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Addition of Hydrocarbon Components to Products in the Catalytic Pyrolysis of Sawdust by Natural Catalysts

Nattadon Pannucharoenwong,[1] Snunkhaem Echaroj,[1,*] Keyoon Duanguppama,[2,*] Suwipong Hemathulin,[3] Chinnapat Turakarn,[2] Kumpanat Chaiphet[2] and Phadungsak Rattanadecho[1]

Abstract

The research aims to enhance the hydrocarbon components in the products acquired from the fast pyrolysis of sawdust, employing natural zeolite and dolomite catalysts. The investigation focuses on assessing the impact on yield, properties, and energy content of the products. The experiment involves utilizing 1 kg of biomass, lasting for 1 hour, and incorporating 1 kg of catalyst. The catalyst was introduced into both the reactor and the hot filter. The results show that the application of natural zeolite and dolomite catalysts in sawdust pyrolysis leads to a reduction in bio-oil yield of ~2 wt% while simultaneously enhancing gas production. This is attributed to the catalysts alteration of the chemical make-up of pyrolysis vapor, resulting in elevated concentrations of carbon and hydrogen in the bio-oil. The results of the analysis of the bio-oil also show that the natural zeolite catalyst increases the heating value up to 38.1 MJ/kg. The results of the chemical composition analysis indicate that the two catalysts helped to increase the composition in the hydrocarbon group. In catalytic pyrolysis, the char product experiences an augmentation in both carbon and hydrogen content, leading to a higher calorific value. The experimental outcomes suggest that for enhancing energy efficiency in bio-oil, the utilization of natural zeolite catalysts is recommended. Conversely, to bolster efficiency in gas products, the preferred choice is the deployment of dolomite catalysts.

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1. Introduction

Energy plays a crucial role in propelling economic activities. Plus, nations worldwide are actively exploring potential energy sources to bolster their national economies. Biomass is prominent as a promising energy source with the capacity to be converted into various forms of energy, including fuel,[1-3] charcoal,[4,5] and fuel gas.[6-8] Numerous studies delve into the transformation of biomass to alternative energy, with the procedure of fast pyrolysis being a notable method that yields concentrated liquid fuel products. Historically, the challenge with this fuel lay in its relatively low quality, making it challenging to utilize effectively. Consequently, ongoing research is dedicated to enhancing the quality of this liquid fuel, both during and after the production process.

Enhancements in fuel quality primarily target elevating the calorific value. The calorific value of fuel is subject to improvement based on the yield of substances within the hydrocarbon group, with hydrogen and carbon constituting the principal components. To introduce hydrogen during the fast pyrolysis of biomass has the ability to influence product distribution and improve quality of the resulting bio-oil. Fast pyrolysis is a swiftly conducted thermal decomposition process carried out at reaction temperatures (typically 450-550 °C)[9] and brief residence times, yielding bio-oil, char, and gas. Catalytic pyrolysis is another method that improves the calorific value of fuel to improve its quality.[2] This phenomenon arises due to the catalyst influence, which facilitates alterations in the chemical composition of the pyrolysis vapor, thereby augmenting the quantities of hydrogen and carbon.[3] Pyrolysis causes the biomass to decompose into vapor under oxygen-free conditions. In

[1] *Department of Mechanical Engineering, Faculty of Engineering, Thammasat School of Engineering, Thammasat University, Bangkok, 10100, Thailand.*
[2] *Department of Mechanical and Mechatronics Engineering, Faculty of Engineering and Industrial Technology, Kalasin University, Kalasin, 46000, Thailand.*
[3] *Department of Mechanical and Industrial, Faculty of Industrial Technology, Rajabhat Sakon Nakhon University, Sakon Nakhon, 47000, Thailand.*
**Email:* snunkha@engr.tu.ac.th (S. Echaroj), keyoon.du@ksu.ac.th, k_duanguppama@hotmail.com (K. Duanguppama)

contact with the surface area and pores of the catalyst, the chemical structure of the pyrolysis vapor cleaves bonds that have large molecules separated from small ones. Large molecule oxygen is separated from smaller molecules hydrogen and carbon. Vapor with smaller molecules travels faster and condenses into a liquid. When vapor containing large molecules is condensed into a liquid, layer separation occurs. As a result, the liquid formed in the part that has hydrogen and carbon as the main components will have an increased heat value.

Most catalysts used in pyrolysis are solid and installed inside the reactor. There are synthetic and natural catalysts such as ZSM-5,[10,11] $CoMo/Al_2O_3$,[12] $NiMo/Al_2O_3$,[13] $CuCO_3$[14,15] $NiCO_3$,[15,16] $SrCO_3$,[15,17] $MgCO_3$,[15,18] $CdCO_3$,[15,19] $FeCO_3$,[20] CaO,[21] Al_2O_3,[22] MgO,[23] kaolin,[3,24] natural zeolite,[2,3,25] and dolomite,[2,3] *etc*. Natural zeolite and dolomite are natural catalysts cheap and easily available. This catalyst preparation method can be calcined at 500 °C for 4 hours[2,3] to form pores and be ready for biomass pyrolysis. It was reported that natural zeolite and dolomite catalysts improved the heating value of bio-oil from *Leucaena Leucocephala* pyrolysis up to 7 MJ/kg.[2] Natural zeolite and dolomite catalysts must undergo a fine grinding process and particle size selection to suit the pyrolysis unit. Because of its use in fluidized-bed reactors, the catalyst must be able to lift itself when carrier gas is released into the system. While in the hot filter, the catalyst must not affect the pressure drop across the system. It is not clear how fast pyrolysis of sawdust in fluidized-bed reactors using natural zeolite and dolomite catalysts will affect hydrogen, carbon, and calorific value of the bio-oil. Moreover, this work wants to study techniques for installing different types of catalysts in a fluidized-bed reactor and a fixed-bed hot filter on the same production process.

Hence, the main emphasis of this document is to enhance the hydrogen content in the products derived from the fast pyrolysis of sawdust employing natural zeolite and dolomite catalysts. The investigation seeks to analyze the impact on yield, properties, and energy content of the products obtained through fast pyrolysis.

2. Materials and methods

2.1 Biomass raw materials

The biomass samples utilized in this document consisted of sawdust sourced from Kalasin Province, Thailand. The biomass underwent a process of sun-drying, grinding, and sieving, resulting in particles ranging from 0.6 to 3 mm. Before conducting the fast pyrolysis experiments, the biomass samples underwent drying using the oven method or standard method, with a temperature set at 105 °C for 24 hours to decrease the moisture components to 7.8 wt%. The analysis of the heating value, conducted in accordance with DIN 51900 using an S.M.D. Torino Bomb Calorimeter, indicated a higher heating value (HHV) of 20.2 MJ/kg.

Lower heating value (LHV) Eq. 1

$$LHV\left(\frac{MJ}{kg}\right) = HHV - 21.822\left(\frac{Hydrogen}{100}\right) \quad (1)$$

Table 1. Characteristics of sawdust.

Analysis	
Proximate (*wt%, dry basis*)	
Volatile matter	82.4±2.1
Fixed carbon	16.2±1.4
Ash	1.4±2.4
Moisture	7.8±1.8
Ultimate (*wt%, dry basis*)	
Carbon	48.2±2.3
Hydrogen	5.7±1.7
Nitrogen	0.3±1.3
Sulfur	0.8±2.2
Oxygen	45.0±1.6
HHV (MJ/kg)	20.2±2.0
LHV[a] (MJ/kg)	19.0±1.3

[a]Tallied by Eq. 1

2.2 Fluidizing medium

Silica sand acts as a heat transfer medium for non-catalytic pyrolysis. Before experimentation, sand underwent a calcined process at 500 °C for 4 hours and was subsequently filtered to achieve a particle dimension ranging from 200 to 500 µm. The sand possessed a denseness of 1,200 kg/m³, and approximately 500 g of sand was utilized for each experiment. The properties of silica sand are mean particle diameter 0.25 mm, coefficient of uniformity (C_u) 1.27, coefficient of curvature (C_c) 0.97.

