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Probing the Pyrolysis Process of Rice Straw over a "Dual-Catalyst Bed" for the Production of Fuel Gases and Value-Added Chemicals

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Abstract: Rice straw is an agricultural byproduct primarily produced in Asian regions. It is crucial to discover an effective method for converting this waste into chemicals that can be utilized to substitute goods derived from fossil fuels. Pyrolysis serves as an interesting procedure to obtain bio-oil from this rice straw. The composition of the bio-oil obtained after the pyrolysis procedure contains a small quantity of value-added chemicals in addition to various gas components in the gas product. Therefore, the development of catalytic systems that improve this pyrolytic reaction is mandatory. Herein, the design of a dual catalyst bed (CEM/ZSM-5) that catalyzes the volatiles that it releases has been developed. The highest output of 42.1 wt.% of bio-oil, 29.9 wt.% of gases and 28.0 wt.% of bio-char was obtained. Nevertheless, the inclusion of single zeolites to biomass yields biofuel outputs of 42.8 wt.%, gas yields of 27.7 wt.%, and a bio-char yielding of 29.5 wt.%. Additionally, the addition of cement to biomass results in a bio-oil yield of 40.4 wt.% and 30.5 wt.% of gas, along with 29.1 wt.% of char. Regarding pyrolysis gas products, the H2 yield in the produced biogas was increased from 35.9 mL/g to 45.7 mL/g, and the CH4 output was increased from 21.1 mL/g to 27.4 mL/g. The bioenergy output was evaluated employing GC-FID and GC-MS (gas and biofuel). The dual catalytic bed had a significant impact on the contents of the generated biofuel, increasing the quantity of hydrocarbons and other value-added compounds.

Keywords: biomass; bio-oil; cement; zeolite; fixed bed reactor

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1. Introduction

Due to the energy dependency of the global economy, the decrease in crude oil supplies and changing prices of fossil energy generate instability. It is predicted that shortly, rising global energy consumption will deplete fossil fuel sources, causing an energy crisis. Additionally, excessive consumption of fossil energy generates dangerous pollutants such as carbon, nitrogen, and sulfur oxides, which endanger the environment by adding to air pollutants and worldwide overheating. Consequently, the world urgently needs resources and methods for energy production that are environmentally safe and sustainable [1]. Oil is the most widely used fossil fuel and the principal energy source that primarily supports global transportation and power industries [2]. Rice straw is perceived as agricultural waste and a significant source of carbon-neutral renewable energy because of its massive production worldwide. The ideal resource for the regular generation of value-added chemicals made up of cellulose, hemicellulose, and lignin, biomass has gained a great deal of attention. Each year, around 731 million metric tons of rice straw are generated, with Asia contributing 92% of this amount [3]. Due to the inert qualities of lignin, this agricultural waste cannot be transformed by many typical chemical techniques and is often thrown in the field or burned, generating numerous environmental hazards. As a result, an effective and simple technique of transforming agricultural residue into a valuable product is required to minimize reliance on fossil-based energy and pollution in the atmosphere. Numerous experiments have lately been conducted to examine environmental challenges technically and theoretically. The simplest immediate conversions technique in these organized technologies is combustion for the generation of steam or electricity, which has limited application owing to the corrosion of alkaline metal on the furnace in the environment at extreme temperatures. Furthermore, agricultural residues are employed as raw resources in the paper industries [4,5]. However, lignin is a key element of rice straw that is not transformed during the paper production procedure. As a result, discharge is required because black fluid is a serious environmental concern; to obtain one ton of pulp, around 7 tons of black liquid are produced. Thus, the efficient conversion of whole rice straw improves the generation of fine chemicals while also boosting the sustainability of the biorefinery industry. When compared to fossil fuels, biofuels have many advantages in terms of their environmental impact and sustainability. However, the pyrolytic oil generated from ultimate biofuels does have some technological constraints, including an elevated accumulation of oxygenates and water, which restricts calorific valuation and thermal effectiveness. An elevated accumulation of acids, aldehydes, and ketone induces destabilization, elevated viscous, strong fluctuations, and nontoxicity, which inhibits pyrolysis process oil from being directly utilized as an appropriate fuel. These limitations, caused by the biomass's low H/C ratio and high oxygen concentration, are what ultimately prevent pyrolysis from being scaled up and commercialized [6].

