.7°(101), 23.7°(110), 24°(110), 25.6°(111), 27.4°(200) and 32.1(210) which slightly exhibited different diffraction peaks than reported in the literature which can be attributed due to the deposition of MgO that leads to the structural modifications of the catalyst[18–22].

<Figure 2>

SEM images displayed the crystalline structure of the fresh catalysts (Figure 3), in which structural alterations were seen after metal oxides impregnation on the ZSM-5, Al_2O_3, TiO_2, ZrO_2 surface. When compared to bare the ZSM-5, Al_2O_3, TiO_2, and ZrO_2 metal impregnation resulted in particle aggregation. The surface elemental composition of the catalyst was qualitatively determined using EDX analysis confirms the deposition of metal oxide loadings which matches closely with the calculated amounts used through the synthesis process. Although, the estimated loadings are lower than the calculated amounts this can be attributed to the surface composition determination using EDX which doesn't represent the bulk concentration. The catalyst composition analysis revealed the following elemental distributions: Modified ZSM-5 showed the presence of oxygen, magnesium, alumina, and silica at approximately 50.5%, 2%, 24.4%, and 23%, respectively; MgO modified Al_2O_3 confirmed 48.4% oxygen, 11.2% magnesium, and 40.4% alumina; MgO modified TiO_2 revealed 48.2% oxygen, 12.2% magnesium, and 39.6% titania; and MgO supported on ZrO_2 revealed the presence of 38.2% oxygen, 4.6% magnesium, and 57.2% zirconia.

<Figure 3>

3.2 Catalytic pyrolysis studies

3.2.1 Effect of different catalysts on product yield

Figure 4 a and b correspond to the pyrolysis product yields obtained with two different C/B ratios such as 1:6 and 1:1. It is seen from figure 4a that no significant differences in the pyrolysis product yields were noticed with different supported MgO catalysts when compared with non-catalytic conditions. Maximum biocrude yield up to ~32 wt% and only marginal changes were observed with gas and char yields with different catalysts which can be attributed to the low contact time of the pyrolysis vapors over the catalyst bed. The pyrolysis product yields with a high C/B ratio (1:1) is shown in Figure 4 b. It is evident from the figure that there is a decline in biocrude yield of ~50 % with ZSM-5, ~35 % with Al_2O_3, ~20 % with TiO_2, and ~16 % with ZrO_2 supported catalysts when compared to non-catalytic pyrolysis (Figure 4 a). While gaseous yields increased by ~18 % marginal changes in char yield were also seen. At higher C/B ratios, the extended interaction between biomass vapors and the catalyst facilitates the cracking reactions that can result in the lowered biocrude and increased gas yields. Similar observations were seen with previously studied sawdust biomass pyrolysis in the presence of MgO/Al_2O_3 at a low C/B ratio higher biocrude yields were seen whereas, with an increase in C/B ratio, the biocrude yields were deceased[14]. Similar studies reported in the literature as well areca *catechu* sawdust pyrolysis over MgO and ZSM-5 catalysts at low C/B biocrude yield increased while biocrude yield decreased with high C/B [23]. The effect of MgO on the cotton seed pyrolysis reported in the literature have shown that with increasing biomass-catalyst mixture the biocrude yields decreased while gas and char yields were reported to be increased[24].

Figure 4 c presents the overall statistical distribution of pyrolysis product yields obtained under different conditions. The violin plot shows the distribution of pyrolysis yields for gas, biocrude, and char, with median values of 31.3%, 29.2%, and 38.9%, respectively. Char yields are larger and more evenly distributed, whereas gas and oil yields are similar but with narrower distributions around the medians. The black bars represent interquartile ranges, indicating the middle 50% of the data for each product. This demonstrates that char has the highest total yield when compared to gas and oil.