2.3 Catalysts

Natural zeolite and dolomite catalysts were calcined in a furnace under atmospheric pressure at 500 °C for 4 hours. Subsequently, they were filtered to attain a particle dimension of 0.2-0.5 mm for the primary reactor and a particle size for the secondary reactor of 0.5-3 mm. The primary and second reactors used approximately 500 g of catalyst. The catalysts, comprising natural zeolite and dolomite, underwent characterization using the Brunauer-Emmett-Teller (BET) approach with the Automatic specific surface area/pore size distribution measurement model Belsorp-mini. The properties of these catalysts are outlined in Table 2.

2.4 Fast pyrolysis instrument

The biomass was pyrolyzed quickly in a fluidized-bed reactor unit designed and built by the Department of Mechanical and Mechatronics Engineering, Faculty of Engineering and Industrial Technology, Kalasin University, Thailand. A schematic diagram depicting its design is presented in Fig. 1. The primary components of this unit include a biomass hopper, a fluidized-bed reactor (primary reactor), a hot filter (secondary reactor), two cyclone separators, a water-cooled condenser, an ESP condenser, and an ice/salt condenser.

Constructed from a glass tube, the biomass hopper possesses a capacity that accommodates approximately 0.01 m³ or 1 kg of sawdust. To facilitate the feeding of biomass

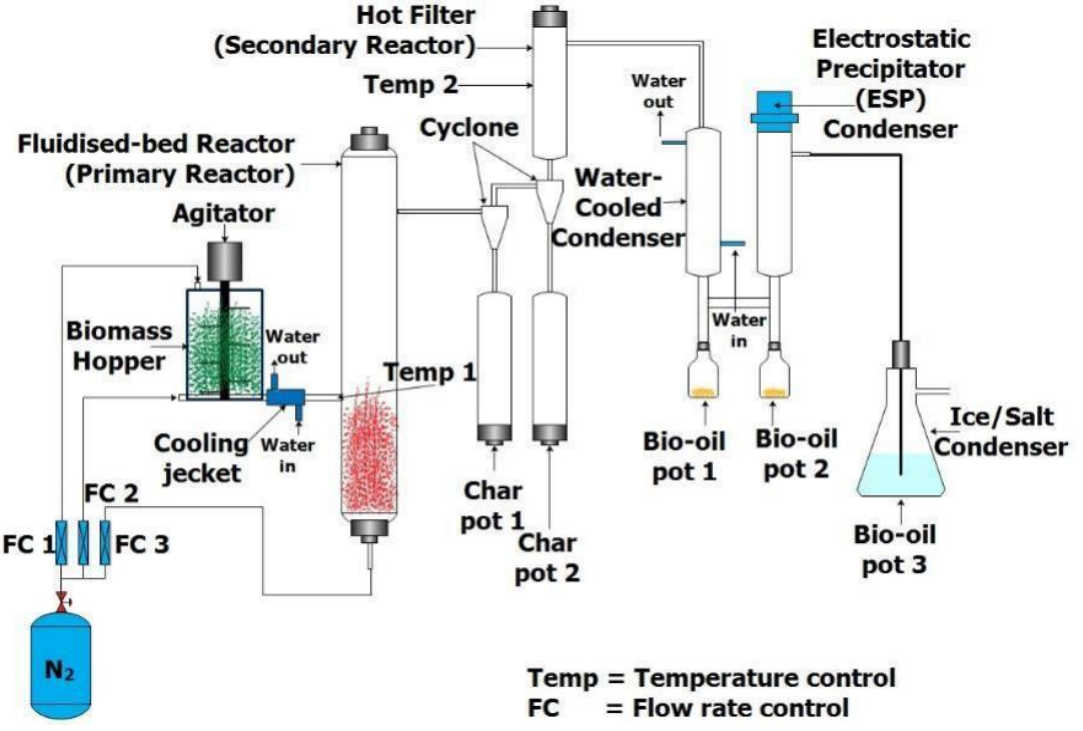

Fig. 1 Diagram of the fast pyrolysis unit. Reproduced with the permission from [25].

Table 2. Catalyst properties.

Catalysts		Bulk density ($kg.m^3$)	Particle density ($kg.m^3$)	BET surface area ($m^2.g^{-1}$)	Mean pore diameter (nm)	Total pore volume ($cm^3.g^{-1}$)	Si/Al ratio
Type	Calcination Temperature/Time						
Natural zeolite	500 °C for 4 hrs	700	1,165	14	25.4	0.068	12.34
Dolomite	500 °C for 4 hrs	1,128	1,728	32.6	13.7	0.20	N/A

particles into the primary reactor, a feeding tube, equipped with a cooling jacket to prevent premature pyrolysis, is employed, with the particles transported by a nitrogen flow entrainment. The primary reactor, cyclones, and secondary reactor are crafted from 304 stainless steel tubing. The primary reactor has an internal diameter of 100 mm and a height of 800 mm. The fast pyrolysis unit utilized in this study is depicted in Fig. 2.

The initial and subsequent cyclones were specifically depicted to eliminate fine char fragments from the pyrolysis vapor then deposit those fragments into the char container. The secondary reactor employed a fixed bed configuration. For the experimental setup, approximately 500 g of catalyst was introduced into the primary and secondary reactors.

The bio-oil collection system comprised a water-cooled condenser (bio-oil pot 1) ~30 °C, an electrostatic precipitator (ESP) condenser (bio-oil pot 2), and an ice/salt condenser (bio-oil pot 3). The condenser that cooled the water functioned as a mechanism that exchanged heat. Operating at 15 kV DC, the ESP was employed to assist in the collection of bio-oil. The ice/salt condenser, operating as a glass tube heat exchanger, maintained a temperature of approximately -15 °C. The primary and second reactors are heated by automatically controlled heating coils. The operation of the heating coil is activated by a temperature controller with a thermocouple acting as a sensor. The heating coil receives a voltage of 220 volts when the detected temperature is lower than the specified temperature and stops receiving voltage when the temperature is reached. The heating coils in each reactor are rated at 2500 watts.

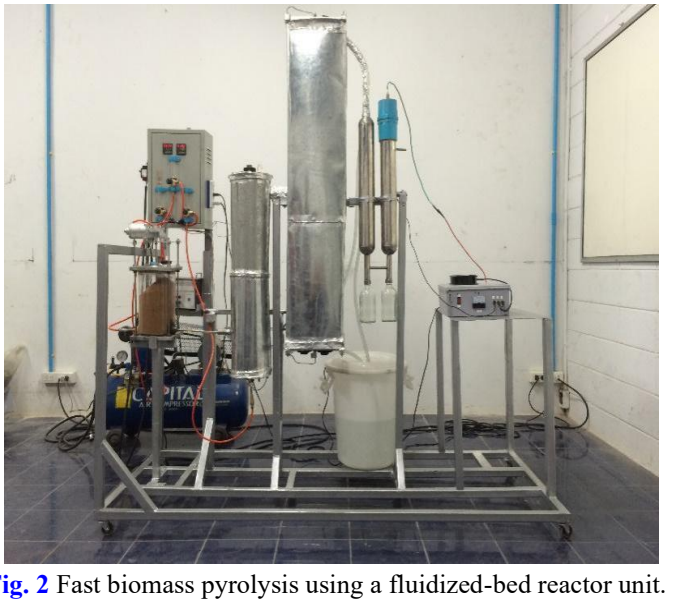

Fig. 2 Fast biomass pyrolysis using a fluidized-bed reactor unit.