HZSM-5 porous structure zeolite is now regarded as the highly appropriate and efficient catalyst for hydrocarbon production owing to its optimal acidic site dispersion and shaped specificity [7]. A variety of microporous and mesoporous catalysts, including zeolites, MCM-41, SBA-15, Al_2O_3, CaO, MgO and so on, can be evaluated. They have a good capability for breaking down complex molecular mixtures into many shorter-strand complexes but have a lower capacity to make desirable aromatic hydrocarbons [8–11]. Thus, combining two catalyst beds has the potential to significantly increase the composition and yield of biofuel. In this work, the dual catalytic bed method was employed to increase the composition of biofuel. The dual catalytic chamber comprising Al-MCM-41 and HZSM-5 had a significant impact on the biofuel pyrolysis process. In comparison to a mixed catalyst system, a greater yield of gasoline-range compounds was produced. Consequently, the use of a dual catalytic bed seems to be crucial for generating desirable compounds. Several studies on the dual catalytic systems have recently been done [12–15]. Rice straw was catalytically pyrolyzed in a fixed bed unit utilizing a dual catalytic bed technique in this work. The first cement catalyst and ZSM-5 have been proposed to promote the production of aromatics, hydrocarbons, and phenols in gas products, particularly hydrogen (H_2) and methane (CH_4). The influence of the catalyst bed on the product yield was examined with favourable results attributed to the cement's remarkable capacity to capture oxygen and dissociate it from the active moieties contained in the biochemical gaps and locations inherent in its crystalline lattice. A thin silica wool layer separates the cement and zeolite in a dual-catalytic bed. In the catalytic bed process, cement-containing silicate minerals and oxides that have functional imperfections may behave as microscopic pores and cages. The molecular holes can promote de-oxygenation, leading to refined biofuel and enhanced gases [14]. As a result, it remains extremely desirable to design a catalyst for pyrolysis and to improve the quality of biofuel. Catalysts enhanced the production of biofuel and gas and decreased the contents of water produced during pyrolysis, according to the experimental data [16,17]. The cement is composed of many crystalline phases, one of which is the ferrite component. A literature study demonstrates that ferrates and ferrites are good water-splitting catalysts [18,19]. Consequently, in our research, the amount of additional compounds in biofuel, hydrogen (H_2) and methane (CH_4) constituents in a gaseous fuel was enhanced, and water was greatly decreased, therefore increasing the integrity of the biofuel. The volatile hydrocarbons were transformed into aromatics due to the large interface region and tiny pore diameter of the conventional zeolite in the dual catalytic bed. This dual catalytic bed (CEM/ZSM-5) reduced the water concentration of biofuel and generated H_2, CH_4, and value-added products.

The goal of employing a dual catalytic bed (CEM/ZSM-5) in the pyrolysis of rice straw is to enrich the hydrocarbon content of the generated biofuel and gas products. At scaled fabrication, the cement in the catalytic bed is generated by an intensive dehydration process at 1400 °C. The cement acts as a clinker material and significantly reduces the amount of water used throughout combustion, also decreasing the percentage of oxygen from 19.09 to 5.40%. For its part, zeolite provides acidity locations and a vast surface region promoting the effective pyrolytic conversion of volatiles into a value-added product. The composition and other essential parameters of the resulting pyrolytic oil and gas were studied. The results of the current study are expected to provide investors and other authorities with useful information.