<Figure 4 (a), (b) & (c)>

3.2.2 Biocrude Composition Analysis

The obtained biocrude mainly comprises of both aqueous and organic fractions and the distribution of these fractions depend on various factors such as the biomass type, reactor type, catalyst, contact time and biomass pretreatment (chemical/thermal). Phase separated aqueous fractions typically contain very low amounts of organic content. The chemical composition of organic fraction of the biocrude was analyzed to determine the different chemical functional groups that are lumped as aldehydes, acids, furans, alcohols, ketones, phenolics, hydrocarbons, aromatics, and other components. Figures 5a and 5b show the major compounds identified in the biocrude with different supported MgO catalysts. In general, catalysts play a crucial role in the pyrolysis process by converting the sugar derivatives from cellulose and hemicellulose into lighter components like alcohols, furans, and ketones. This happens through cracking, dehydration, decarboxylation, and decarbonylation reactions. Eventually, these compounds are converted into hydrocarbons, phenols, and aromatics compounds. Major phenolic compounds that were observed in the presence of catalysts were phenol, cresol, 2-methoxy phenol, and 2,6-dimethoxy phenol. Some aromatic compounds such as toluene, naphthalene, 3,5-dimethoxy-4-hydroxytoluene, and benzene,1,2,3-trimethoxy-5-methyl were also detected. Alcoholic compounds pentanol, 1-hexacosanol, and 3,5-dimethylpyrazole-1-methanol were also noticed. Hydroxymethyl-furfural, furfural, furfuryl-alcohol, 3-methyl-2-cylcopentenone, and cyclopentenone, found in the biocrude are typically generated from cellulose and hemicellulose dehydration. The biocrude obtained consisted of specific components in significantly relative higher amounts such as *p*-cresol, 2-methoxy phenol, furfural, 3,5-dimethyl pyrazole, and cyclopentanone, with metal oxide modified Al_2O_3 and ZSM-5 while, naphthalene and decane were noticed in the biocrude with metal oxide modified ZrO_2 and TiO_2 supported catalysts.

Non-catalytic and catalytic biocrude obtained with varied C/B ratio showed noticeable differences in their chemical composition. The biocrudes obtained without catalyst have low concentrations of phenolics ~38 wt%, aromatics ~ 5wt%, and hydrocarbons ~4 wt% compared to biocrude containing MgO with various supports as shown in Figure 5a and 5b. Previous studies reported that bare MgO produced a biocrude containing over 70% phenolics, with specific compounds like phenol (12%), p-cresol (25%), and 2-methoxyphenol (16%) in notable proportions [14]. The increased selectivity toward aromatics and decreased phenolic content with all supported catalysts suggest that phenolic compounds may undergo conversion to deoxygenated aromatics through dehydroxylation and demethoxylation reactions, facilitated by the cooperative action of acid and base sites[25]. Particularly with ZSM-5 at high C/B ratios, the highest aromatic hydrocarbon content was observed in the biocrude. The MgO deposition on ZSM-5 alters the acidic properties of the parent zeolite by reducing acid sites and introducing a substantial number of basic sites. This modification creates a balanced synergy between the acidic sites of ZSM-5 and the basic sites of MgO, promoting deoxygenation and enhancing the formation of aromatic hydrocarbons[26]. Alumina and zirconia supports also reduced phenolic compounds relative to bare MgO, suggesting these supports are effective for deoxygenation; however, their acidity and basicity are not high enough to fully convert intermediates into aromatic products. Additionally, higher coke deposition observed on ZrO_2 and Al_2O_3 supports, compared to ZSM-5, implies that phenolic compounds were more prone to polymerization into coke, limiting aromatic formation. The larger pore structure of alumina and ZrO_2 support likely facilitated condensation and polymerization reactions [25], contributing to the increased coke formation (Refer Table 1 and Figure 7c). With TiO_2 support, the biocrude exhibited a high proportion of furan compounds and limited aromatic content at higher C/B ratios, suggesting that TiO_2 support is not sufficiently active to promote effective deoxygenation reactions [27]. Significant amounts of hydrocarbons were obtained from TiO_2 with lower amounts of aldehydes, ketones, alcohols, and furans. Whereas, with high C/B the phenolics decreased up to ~18 wt%, and aromatics enhanced up to ~10 wt% with ZSM-5 support.