2.5 Fast pyrolysis experimentations

The pyrolysis temperatures, as indicated and regulated at Temp1 (Fig. 1), were maintained at 500 °C. The hot filter and cyclone (Temp2) were set to a reaction temperature of 500 °C. The heat source received by the reactor and hot filter is a 2500-watt heating coil. Automatic operation control with temperature controller and K type thermocouple. The reaction temperature detection error is approximately ± 3 °C. The nitrogen flow rates at the upper section (FC1) and the side section (FC2) of the hopper were roughly 5 L/min, with the fluidizing nitrogen flow (FC3) configured at 20 L/min. In each experiment, biomass in the region of 1 kg was inserted into the reactor at a feeding 1 hr. The heated components and reactor finally cooled to room temperature once the pyrolysis experimentation ended. Afterward, the reactor was weighted for mass balance calculations.

Non-catalytic pyrolysis is used, 500 g of silica sand is loaded in the reactor and another 500 g in hot filter. In the catalytic pyrolysis process, two types of catalysts, as dictated by the experimental conditions, were strategically placed in the reactor and hot filter. This involved the use of 1 kg of catalyst inserted in the reactor and the hot filter to react with the biomass and pyrolysis vapor. To ensure control over experimental variables, the catalysts were replaced after every fast pyrolysis experiment involving sawdust.

2.6 Product and energy

The prominent output from fast pyrolysis encompassed bio-oil in liquid form, char, and non-condensable gases. To quantify the return for every part, all components of the fast pyrolysis network, including biomass, catalyst, fluidized-bed reactor, cyclone separators, hot filter, and the product collection unit, were weighed both before and after each experiment. The determination of total bio-oil yields contained the liquid weight collected from the product collection unit, which includes the water-cooled condenser (bio-oil pot 1), ESP condenser (bio-oil pot 2), and ice/salt condenser (bio-oil pot 3). Char yields were established by combining the solid masses gathered from the cyclones, reactor, transfer line and char pot. Gas yields were computed by taking the remainder in mass.

$$Bio-oil\ yield\ (wt\%) = \frac{W_{bio-oil\ pot\ 1}+W_{bio-oil\ pot\ 2}+W_{bio-oil\ pot\ 3}}{W_{biomass,\ db}} \times 100 \quad (2)$$

$$Char\ yield\ (wt\%) = \frac{W_{solid\ in\ reacter,\ hot\ filter,\ cyclone,\ db}}{W_{biomass,\ db}} \times 100 \quad (3)$$

$$Gas\ yield\ (wt\%) = 100 - (Bio-oil\ yield, wt\%) - (Gas\ yield, wt\%) \quad (4)$$

$$Heavy\ bio-oil\ yield\ (wt\%) = \frac{W_{bio-oil\ pot\ 1}+W_{bio-oil\ pot\ 2}}{W_{biomass,\ db}} \times 100 \quad (5)$$

$$Light\ bio-oil\ yield\ (wt\%) = \frac{W_{bio-oil\ pot\ 3}}{W_{biomass,\ db}} \times 100 \quad (6)$$

$$Heavy\ bio-oil\ in\ WC\ condenser\ yield\ (wt\%) = \frac{W_{bio-oil\ pot\ 1}}{W_{biomass,\ db}} \times 100 \quad (7)$$

$$Heavy\ bio-oil\ in\ ESP\ condenser\ yield\ (wt\%) = \frac{W_{bio-oil\ pot\ 2}}{W_{biomass,\ db}} \times 100 \quad (8)$$

$$Energy\ yield\ (\%) = \frac{HHV_{product} \times Product\ yield}{HHV_{biomass}} \times 100 \quad (9)$$

$$Energy\ efficiency = \frac{Energy\ yield}{Product\ yield} \quad (10)$$

2.7 Bio-oil analysis

Elements that come from heavy bio-oil have two sources: electrostatic precipitator (ESP) and the water-cooled heat exchanger. These heavy bio-oil products were subjected to a comprehensive examination covering the contents of various materials such as water, solids, ash, density, pH value, high heating value, stability, and viscosity.

Heavy bio-oil is denser than water while light bio-oil is less dense than water. As light bio-oil cannot ignite or help fire and is highly acidic, it was not used for fuel properties analysis. All analyses were conducted in triplicate to guarantee the precision and dependability of the outcomes.

2.7.1 Water content

The determination of water content in the bio-oil followed ASTM E203 standards, employing volumetric Karl Fischer titration with a Mettler Toledo V20 instrument. The titration reagent utilized was Merck Combi titrant 5 keto, and Merck Combi solvent keto served as the titration solvent. This titration process was conducted in triplicate to ensure accuracy and consistency in the results.

2.7.2 Solids content

The determination of solids components in the bio-oil adhered to ASTM D7579 standards, involving the use of a methanol-dichloromethane (1:1) mixture to identify indissoluble substance through a filtering method. About 1-2 g of pyrolysis -oil was purified using a previously dry and weight Whatman No. 3 quality filter paper with a 6 µm particle retention. Subsequently, the pyrolysis-oil underwent washing with dichloromethane until the filtered solution became transparent, ensuring the filter paper was free of any remaining organic liquid. The filler paper that had contents left over, spent a duration of 15 minutes drying, before being placed in a stove for 30 minutes at 105 °C, before being inserted into a glass container to bring the temperature down and then its weight was measured. Then, utilizing the technique recommended by Oasmaa and Peacocke.[26] The contents were then added as the percentage of solid leftovers.

2.7.3 Ash content

In agreement with DIN EN 7 standards, the bio-oil and its ash components were evaluated. Around 3 g of bio-oil placed in a container that had been already heated and dried underwent heating for 12 hours at 105 °C. This process was to prevent foaming and splashing by eliminating volatile compounds and water. Subsequently, the sample was heated again for 24 hours at 775 °C or whenever a constant weight was achieved. The

number of rigid sediments during the previous pyrolysis-oil was then tallied up as the ash component.

2.7.4 pH value

The pH of the pyrolysis-oil was determined using a UB-10 Denver instrument pH meter. Before analysis, the pH meter was calibrated using buffer solutions with pH values of 4, 7, and 10. For each experimental run, approximately 10 ml of bio-oil sample was analyzed.

2.7.5 Density

A 5 ml density vial at room temperature (~30 °C) determined the density of pyrolysis-oil.

2.7.6 Flash and fire point

The flash and fire points represent the lowest temperature where a fluid converts to a vapor capable of creating an ignitable blend with the air near its surface. Lower flash points and fire points indicate greater ease of igniting a liquid solvent. In the case of bio-oil, these properties were measured in line with ASTM D93 standards.

2.7.7 Heating value

Using the DIN 51900 approach, the higher heating value (HHV) of bio-oil which was determined on an as-produced basis, was assessed utilizing the S.M.D. Torino bomb calorimeter. Bio-oil sample of around 1 g, contained in a cup, was positioned in a reaction chamber or a bomb. The bomb contained an inordinate level of oxygen and subsequently submerged in a container holding 2,000 ml of water. Using electrically heated cables the bio-oil sample was set alight, and any variation in the temperature of the water was captured electronically. The bomb calorimeter has been calibrated using benzoic acid.