2. Materials and Methods

2.1. Materials and Techniques

One of the most important agricultural by-products of China is rice straw, which is abundantly found in the farms of Guangxi province. Clay and soluble materials were removed from rice straw by pre-treating it with tap and distilled water [20] and then drying it in an open-air fuming hood under ambient laboratory conditions for 48 h. Size reduction machinery was used to grind the product down to a fine powder. Fine biomass powders with a mean width of 0.4 mm were produced by sieving the biomass. It was expected that this mechanical processing would alter the lignocelluloses' inherent structure while also decreasing particle size and crystallinity. As a result of the reduction in particle size, the amount of specified surface area accessible and the amount of cellulose polymerization were reduced. The aforementioned factors are essential to enhance the total hydrolysis yield and decrease the digestion time [21]. The Portland cement employed in the research was obtained from a Chinese cement factory, and the Zeolite (ZSM-5 (50) was obtained from Nankai Academic Catalyst Co., Ltd. (NKC), Tianjin, China. In analysis, one cement of a certain mass and ZSM-5 were mechanically mixed individually with the biomass and then loaded into the relevant reactor. In a few experiments, however, the rice straw was not mechanically mixed with a catalyst since the volatiles from the biomass flowed via the dual CEM/ZSM-5 reaction chamber. Rice straw was explored at 600 °C in our fast pyrolysis study effort, and reactions were carried out in a static bed reactor for 30 min using nitrogen gas as an inert atmosphere.

The pyrolysis of the rice straws was carried out in locally constructed reactors with the appearance of a fixed bed reactor. The device comprised a steel cylinder wrapped with a thermal barrier to keep the temperature consistent. The materials contained within the tube were attached by a long steel wire that could accommodate only 15 g of biomass upon each trial. While in other studies the catalyst was not manually combined with the biomass, in this instance the static catalyst bed was employed, and the composition of catalysts and rice straw 10 g was poured into the materials container. At elevated calcination, the biomass pyrolyzed and flowed through the dual catalyst bed. After its temperature was recorded, the sample container was positioned away from the reaction chamber, as shown in Figure 1. The chamber consisted of two thermo-couples (T), one on either side of the reactor, which showed the outside temperature, and the other on the bottom, which showed the temperature within the reaction chamber. First, a piece of stainless tubing was heated and then cooled to achieve the correct balance. The material container was placed inside the reaction chamber using the metal hook on the top, and the time was recorded after it reached the desired temperature. The biomass disintegrated at elevated temperatures to preserve an inert environment while also filtering out all the gases, releasing volatiles that were then passed through the catalyst beds by nitrogen gas supplied from the top of the reactor. For 30 min, the pyrolysis reaction temperature was held at 600 °C. Volatiles generated during the pyrolysis process were collected in dichloromethane solvent and then passed over an ice-water condenser for further processing. Finally, the bio-char was kept to settle at ambient temperatures before being stored in a desiccator on top of the dry silica gel.