Figure 5c shows the relative content of different compounds such as acids, alcohols, ketones, phenolics, aldehydes, furans, aromatics, hydrocarbons, and other compounds. The order of components in the biocrude is typically in the form of phenolics > aromatics > ketones >hydrocarbons > furans > acids, aldehydes, and alcohols. Figure 5c represents the statistical analysis presented in the form of violin plot which represents the overall composition of the biocrude obtained under different conditions. The median values of acids, aldehydes, phenolics, ketones, furans, hydrocarbons, aromatics, and others were found to be 2.1, 1.5, 47.3, 15.2, 5.8, 2.6, 17.8, and 0.9 respectively. Phenolics have the highest content with a wide distribution, followed by ketones and aromatics, whereas acids and aldehydes have significantly lower content. The black bars in each violin reflect the interquartile range, which highlights the middle 50% of the data for each component. It is evident from the figure that phenolics are the most prevalent components in the biocrude, with other smaller components.

<Figure 5 (a), (b) & (c)>

3.2.2.1 Carbon number distribution

The carbon number distribution in the biocrude, obtained at various C/B ratios (1:6) and (1:1), is depicted in Figures 6a and 6b respectively. Biocrude consists of diverse carbon compounds spanning from C_2-C_{50}. The lower C/B ratio in biocrude has lighter components up to ~10% distribution of C_2-C_5, however, as the C/B ratio increases, these lighter compounds are converted into the gaseous phase. The major components present in the C_2-C_5 carbon distribution are penten-2-one, cyclopentanone, 2-butanone, 2-methoxytetrahydrofuran, 2-furanmethanol, furfural, and 2-furanmethanol, tetrahydro-, which were present in both lower as well as higher C/B ratios. At low C/B ratios, C_2-C_5 compounds were present in higher concentrations compared to higher C/B ratios. ~10% of C_2-C_5 components were seen with ZSM-5 catalyst at low C/B ratio whereas only ~1% of these components were seen with high C/B ratio. With TiO_2 at a lower to higher C/B ratio, these lighter components increased from ~7% to ~15%. whereas no major changes were seen with ZrO_2 and Al_2O_3. In contrast, C_6-C_{10} compounds increased from 55% to a maximum of 80% from low to higher C/B ratio. The major components present in these are creosol, phenol, 2-methoxy-, eugenol, phenol, phenol, 4-ethyl-2-methoxy-, toluene, p-xylene, benzene, 1-ethyl-2,4-dimethyl-, and benzene, 1,3-

dimethyl-. At higher C/B ratios the large molecules broke into small components due to higher catalyst-to-biomass interaction. The distribution of C_{11}-C_{15} compounds varies, rising from ~5% to ~28% at a low C/B ratio whereas, with higher C/B loading, these compounds subsequently decreased up to ~6% as these higher carbon-containing components broke down into C_6-C_{10} compounds. Additionally, At 1:6 C/B ratio C_{16}-C_{20} compounds were observed up to 12% but not seen in the 1:1 C/B ratio. At a higher C/B ratio, most of the large components broke down into smaller components. Moderate changes were noticed in C_{21}–C_{25} and C_{26}-C_{30}, whereas > C_{30} compounds were seen in low C/B ratio in the biocrude but not in higher C/B ratio. It was reported in the literature that the catalytic pyrolysis of Douglas fir with MgO and biomass-derived activated carbon catalysts in high C/B results in significant C_5-C_{10} components with phenols and furans accounting for 42% and 24%, respectively. The primary components of the biocrude were found to be furfural, 5-methyl-2-furancarboxaldehyde, and 4-ethyl-2-methoxyphenol along with some ketones and aldehydes in Douglas fir pyrolysis [28]. Similarly, during *in situ* catalytic pyrolysis of lignocellulosic biomass using ZSM-5 catalyst, the main components were C_5-C_{10} compounds. These include phenol, 2-methoxyphenol (guaiacol), 2-methoxy-4-vinylphenol, toluene, indene, 2-cyclopenten-1-one, and 2-hydroxy-2-cyclopenten-1-one. ZSM-5 was reported to efficiently convert the lignocellulosic feedstocks into aromatic and oxygenated compounds in the C_5-C_{10} carbon range, producing valuable chemicals [29]. In the catalytic co-pyrolysis of cellulose and LDPE, MgO-impregnated catalysts exhibited distinct selectivity based on the active sites present. Zirconia supported catalyst with active basic sites improved the synthesis of aliphatic and aromatic hydrocarbons, including decane, and methoxy toluene. Alumina support with acidic sites showed better selectivity towards furans and ketones, such as furfural and 2-cyclopenten-1-one. The products mainly contained C_5-C_{15} components, demonstrating the catalyst's specialized functionality in the pyrolysis process [8]. At a higher C/B ratio, the interaction between catalyst to biomass pyrolysis vapors was very high which enhances the breakdown of larger components into smaller ones, leading to the formation of C_6-C_{10}, and C_{11}-C_{15} compounds. Therefore, it can be concluded that higher C/B ratios are required to effectively produce these smaller compounds.