2.7.8 Viscosity and storage stability

ASTM D445 method was employed to investigate bio-oil's kinematic viscosity. At a size of -350, an opaque Cannon-Fenske viscometer, at a constant temperature of 40 °C was used. The rate at which the change of bio-oils, new and old, determined the stability of pyrolysis-oil. Within 24 hours, the viscosity of the fresh pyrolysis-oil (ν_{fresh}) was calculated. In contrast, after storing pyrolysis-oil was kept in an airtight vessel at 80 °C up to 24 hours, similar to reserving it for 1 year at room temperature[27] the viscosity of aged bio-oil (ν_{aged}) was calculated.

$$viscosity = \frac{\nu_{aged} - \nu_{fresh}}{\nu_{fresh}} \times 100\ (\%) \quad (11)$$

$$Ageing\ rate = \frac{\nu_{aged} - \nu_{fresh}}{24}\ cSt/hr \quad (12)$$

2.7.9 Elemental in bio-oil

The elemental examination of pyrolysis-oil, aiming to determine the quantities of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S), was carried out applying CHNS elemental analyzer, specifically the Micro-Tru Spec CHNS/O model. In this process, approximately 0.2 grams of the sample, contained in a tin cup, was placed in a combustion chamber (Lodding chamber) where oxygen aided in combustion. The combustion yielded carbon dioxide (CO_2), nitrogen (N), and sulfur dioxide (SO_2), and then conveyed into the inspection system using helium gas.

In the analysis, the system assessed the carbon (C), hydrogen (H), and sulfur (S) content by absorbing infrared in the IR cell. Concurrently, the nitrogen (N) content was determined by eliminating the heat of carbon dioxide (CO_2) and water (H_2O) using Lecosorp and Anhydrous, respectively. The resulting values were expressed as percentages for carbon (C), hydrogen (H), nitrogen (N), and sulfur (S). The element oxygen (O) content was calculated by subtracting the combined weight percentages of carbon, hydrogen, nitrogen, and sulfur from 100.

2.8 GC/MS of pyrolysis-oil analysis

Bio-oil was diluted in methanol-dichloromethane (1:1) to achieve a 10 wt%. After injection, the sample group underwent filtration through a Filtrex nylon filter with a pore size of 0.2 µm. Afterwards, gas chromatography/mass spectrometry (GC/MS) examination of the pyrolysis-oil was conducted with a SHIMADZU Gas Chromatograph Mass Spectrometer model GCMS-QP2010. The separation occurred on a Restek Rtx-5MS column (30 m × 0.25 mm id, USA) with a film thickness of 0.25 µm, characterized by a phase composition of 95% dimethylpolysiloxane and 5% diphenyl. The first GC oven was set for 2 minutes at 60 °C, and then scheduled to increase from 60 °C to 270 °C at a rate of 5°C/min. The injector temperature was set at 270°C with a split ratio of 100, helium used as the carrier gas with a linear velocity of 40 cm/s. Connected directly to a metal quadrupole mass filter was the capillary column, with a pre-rod Mass Analyzer and Electron Multiplier detector.

Data acquisition was performed for compounds with molecular weight range from 20 to 650 m/z and analysed using the SHIMADZU LabSolutions GCMS solution software. This analytical approach was suggested by Duanguppama et al.[28] The mass spectrometer has an ionization energy of 70 eV, operated under the electron impact (EI) mode and an ion sources/interface temperature of 230 and 250 °C, respectively.

2.9 Char analysis

The analysis involved examining both char composition and various properties of the biomass. These properties encompassed ash content, bulk density, particle density, high heating value, low heating value, and elemental composition.

2.10 Non-condensable gas analysis

Non-condensable gases that are analyzed are samples collected during experiments using vacuum tubes. After the experiment ended, the gas was immediately sent for analysis. The columns used to analyse composition of non-condensable gas were Porapak N (80/100 SS 2.3 mm I.D. × 1 m) and

Unibeads C (60/80 SS Col. 3 mm I.D. × 2 m). High-purity argon (99.995%) was employed as the carrier gas. The hydrogen concentrations value (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), ethene (C_2H_4), nitrogen (N_2) and ethane (C_2H_6) were measured.

3. Results and discussion

The experimental results and discussion encompass product yield, bio-oil properties, char characteristics, gas composition, and product energy. All experiments were conducted under consistent conditions, with a reaction temperature of 500°C, biomass feed rate of 1 kg/hr, and an experimental period of 1 hr.

3.1 Product yields

In Fig. 3, NZ is Natural Zeolite Catalyst and DM is Dolomite Catalyst. The product yield indicates that pyrolysis without a catalyst resulted in the highest bio-oil yields, reaching 65.4 wt%. Conversely, pyrolysis with natural zeolite and dolomite catalysts a bio-oil yields was decreased. The bio-oil yield experienced a slight decrease within the range of 63.1-63.9 wt%. This decline can be attributed to the second cracking of pyrolysis vapor, leading to increased gas production. Notably, the use of the catalyst gave rise to a higher gas yield, exceeding 21 wt%.

Upon examining Fig. 3, the char obtained from the fast pyrolysis of sawdust, both with and without a catalyst, exhibits a slightly different yield in the range of 15.1-15.8 wt%. The product yield from the fast pyrolysis of sawdust in this study aligns with the quantity of bio-oil observed in the experimentation already processed by Duanguppama et al.[2], focusing on the fast pyrolysis of *Leucaena Leucocephala*.

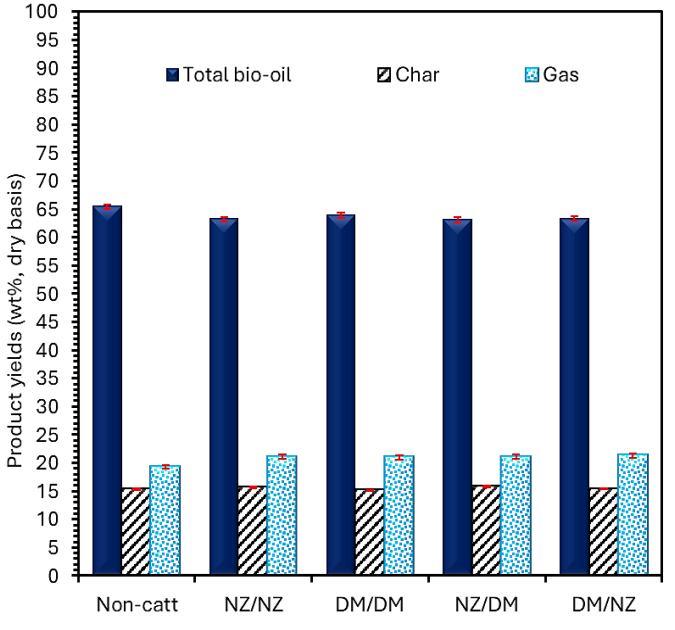

Fig. 3 Effect of catalysts on main product yields.

In Fig. 4, the distribution of pyrolysis-oil generated from the manufacturing procedure is illustrated, highlighting that substantial pyrolysis-oil constitutes the predominant portion of the total bio-oil. Heavy bio-oil is the main proportion of total bio-oil. But when pyrolysis was carried out with a catalyst, the proportion of light bio-oil increased more than twofold. It is therefore possible that the catalyst helped the pyrolysis vapor become so small that it could not be condensed by the primary condenser. The yield of bio-oil in the case of using the two types of catalysts is not much different.