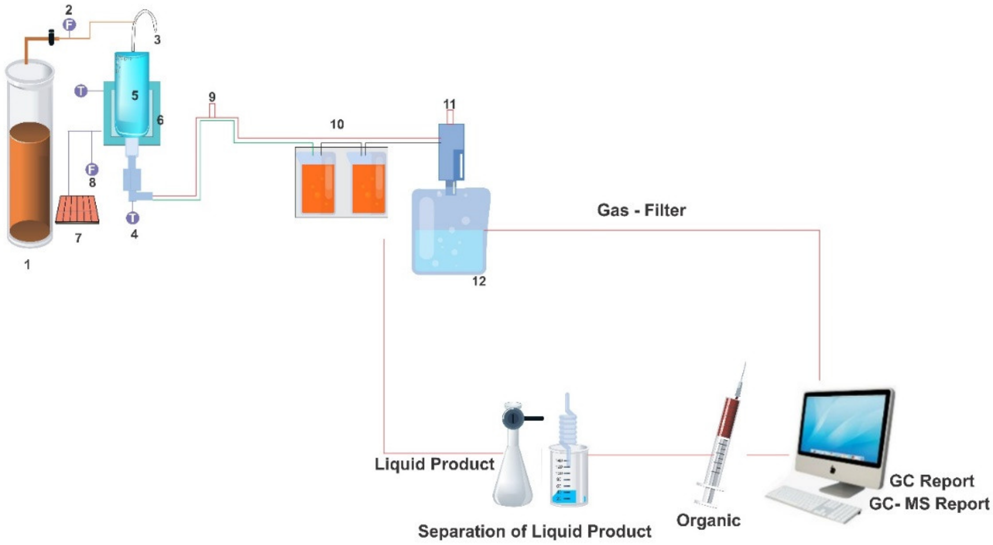

Figure 1. An illustration of the pyrolysis process in the bed reactor. Elements of the scheme: 1. N_2 container; 2. Flowmeter; 3. Exterior hook; 4. Thermo-couples; 5. Metallic tubes; 6. Thermal insulation; 7. Thermal regulator; 8. Electrical energy; 9. Air valves; 10. The air conditioning device; 11. Windbag, and 12. Gasbag.

The outputs of the gaseous components outputs were calculated using the formula below [22]:

$$V_{H_2} = \frac{V'H_2}{V_{N_2}} \times V'_{N_2} \tag{1}$$

where; V'_{H_2} is the percentage of gaseous content.
V_{N_2} = % content of N_2.
V'_{N_2} = Progression of N_2 × time

$$V_{H_2} = \frac{V_{mL}}{W_s} \qquad (V_{H_2} = mL/g) \tag{2}$$

where; W_S = Weight of sample, V_{mL} = Volume of gas in mL

$$W_{H_2} = \left(\frac{V_{H_2}}{(1000 \times 22.4)}\right) \times MW \qquad MW(\text{Molecular weight}) \tag{3}$$

W_{H_2} = weight of H_2 in g

Employing the succeeding formula, the overall Volumetric Composition of Gas in grams was determined:

$$W_{Gas} = W_{H_2} + W_{CO} + W_{CH_4} + W_{CO_2} + W_{C_2H_4} + W_{C_2H_6} \tag{4}$$

$$Y_{Gas} = \frac{W_{Gas}}{W_S} \times 100 \tag{5}$$

$$Y_{Char} = \frac{W_{Char}}{W_S} \times 100 \tag{6}$$

$$Y_{Liquid} = 100 - (Y_{Gas} + Y_{Char}) \tag{7}$$

where; $W_{Gas\,=}$ Weight of gas, Y = yield.

2.2. The Ultimate, Proximate Analysis and Chemical Composition of the Feedstock

Elemental composition Vario EL cubes were used to examine the primary materials, which measured the basic composition of raw materials. The quantities of C, H_2, and N_2 were measured to establish the percentage weight of O_2: C = 39.78%, H = 5.37%, O = 53.41%, and N = 1.44%. Therefore, H/C was found to be 1.61, whereas O/C and N/C were both found to be 1.01 and 0.03, respectively. Vital to note, proximate analysis uses weight percentages to calculate the amount of four variables: moistures (M), volatile material (VM), fixed carbon (FC), and ash (A). Rice straw manifested massive moisture and an ash amount that were recorded as 7.53% ± 0.05 and 18.53% ± 0.20, respectively. The biomass comprised 66.61% ± 0.30 of volatile matter and 14.98% ± 0.10 of fixed carbon. Similarly, the rice straw composition was determined by using the alkaline treatment method [23,24], which is composed of 35.20% ± 0.50 of cellulose, 18.59% ± 0.40 of hemicellulose, 16.60% ± 0.60 of lignin and 11.12% ± 0.20, of water-soluble substances.

The following equations were used to determine the consequential assessment of biofuels [25]:

$$\text{Moisture}\ \% = \frac{\text{Loss in weight due to moisture}}{\text{Initial weight of biomass}} \times 100 \tag{8}$$

$$\text{Moisture}\ \% = \frac{\chi - \chi 1}{\chi} \times 100 \tag{9}$$

where, χ = initial mass of the material, χ^1 = mass of materials after annealing at 110 °C.