<Figure 6 (a), &(b)>

3.3 Spent catalyst characterization

Catalyst deactivation remains a central challenge in catalytic pyrolysis of biomass, largely due to the complex feedstock composition and pyrolysis conditions. Catalyst deactivation in this context is influenced by multiple interdependent factors, including feedstock type, catalyst-vapor contact time, the location of the catalyst bed relative to the pyrolysis zone, tar concentration in the pyrolysis vapors, and carbonaceous residue carried by the vapor stream. These factors collectively determine the rate and nature of catalyst deactivation, necessitating a detailed understanding of deactivation mechanisms for process optimization.

The coke deposition was studied using FTIR, BET, XRD, SEM, and EDX analysis of spent catalysts. FTIR spectra of the spent catalysts showed minimal deviation from those of fresh catalysts, suggesting limited alteration in functional groups on the catalyst surface. The dominant peaks observed at 3863 cm^{-1} and 3601 cm^{-1} were attributed to -OH stretching, indicative of surface-bound moisture, while the peak at 2342 cm^{-1} reflected C-H stretching, possibly from residual organic compounds or carbonaceous deposits. Peaks at 1617 cm^{-1} and 1525 cm^{-1} correspond to C=C bonds, and the 1056 cm^{-1} band suggest C-H stretch arising from carbon deposition. The 550 cm^{-1} peak, represents Mg-O bonding, was consistent with the fresh catalyst spectrum, as shown in Figure 7a.

XRD analysis of these spent catalysts revealed nearly identical patterns to those of fresh catalysts as shown in Figure 7b. This similarity indicates that structural degradation or phase transformation did not significantly contribute to catalyst deactivation under the given conditions. Further BET analysis confirmed a reduction in surface area, consistent with the hypothesis of coke deposition on active sites, which SEM and EDX analyses corroborated by revealing carbon deposits on the catalyst surface. SEM and EDX analysis of the spent catalysts shown in Figure 7c indicate that around ~5% carbon was deposited on the Al_2O_3 and ZrO_2 supported catalyst surface. Additionally, 2% carbon deposition was observed on the ZSM-5 supported catalyst while the TiO_2 support exhibited 3% carbon deposition indicating the catalyst deactivation was due to coke accumulation on the catalyst.

<Figure 7a), b), & c)>

Table 2 lists the physicochemical properties (surface area, total pore volume, and pore diameter) of spent catalysts. Where spent MgO modified Al_2O_3 surface area was decreased up to 58 m^2g^{-1}, minor changes were seen in pore volume and pore diameter, whereas no major changes were seen in surface structure, pore volume and pore diameter of spent MgO modified supports such as ZSM-5, ZrO_2, and TiO_2 as compared to fresh catalysts. These changes are attributed to the thermal stability of these catalysts as a result of changes in the catalyst crystallinity, structural integrity, and rearrangement in the structure of catalysts[30,31].