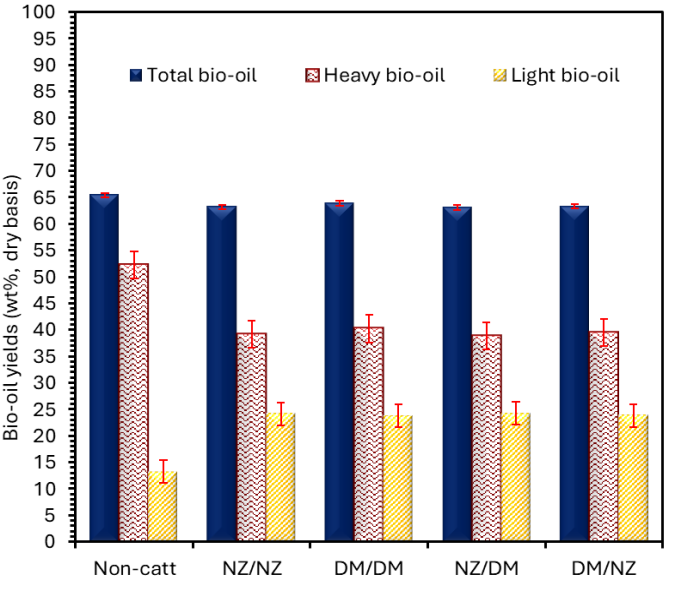

Fig. 4 Effect of catalysts on bio-oil yields.

The decrease in heavy bio-oil pertains to the conversion of the initial, more substantial bio-oil constituents into lighter and more valuable products. It may be influenced by the following factors. Catalytic pyrolysis encompasses cracking reactions, where the larger and heavier molecules present in the bio-oil[29] undergo decomposition into smaller and lighter hydrocarbons. During catalytic pyrolysis, hydrogen transfer reactions[30] may take place, causing the saturation of double bonds in the bio-oil components. This, in turn, causes a drop in the molecular weight of the bio-oil. Catalytic pyrolysis facilitates deoxygenation reactions,[31,32] wherein oxygen is eliminated from these functional groups, resulting in the formation of lighter hydrocarbons.

As depicted in Fig. 5, heavy bio-oil containing substantial macromolecules is prone to condensation by the water-cooled condenser. This outcome stems from the combination of pyrolysis vapor until it achieves sufficient density to overcome gravity and transition into a substantial liquid state. The vapor produced from pyrolysis without a catalyst may encompass larger molecules, allowing for a more substantial condensation into liquid form.

Upon evaluating the type and placement of catalyst installation in relation to the product obtained from the fast pyrolysis of sawdust, no differences in yields are observed. Consequently, it can be inferred that fast pyrolysis of sawdust with regular zeolite and dolomite catalysts led to a drop in bio-

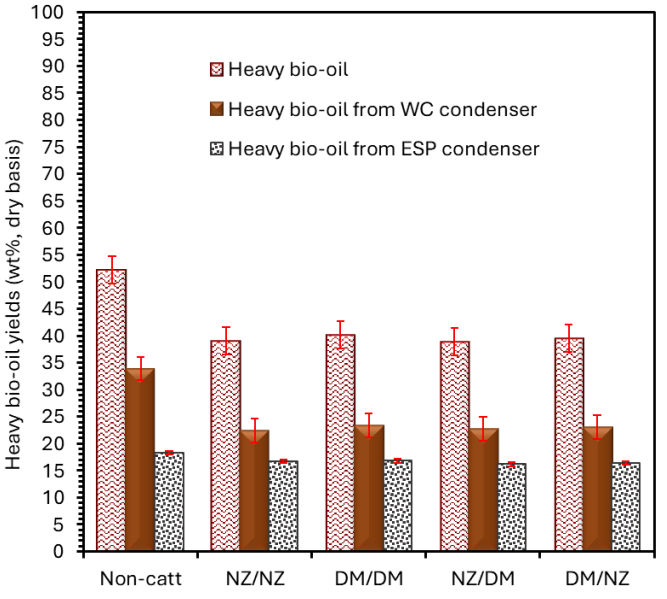

Fig. 5 Effect of catalysts on heavy bio-oil yields.

oil yield and an elevation in gas supply. However, the outcomes of pyrolysis with both catalysts and different installation locations demonstrated no variance in product yields.

3.2 Bio-oil properties

Bio-oil or pyrolysis-oil acquired through the fast pyrolysis of sawdust is categorized in two segments: substantial pyrolysis-oil and insubstantial pyrolysis-oil. The primary focus of analysis is substantial pyrolysis-oil because of the significance it holds in terms of properties. Light bio-oil, comprising over 60% water, is excluded from fuel properties examination. The bio-oil for properties analysis was bio-oil from the water-cooled condenser (WC condenser) and the electrostatic precipitator condensing unit (ESP condenser).

The results of the analysis of the water content in bio-oil found that in the case of pyrolysis with natural zeolite and dolomite catalysts, the water content in bio-oil decreased. The bio-oil from the electrostatic precipitator condenser had a water content approximately 2 wt% lower than the bio-oil from the water-cooled condenser. Natural zeolite catalysts reduce water formation in bio-oil more than dolomite catalysts. As illustrated in Table 3, the fast pyrolysis of sawdust with catalysts caused a twofold reduction in solid components within the bio-oil. Specifically, installing a natural zeolite catalyst in the hot filter and reactor resulted in a solid content as low as 0.1 wt%. This decline in solid content in pyrolysis-oil is likely accredited to various factors. The catalyst promotes the cracking of larger molecules into smaller liquid hydrocarbons, thereby extenuating the formation of solid char.[33,34] The catalysts demonstrate a preference to produce pyrolysis-oil over solid char or other by-products.[35-37] The catalysts selectively enhance the manufacturing of liquid contents, resulting in a decrease in solid content.[38,39] Consequently, it is noted that the dolomite catalyst facilitates this reaction more effectively than the natural zeolite catalyst. In both solid pyrolysis and vapor pyrolysis positions, such reactions can occur comprehensively. This effectiveness is anticipated due to the sizable exterior region and small pore structure of the dolomite catalyst, promoting the reaction exceptionally well.

The drop in solids in the pyrolysis-oil can improve properties across various aspects of the bio-oil. The ash components of the bio-oil saw a significant reduction of up to three times when pyrolysis was conducted with natural zeolite and dolomite catalysts. Consequently, the resulting bio-oil exhibits a reduced density that closely aligns with that of petroleum fuels. Moreover, the catalyst brings about a more than threefold reduction in the fluidness of the pyrolysis-oil. During an examination of the storage durability of this bio-oil, it was found that the rate of change in viscosity was very low. The reduction in solids content in the bio-oil imparts several beneficial characteristics to the bio-oil.

The catalyst significantly reduces the solid content in the bio-oil, resulting in a noticeable reduction in viscosity. Therefore, a reduction in solid content may mitigate the likelihood of sedimentation and agglomeration, contributing to enhanced storage stability.[40] Lower solid content also diminishes the risk of clogging in pipelines and storage tanks.[41] Over time, solid particles have the potential to settle, causing blockages, particularly in systems with low flow rates. The decrease in solid content can enhance the filterability of bio-oil, facilitating the filtration of remaining particles and impurities.[42] in the production process or before end-use. If the reduction in solid content is coupled with smaller particle sizes, the suspension of residual particles in the bio-oil may exhibit greater stability.[43] Furthermore, pyrolysis-oil with lesser solid components is further readily ignited. Table 3 indicates that bio-oil obtained from catalytic pyrolysis is up to 50% more flammable.

The elemental content in Table 3 indicates an obvious drop in the oxygen content of pyrolysis-oil by catalytic pyrolysis. In particular, the hefty pyrolysis-oil from the ESP condenser, obtained by pyrolysis with a natural zeolite catalyst, exhibited the lowest oxygen content, reduced to 15.8 wt%. Concurrently, there was a substantial increase in the carbon and hydrogen contents of the pyrolysis-oil. The increased amount of hydrogen in catalytic pyrolysis results from a proportion of hydrogen being separated from oxygen, which is water in the bio-oil. The natural zeolite catalyst elevated the carbon and hydrogen contents of the bio-oil to 70.5% and 13.4 wt%, respectively. Due to these changes, the pyrolysis-oil obtained from this catalyst exhibits the most calorific content. Specifically, the substantial pyrolysis-oil from the ESP condensing unit reached a maximum heating rate of 38.1 MJ/kg. When comparing the catalyst types, natural zeolite demonstrates a more significantly improved heating value compared to dolomite, especially when installed at the hot filter position.