Table 2 Physicochemical properties of spent catalysts

Catalyst	**BET surface area ($m^2\,g^{-1}$)**	**Total pore volume ($cm^3\,g^{-1}$)**	**Pore diameter (nm)**
MgO/ZSM-5 (Spent)	89	0.1	4
MgO/Al_2O_3 (Spent)	106	0.3	9
MgO/TiO_2 (Spent)	10	0.1	38

MgO/ZrO_2 (Spent)	16	0.1	18

Biomass pyrolysis vapors result in more coke formation on the catalyst surface which is confirmed with the characterization results of our study. Indeed, more studies are also required in the future to evaluate the catalyst performance through reusability and long-duration studies which aid in the development of designer catalysts possessing high activity and stability for a continuous process. The distinct carbon deposition characteristics of various catalysts directly impact their reactivity by influencing the active sites available for the catalytic process. When carbon deposits accumulate on the surface, especially in catalyst supports like ZrO_2 and Al_2O_3, which exhibit higher carbon deposition, the catalyst's active sites become blocked. This reduces the catalyst's ability to promote reactions, eventually leading to deactivation and stopping the reaction. In contrast, catalyst supports like ZSM-5 and TiO_2 show less carbon deposition, which suggests they maintain more active sites for longer periods, enhancing their reactivity and extending their lifespan. Therefore, the extent of carbon deposition determines how quickly a catalyst deactivates, with high deposition leading to reduced reactivity and shorter operational time.

The differential weight loss curves of biochar typically show a single peak between 350 – 650°C (not shown) indicating its decomposition range. During catalytic biomass pyrolysis, the volatiles from biomass undergo catalytic reactions on the catalyst surface which result in different types of coke residues deposited on the catalyst surface that have a different thermal decomposition ranges when compared to biochar alone. To improve catalyst reliability and activity, it is critical to reduce vapor residence time on the catalyst surface. Furthermore, the location of the catalytic bed within the pyrolysis unit is also critical in understanding the catalyst deactivation mechanism.

4 Conclusion

Herein, we studied the influence of different catalysts made of MgO loaded on different supports (ZSM-5, Al_2O_3, ZrO_2, and TiO_2) that are evaluated in terms of catalytic pyrolysis behavior on pyrolysis product yields and biocrude composition at different C/B loadings. At a low C/B ratio (1:6) the presence of catalyst did not have a significant change on product yields (biocrude, gas, and char) but an increase in char, and gas yield and decrease in biocrude yields was observed with higher C/B (1:1) ratio. The composition of biocrude produced at the lower C/B ratio (1:6) showed higher phenolics as well as aromatics with MgO/ZSM-5. While, at high C/B (1:1) ratio a clear distinction in terms of biocrude composition is noticed in terms of the functional groups as well as the carbon chain length. Higher C/B ratio favored the production of aromatics and hydrocarbons and reduced the phenolics due to the promotion of deoxygenation reactions facilitated by the presence of a catalyst. This resulted in a reduction of phenolics and an increase in aromatics as well as hydrocarbons with ZSM-5 and Al_2O_3 supports respectively. A significant amount of coke deposition was also noticed on the surface of the spent catalyst suggesting the need for more studies in terms of reusability/continuous pilot scale studies for evaluating the catalyst feasibility for large-scale operations.

Acknowledgements:

The authors thank the Manipal University Jaipur (MUJ) for providing access to the Central Analytical Facilities (CAF) for GCMS and, FTIR analysis and Sophisticated Analytical Instrumentation Facility (SAIF) for carrying out the XRD, SEM and EDX analysis.