From Table 3, it becomes evident that natural zeolites are

Table 3. Characteristics of heavy pyrolysis-oil.

Characteristics	Heavy bio-oil from		Non-catt	NZ/NZ	DM/DM	NZ/DM	DM/NZ
Water content (wt%)	WC condenser		14.6±0.8	12.7±0.9	13.2±0.1	13.8±0.2	13.4±0.2
	ESP condenser		12.6±0.9	10.4±0.8	11.2±0.1	11.3±0.8	11.1±0.6
Solids quantity (wt%)	WC condenser		0.5±0.1	0.2±0.1	0.1±0.1	0.2±0.1	0.2±0.1
	ESP condenser		0.4±0.1	0.2±0.1	0.1±0.1	0.1±0.1	0.2±0.1
Ash (wt%)	WC condenser		0.3±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1
	ESP condenser		0.3±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1
pH	WC condenser		2.1±0.2	3.3±0.2	3.3±0.2	3.2±0.1	3.3±0.2
	ESP condenser		2.6±0.2	4.5±0.2	4.4±0.1	4.6±0.1	4.5±0.2
Density (kg/m^3)	WC condenser		1132±3.2	1031.7±2.5	1072.3±2.6	1052.1±2.1	1013.8±2.2
	ESP condenser		1283.1±2.4	1150.7±3.1	1131.8±2.8	1108.9±2.7	1143.6±2.5
Flash point (°C)	WC condenser		218.9±2.1	139.4±1.7	133.7±2.6	134.9±1.4	130.5±1.1
	ESP condenser		205.6±3.4	117.8±2.5	115.4±1.5	119.1±2.5	110.3±2.7
Fire point (°C)	WC condenser		272.1±2.2	194.3±3.2	197.6±1.9	193.8±3.1	190.4±3.1
	ESP condenser		281.6±1.8	124.2±1.8	126.4±2.4	129.3±2.4	122.4±1.8
HHV (MJ/kg)	WC condenser		29.2±1.2	36.2±1.5	33.4±1.2	34.7±1.1	35.3±1.3
	ESP condenser		31.4±1.4	38.1±1.1	36.7±0.9	36.9±1.2	37.5±1.2
LHV (MJ/kg)	WC condenser		24.6±1.2	29.9±1.5	26.9±1.2	27.3±1.1	28±1.3
	ESP condenser		27.1±1.4	33.9±1.1	32.7±0.9	32.5±1.2	33.1±1.2
Viscosity at 40 °C (cSt)	WC condenser	Fresh	184.1±2.8	50.3±1.4	42.2±1.4	43.8±2.4	46.2±2.4
		Aged	403.9±2.4	98.9±1.4	67.3±2.8	73.8±1.4	80.3±2.4
	ESP condenser	Fresh	209.2±2.4	69.7±1.4	60±1.4	66.5±1.4	66.5±1.4
		Aged	477.7±2.8	137.1±1.4	111.9±2.4	116.8±2.4	121.7±2.4
Viscosity change (%)	WC condenser		119.4±4.5	96.8±2.7	59.6±1.3	68.8±6.9	73.8±3.9
	ESP condenser		128.3±1.6	96.6±6	86.5±2.2	75.7±7	82.9±2
Ageing rate (cSt/h)	WC condenser		9.2±0.2	2.0±0	1.0±0.1	1.3±0.1	1.4±0
	ESP condenser		11.2±0.1	2.8±0.1	2.2±0.1	2.1±0.2	2.3±0.1
Elemental in heavy bio-oil (wt%)	WC condenser	Carbon	52.2±0.1	60.5±0.1	57.8±0.1	56.6±0.1	56.1±0.1
		Hydrogen	2.2±0.1	8.2±0.1	9.4±0.1	8.4±0.1	9.7±0.1
		Nitrogen	0.1±0.1	0.4±0.1	0.3±0.1	0.4±0.1	0.6±0.1
		Sulfur	0.1±0.1	0.1±0.1	0.2±0.1	0.2±0.1	0.2±0.1
		Oxygen	45.3±0.1	30.8±0.1	32.3±0.1	34.4±0.1	33.3±0.1
	ESP condenser	Carbon	58.3±0.1	70.5±0.1	67.7±0.1	66.7±0.1	66.2±0.1
		Hydrogen	2.3±0.1	13.4±0.1	11.5±0.1	12.1±0.1	12.6±0.1
		Nitrogen	0.3±0.1	0.2±0.1	0.4±0.1	0.4±0.1	0.3±0.1
		Sulfur	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1
		Oxygen	39±0.1	15.8±0.1	20.3±0.1	20.7±0.1	20.8±0.1

more proficient in catalyzing oxygen removal reactions compared to dolomite. That's because natural zeolite catalysts clearly reduce the water content in bio-oil better. For this reason, the resulting bio-oil will have a reduced amount of oxygen. In summary, the dolomite catalyst appears to have the most pronounced impact on improving the viscosity, ash content, and storage stability of bio-oil. Conversely, natural zeolite catalysts exhibit a significant reduction in oxygen content and a notable increase in carbon and hydrogen. Notably, the installation of natural zeolite catalysts in hot filters results in a substantial enhancement of carbon and hydrogen content. As a result, it can be inferred that natural zeolite catalysts are particularly effective in enhancing the thermal properties of bio-oil.

Figure 6 illustrates that heavy bio-oil acquired from the WC condenser without a catalyst exhibited the highest acid content. The predominant acid identified was $C_8H_{14}O_2$ (2-Octenoic acid), constituting as much as 24.4%. Bio-oil produced via pyrolysis typically consists of a wide range of organic compounds. The presence of acids in the bio-oil is primarily attributed to the formation of carboxylic acids during the pyrolysis process. Pyrolysis entails the thermochemical breakdown of organic materials at elevated temperatures in an oxygen-deprived environment. During pyrolysis, intricate organic compounds like lignin, cellulose, and hemicellulose present in biomass undergo decomposition into smaller molecular fragments. Carboxylic acids are one class of compounds produced during this pyrolytic process.[44] Carboxylic acids are organic acids characterized by the presence of a carboxyl group (-COOH). The presence of oxygenated functional groups, notably carboxylic acids, in bio-oil can have a significant impact on its characteristics and

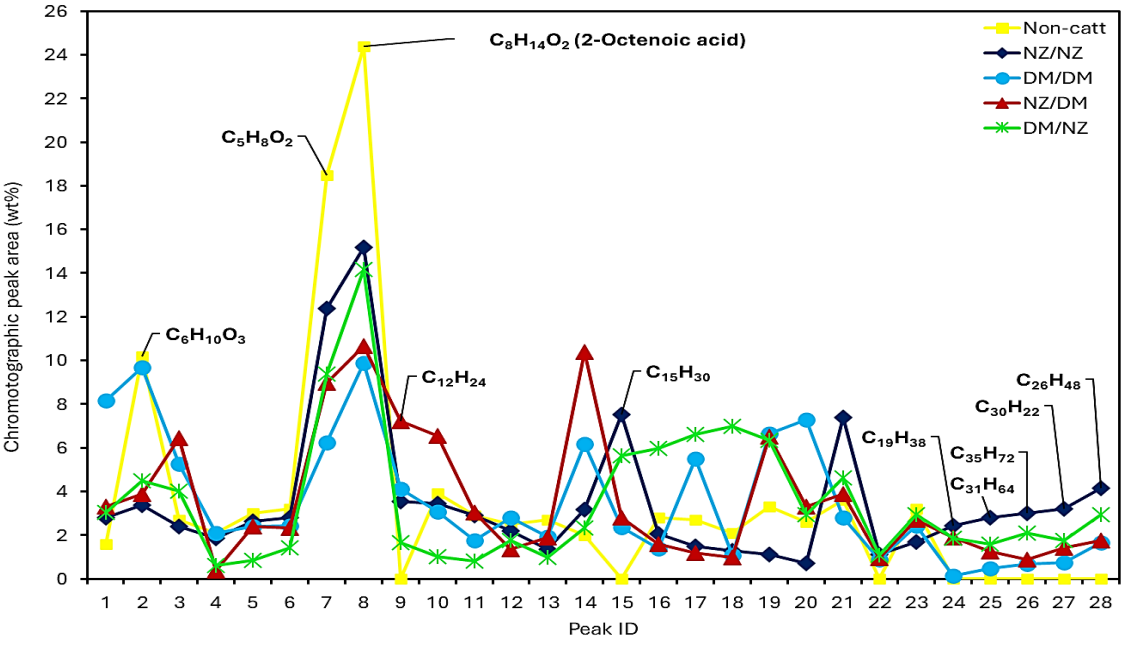

Fig. 6 Chromatograms in heavy bio-oil in WC condenser.

hold significant implications for its potential utilization, particularly in the realms of biofuels and chemical processes. During pyrolysis with natural zeolite and dolomite catalysts, a noticeable reduction in acid content is observed with an increased proportion of carbon and hydrogen. Consequently, pyrolysis-oil acquired from catalytic pyrolysis exhibits a high heating value. Natural zeolite catalysts notably augment the chemical composition of hydrocarbons, including but not limited to $C_{19}H_{38}$, $C_{31}H_{64}$, $C_{35}H_{72}$, $C_{30}H_{22}$, and $C_{26}H_{48}$. As a result, bio-oil obtained from pyrolysis with this catalyst demonstrates the highest heat value.

The chemical make-up analysis of the pyrolysis-oil from the ESP contractor in Fig. 7 reveals that acids constitute a predominant component in the bio-oil. During catalytic pyrolysis, there is a discernible trend of decreasing acid content. Peaks ID 14-20 distinctly illustrates that the reduction in acid content corresponds to an increase in the chemical composition of hydrocarbons. Consequently, bio-oil derived from catalytic pyrolysis exhibits a higher heat value. Notably, the chemical composition doesn't change depending on the kind of catalyst and where it is installed.

3.3 Characteristics of char

The properties of the char outlined in Table 4 indicate that the catalyst played a role in diminishing ash components of the char. This reduction in ash components is presumed to be a result of the catalyst enhancing the thorough decomposition of organic compounds in the biomass into gas. Consequently, this process may lower the carbon content in the final char, contributing to a reduced ash content. A decline in ash content in char also corresponds to a decrease in density, implying that reduced ash contributes to a lighter char.

Analysis of the elemental composition of char reveals that the catalyst can notably decrease the oxygen content while increasing the carbon and hydrogen content. Consequently, the calorific value of char experiences an approximate increase of 2 MJ/kg. The catalyst facilitates the cracking of larger molecules within biomass into smaller fragments during pyrolysis. This process leads to the elimination of oxygen functional groups including hydroxyl, carbonyl, and carboxyl groups,[45] resulting in the production of char with a higher carbon content. Oxygenated compounds present in biomass, such as alcohols, phenols, and acids, can undergo

Table 4. Char characteristics.

Characteristics		Non-catt	NZ/NZ	DM/DM	NZ/DM	DM/NZ
Ash	(wt%)	18.3±0.9	16.8±0.7	16.6±0.7	16.5±0.3	16.6±0.5
Bulk density	(kg/m^3)	112.4±2.5	104.2±2.9	105.4±1.3	107.5±0.8	105.6±1.1
Particle density	(kg/m^3)	388.4±2.6	370.2±3.1	370.9±1.7	370.4±1.4	373.3±2.5
HHV	(MJ/kg)	26.9±0.1	29.6±0.2	29.5±0.2	29.5±0.2	29.4±0.2
LHV	(MJ/kg)	26.2±0.1	28.4±0.2	28.3±0.2	28.4±0.2	28.2±0.2
Elemental in char (wt%)	Carbon	66.5±0.1	68.3±0.1	69.3±0.1	68.6±0.1	67.1±0.1
	Hydrogen	3.3±0.1	5.2±0.1	5.5±0.1	5.3±0.1	5.7±0.1
	Nitrogen	1.4±0.1	1.9±0.1	1.6±0.1	1.5±0.1	1.4±0.1
	Sulfur	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1
	Oxygen	28.7±0.1	24.6±0.1	23.6±0.1	24.6±0.1	25.8±0.1

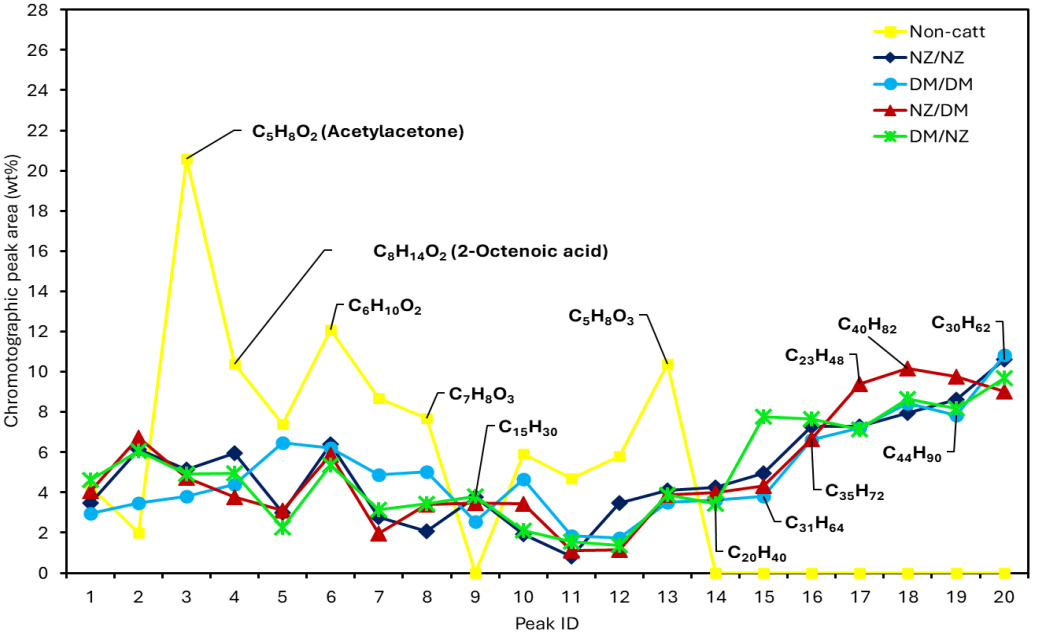

Fig. 7 Chromatograms in heavy pyrolysis-oil from the electrostatic precipitator condenser.

hydrodeoxygenation,[46] a process in which oxygen is replaced by hydrogen. Catalysts may enhance the polymerization of aromatic compounds,[47] resulting in the development of a more condensed and carbon-rich char structure.

Hence, it can be inferred that both natural zeolite and dolomite catalysts contribute to enhancing the char's quality. The reduction in ash and oxygen content leads to an increase in carbon, hydrogen, and calorific value. Both catalysts exhibit a similar capacity to enhance char quality.