Credit Author Statement:

Ranjita Singh contributed to the investigation, data curation, and writing of the original draft. Vaibhav Anand contributed to the investigation, data curation, and writing of the original draft. Nandana Chakinala carried out the formal analysis, supervised the project, and was involved in the review and editing. Kaustubha Mohanty was involved in the review and editing. Anand G. Chakinala conceptualized the study, administered the project, validated the findings, supervised the project, and wrote the review and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper**.**

Data Availability

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

5 References

[1] S. Sankaranarayanan, W. Won, Catalytic pyrolysis of biomass to produce bio-oil using layered double hydroxides (LDH)-derived materials, GCB Bioenergy. 16 (2024) 1–22. https://doi.org/10.1111/gcbb.13124.

[2] Y. Hu, M. Li, Y. Fang, T. Tan, Resolving challenges in biomass catalytic pyrolysis by co-optimization of process and catalyst: Removal of heavy fraction in pyrolysis vapours and application of novel zeolite catalyst with high thermal conductivity, Renew. Energy. 156 (2020). https://doi.org/10.1016/j.renene.2020.04.103.

[3] Q. Che, M. Yang, X. Wang, X. Chen, W. Chen, Q. Yang, H. Yang, H. Chen, Aromatics production with metal oxides and ZSM-5 as catalysts in catalytic pyrolysis of wood sawdust, Fuel Process. Technol. 188 (2019) 146–152. https://doi.org/10.1016/j.fuproc.2019.02.016.

[4] M. Sharifzadeh, M. Sadeqzadeh, M. Guo, T.N. Borhani, N.V.S.N. Murthy Konda, M.C. Garcia, L. Wang, J. Hallett, N. Shah, The multi-scale challenges of biomass fast pyrolysis and bio-oil upgrading: Review of the state of art and future research directions, Prog. Energy Combust. Sci. 71 (2019). https://doi.org/10.1016/j.pecs.2018.10.006.

[5] T.S. Kim, S. Oh, J.Y. Kim, I.G. Choi, J.W. Choi, Study on the hydrodeoxygenative upgrading of crude bio-oil produced from woody biomass by fast pyrolysis, Energy. 68 (2014) 437–443. https://doi.org/10.1016/j.energy.2014.03.004.

[6] S. Zhang, J. Wang, S. Zhu, X. Liu, Y. Xiong, H. Zhang, Effects of MgCl2 and Mg(NO3)2 loading on catalytic pyrolysis of sawdust for bio-oil and MgO-impregnated biochar production, J. Anal. Appl. Pyrolysis. 152 (2020) 104962.

https://doi.org/10.1016/j.jaap.2020.104962.

[7] M. Zhang, B. Gao, Y. Yao, Y. Xue, M. Inyang, Synthesis of porous MgO-biochar nanocomposites for removal of phosphate and nitrate from aqueous solutions, Chem. Eng. J. 210 (2012). https://doi.org/10.1016/j.cej.2012.08.052.

[8] H.W. Ryu, Y.F. Tsang, H.W. Lee, J. Jae, S.C. Jung, S.S. Lam, E.D. Park, Y.K. Park, Catalytic co-pyrolysis of cellulose and linear low-density polyethylene over MgO-impregnated catalysts with different acid-base properties, Chem. Eng. J. 373 (2019) 375–381. https://doi.org/10.1016/j.cej.2019.05.049.

[9] P. Kim, T.G. Rials, N. Labbé, S.C. Chmely, Screening of Mixed-Metal Oxide Species for Catalytic Ex Situ Vapor-Phase Deoxygenation of Cellulose by py-GC/MS Coupled with Multivariate Analysis, Energy and Fuels. 30 (2016) 3167–3174. https://doi.org/10.1021/acs.energyfuels.6b00347.

[10] R. Kumar, V. Strezov, E. Lovell, T. Kan, H. Weldekidan, J. He, B. Dastjerdi, J. Scott, Bio-oil upgrading with catalytic pyrolysis of biomass using Copper/zeolite-Nickel/zeolite and Copper-Nickel/zeolite catalysts, Bioresour. Technol. 279 (2019) 404–409. https://doi.org/10.1016/j.biortech.2019.01.067.