3.4 Composition of gaseous products

The make-up of the gas, which cannot be condensed any further in Fig. 8 reveals a clear influence of the catalyst on the increased presence of Hydrogen, Methane, Ethene, and Ethane. The natural mineral-like solid catalyst, specifically, greatly enhances the composition of Hydrogen and Methane gases, whereas the dolomite catalyst significantly improves the composition of Ethene and Ethane gases. These gases are recognized for their high calorific values. Consequently, the augmentation of these gases contributes to an overall increase in the calorific value of the gas.

Catalysts play a crucial role in promoting reforming reactions that contribute to hydrogen production.[48] These catalysts aid in the decomposition of complex biomass molecules into smaller fragments, ultimately yielding hydrogen-rich compounds. Moreover, catalysts facilitate dehydrogenation reactions, converting hydrocarbons generated in pyrolysis into methane.[38] This secondary reaction typically follows the initial pyrolysis step, where catalysts actively promote the methanation of carbon-

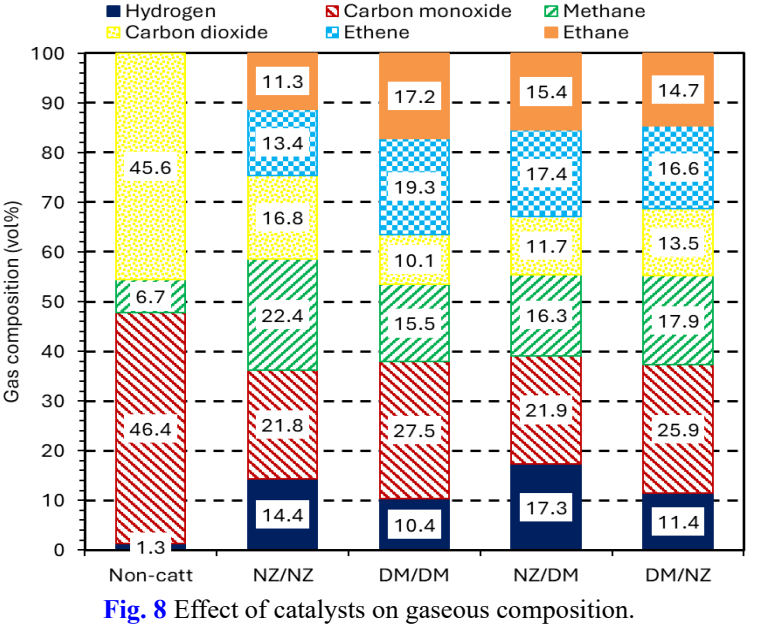

Fig. 8 Effect of catalysts on gaseous composition.

containing species, resulting in the formation of Ethene (C_2H_4) and Ethane (C_2H_6).[49] Catalysts are key in influencing the dehydrogenation of hydrocarbons,[50] leading to the production of ethene. Furthermore, ethene can undergo polymerization reactions, giving rise to higher hydrocarbons, including ethane.

3.5 Energy

The energy yields in pyrolysis-oil are reduced using a catalyst, as the pyrolysis-oil drops during catalytic pyrolysis. Although the catalyst increases the carbon and hydrogen component in pyrolysis-oil, leading to an uptick in calorific value, the overall yield diminishes. It's noteworthy that, among the two catalysts considered, natural zeolite exhibits a more pronounced increase in the energy yields of bio-oil in Fig. 9.

Although the energy content in bio-oil obtained from catalytic pyrolysis is relatively low, as depicted in Fig. 10, it is noteworthy that this catalyst yields the highest energy efficiency for the bio-oil. This suggests that the catalyst-induced alteration of the chemical structure of pyrolysis vapor, leading to an increased concentration of carbon and hydrogen, contributes to enhanced energy efficiency of the product. In the case of the dolomite catalyst, the highest energy efficiency in gas is achieved by augmenting the gas components Ethene (C_2H_4) and Ethane (C_2H_6). These insights provide valuable information for future experiments, guiding decisions on which products to prioritize in the biomass fuel production process.

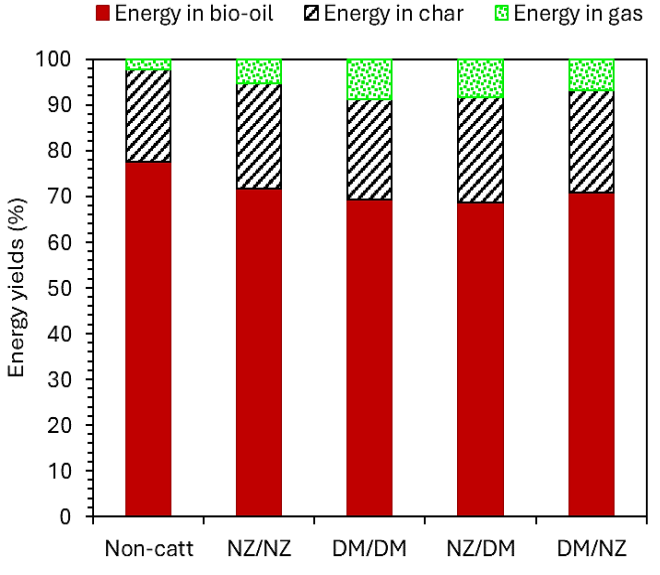

Fig. 9 Effect of catalysts on energy yields.

4. Conclusions

Application of the natural zeolite and dolomite catalysts in sawdust pyrolysis leads to a reduction in bio-oil yield was ~2 wt% while simultaneously enhancing gas production. This is attributed to the catalysts alteration of the chemical make-up of pyrolysis vapor, resulting in elevated concentrations of carbon and hydrogen in the bio-oil. Consequently, the produced fuel gas exhibits a substantial increase in hydrogen

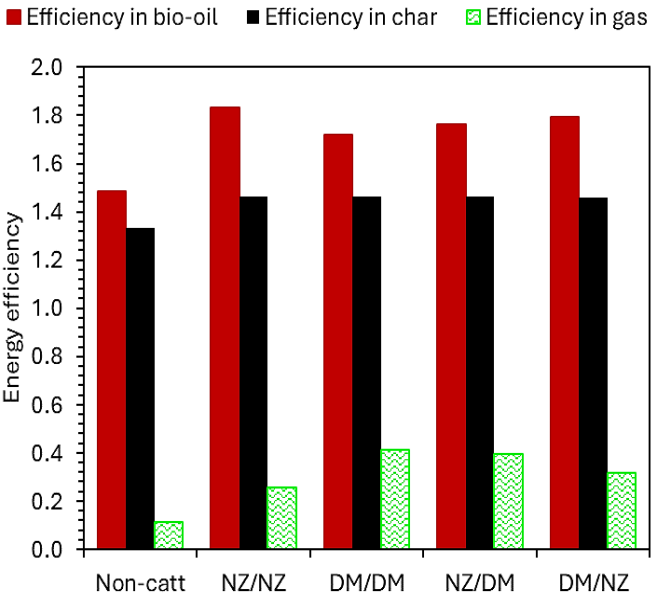

Fig. 10 Effect of catalysts on energy efficiency.

content. The results of the analysis of the properties of the bio-oil found that the natural zeolite catalyst reduces the water content, reduces the solid content, reduces the ash content, and increases the heating value up to 38.1 MJ/kg. The results of the chemical composition analysis found that the two catalysts helped to reduce the amount of acid in the bio-oil and clearly increase the composition in the hydrocarbon group. In catalytic pyrolysis, the char product experiences an augmentation in both carbon and hydrogen content, leading to a higher calorific value. The experimental outcomes suggest that for enhancing energy efficiency in bio-oil, the utilization of natural zeolite catalysts is recommended. Conversely, to bolster efficiency in gas products, the preferred choice is the deployment of dolomite catalysts.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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