[11] P. Kaewpengkrow, D. Atong, V. Sricharoenchaikul, Catalytic upgrading of pyrolysis vapors from Jatropha wastes using alumina, zirconia and titania based catalysts, Bioresour. Technol. 163 (2014). https://doi.org/10.1016/j.biortech.2014.04.035.

[12] X.N. Ye, Q. Lu, X. Wang, H.Q. Guo, M.S. Cui, C.Q. Dong, Y.P. Yang, Catalytic Fast Pyrolysis of Cellulose and Biomass to Selectively Produce Levoglucosenone Using Activated Carbon Catalyst, ACS Sustain. Chem. Eng. 5 (2017) 10815–10825.

https://doi.org/10.1021/acssuschemeng.7b02762.

[13] Q. Lu, X.N. Ye, Z.B. Zhang, M.S. Cui, H.Q. Guo, W. Qi, C.Q. Dong, Y.P. Yang, Catalytic Fast Pyrolysis of Bagasse Using Activated Carbon Catalyst to Selectively Produce 4-Ethyl Phenol, Energy and Fuels. 30 (2016). https://doi.org/10.1021/acs.energyfuels.6b02628.

[14] R. Singh, N. Chakinala, K. Mohanty, A.G. Chakinala, Catalytic upgrading of biomass pyrolysis vapors for selective production of phenolic monomers over metal oxide modified alumina catalysts, J. Environ. Chem. Eng. 11 (2023) 111518. https://doi.org/10.1016/j.jece.2023.111518.

[15] Y. Chen, H. Yang, Q. Yang, H. Hao, B. Zhu, H. Chen, Torrefaction of agriculture straws and its application on biomass pyrolysis poly-generation, Bioresour. Technol. 156 (2014) 70–77. https://doi.org/10.1016/j.biortech.2013.12.088.

[16] S. Kakku, S. Naidu, M. Bhatt, A.G. Chakinala, J. Joshi, S. Gautam, K. Mohanty, G. Kataria, A. Sharma, Pyrolytic conversion of agricultural residue using continuous auger reactor for resource recovery, J. Anal. Appl. Pyrolysis. 171 (2023) 105951. https://doi.org/10.1016/j.jaap.2023.105951.

[17] Ł. Szkudlarek, K. Chałupka, W. Maniukiewicz, J. Albińska, M.I. Szynkowska-Jóźwik, P. Mierczyński, The influence of si/al ratio on the physicochemical and catalytic properties of mgo/zsm-5 catalyst in transesterification reaction of rapeseed oil, Catalysts. 11 (2021). https://doi.org/10.3390/catal11111260.

[18] A. Glisenti, A. Frasson, A. Galenda, M. Ferroni, I. Concina, M.M. Natilea, Synthesis and characterization of Ag/CeO2 nanocomposites, Mater. Res. Soc. Symp. Proc. 1257 (2010)

323–328. https://doi.org/10.4172/2157-7439.1000329.

[19] S. Qu, C. Chen, M. Guo, J. Lu, W. Yi, J. Ding, Z. Miao, Synthesis of MgO/ZSM-5 catalyst and optimization of process parameters for clean production of biodiesel from Spirulina platensis, J. Clean. Prod. 276 (2020). https://doi.org/10.1016/j.jclepro.2020.123382.

[20] Y.A. Al-Baqmaa, A.S. Al-Fatesh, A.A. Ibrahim, A.A. Bagabas, F.S. Almubadde, A.I. Alromaeh, J.K. Abu-Dahrieh, A.E. Abasaeed, A.H. Fakeeha, Effects of MgO on Ni/Al2O3 catalysts for CO2 reforming of methane to syngas, Res. Chem. Intermed. 49 (2023) 5015–5028. https://doi.org/10.1007/s11164-023-05117-0.

[21] N. Patel, A.S. Al-Fatesh, N.A. Bamatraf, A.I. Osman, S.B. Alreshaidan, A.H. Fakeeha, I. Wazeer, R. Kumar, 5Ni/MgO and 5Ni/MgO + MOx (M = Zr, Ti, Al) Catalyst for Hydrogen Production via Dry Reforming of Methane: Promotor-Free, Cost-Effective, and Handy Catalyst System, Catal. Letters. 154 (2024) 3441–3456. https://doi.org/10.1007/s10562-023-04548-z.

[22] M.B. Gawande, P.S. Branco, K. Parghi, J.J. Shrikhande, R.K. Pandey, C.A.A. Ghumman, N. Bundaleski, O.M.N.D. Teodoro, R. V. Jayaram, Synthesis and characterization of versatile MgO-ZrO2 mixed metal oxide nanoparticles and their applications, Catal. Sci. Technol. 1 (2011) 1653–1664. https://doi.org/10.1039/c1cy00259g.

[23] R.K. Mishra, K. Mohanty, Fuel properties and compositional analysis of Areca catechu sawdust over MgO and ZSM-5 catalysts, J. Energy Inst. 94 (2021) 252–262. https://doi.org/10.1016/j.joei.2020.09.009.

[24] E. Pütün, Catalytic pyrolysis of biomass: Effects of pyrolysis temperature, sweeping gas

flow rate and MgO catalyst, Energy. 35 (2010) 2761–2766. https://doi.org/10.1016/j.energy.2010.02.024.

[25] H.W. Ryu, H.W. Lee, J. Jae, Y.K. Park, Catalytic pyrolysis of lignin for the production of aromatic hydrocarbons: Effect of magnesium oxide catalyst, Energy. 179 (2019) 669–675. https://doi.org/10.1016/j.energy.2019.05.015.

[26] H. Hernando, I. Moreno, J. Fermoso, C. Ochoa-Hernández, P. Pizarro, J.M. Coronado, J. Čejka, D.P. Serrano, Biomass catalytic fast pyrolysis over hierarchical ZSM-5 and Beta zeolites modified with Mg and Zn oxides, Biomass Convers. Biorefinery. 7 (2017) 289–304. https://doi.org/10.1007/s13399-017-0266-6.

[27] Q. Lu, Z.F. Zhang, C.Q. Dong, X.F. Zhu, Catalytic upgrading of biomass fast pyrolysis vapors with nano metal oxides: An analytical Py-GC/MS study, Energies. 3 (2010). https://doi.org/10.3390/en3111805.

[28] E. Huo, D. Duan, H. Lei, C. Liu, Y. Zhang, J. Wu, Y. Zhao, Z. Huang, M. Qian, Q. Zhang, X. Lin, C. Wang, W. Mateo, E.M. Villota, R. Ruan, Phenols production form Douglas fir catalytic pyrolysis with MgO and biomass-derived activated carbon catalysts, Energy. 199 (2020). https://doi.org/10.1016/j.energy.2020.117459.

[29] S.D. Stefanidis, S.A. Karakoulia, K.G. Kalogiannis, E.F. Iliopoulou, A. Delimitis, H. Yiannoulakis, T. Zampetakis, A.A. Lappas, K.S. Triantafyllidis, Natural magnesium oxide (MgO) catalysts: A cost-effective sustainable alternative to acid zeolites for the in situ upgrading of biomass fast pyrolysis oil, Appl. Catal. B Environ. 196 (2016) 155–173. https://doi.org/10.1016/j.apcatb.2016.05.031.

[30] M.A. Ebiad, D.R. Abd El-Hafiz, R.A. Elsalamony, L.S. Mohamed, Ni supported high

surface area CeO2-ZrO2 catalysts for hydrogen production from ethanol steam reforming, RSC Adv. 2 (2012) 8145–8156. https://doi.org/10.1039/c2ra20258a.

[31] M.A. Khan, M.T. Mehran, S.R. Naqvi, A.H. Khoja, F. Shahzad, U. Sikander, S. Hussain, R. Khan, B. Sarfaraz, M.M. Baig, Reutilizing Methane Reforming Spent Catalysts as Efficient Overall Water-Splitting Electrocatalysts, ACS Omega. 6 (2021) 21316–21326. https://doi.org/10.1021/acsomega.1c01558.