$$\text{VM}\ \% = \frac{\text{Loss in weight due to volatile matter}}{\text{Initial weight of sample}} \times 100 \tag{10}$$

$$\text{VM}\ \% = \frac{\chi 1 - \chi 2}{\chi} \times 100 \tag{11}$$

where, χ^1 = Mass of materials after annealing at 110 °C, χ^2 = mass of materials after annealing at 925 °C ± 10, and χ = initial mass of the material.

$$\text{A}\ \% = \frac{\text{Weight of Ash}}{\text{Weight of sample after heating at 110 °C}} \times 100 \tag{12}$$

$$\text{A}\ \% = \frac{\chi 3}{\chi 1} \times 100 \tag{13}$$

where, χ^3 = mass of materials after annealing at 625 °C ± 10, χ^1 = mass of materials upon annealing at 110 °C.

$$\text{FC}\% = 100 - (\text{VM}\ \% + \text{A}\ \%) \tag{14}$$

2.3. Determination of Biofuel Output

The chemical composition of pyrolysis-produced biofuel was determined by using gas chromatographic analysis. GC-FID and GC-MS studies were used to characterize these compounds. In quantitative analysis, GC-FID is a reduced-price approach for optimizing dissociation circumstances, while GC-MS was employed to detect the chemicals in the oil and gas samples [26]. The GC-FID of Agilent Technologies (7890B GC system) and Agilent

5977A MSD system were used for these analyses. While the GC-FID was running in split mode with a 35:1 split ratio, the GC-MS was running in a splitting manner. Assuming a fusion capillaries row HP-5 with an inner diameter of 0.32 millimetres and a film depth of 0.25 micrometres, each step of the reaction device was carried out utilizing the same kind of columns. The reaction device was employed at flow rates of 1.8 mL/min for GC-MS and GC-FID. The fixed phase was polydimethylsiloxane (PDMS), while the carrier gas was helium. The oil sample was injected into the GC-FID and GC-MS with a 0.1% dichloromethane solution at 300 °C. A ramping rate of 5 °C/min was used to make the column isothermal for two minutes at 50 °C. The temperature subsequently increased to 180 °C at 10 °C/min, and then from 250 to 300 °C at 20 °C/min, as the heating rate had been pre-set (5 min). A mass spectrometer employed electron impact to ionize materials. The electron had the potential energy of 70 eV. Water content was determined as follows: the water and bio-oil immiscible layers were separated through a separating funnel, and the loss in weight of the initial bio-oil was calculated.

2.4. ZSM-5 Catalysts

The zeolite ZSM-5 (50) was obtained from Nankai University Catalyst Co., Ltd. (NKC), Tianjin, China. Prior to the process, the catalysts were pre-treated, and the annealing temperature was 450 °C in an electric stove for 8 h at 5 °C/min. The catalysts were then processed at 450 °C in an H_2 environment to decrease the O_2 on the reactive site. The catalysts were suitable for usage after pre-treatment. SiO_2 is represented by the numeral "50" in "ZSM-5(50)": Al_2O_3 = 50. The interface of the catalyst region and crystalline structure were determined to be 340 m^2/g and 95%, correspondingly [27]. In addition, Figure S1 illustrates the particular assessment of zeolite, including XRD and SEM.

2.5. Detailed Analysis of the Cement Catalyst

Micromeritics ASAP2460 was used to perform an absorption–desorption BET (N_2) evaluation of Portland concrete. The Brunauer–Emmett–Teller (BET) technique was used to compute the particular surface domain of the cements, which included porosity and pore structure, as illustrated in Figure 2a,b. Prior to measuring, a 20 to 40 mesh-cemented particle was formed through chemical sieve analysis and refluxed for 4 h at 300 °C. The cement had a particular surface area of 2.792 (m^2/g) ± 0.125, a porous diameter of 5.59 (nm) ± 0.14, and a high porosity of 0.00812 (cm^3/g) ± 0.00026. Since cement is frequently synthesized by burning at elevated heat, the surface region and pores dimension is significantly lower when contrasted to conventional synthesized Al_2O_3. Even though the reaction efficiency is reduced on average from that of a catalyst with a larger particular surface area and pore diameter, the cement material shows excellent temperature stability.

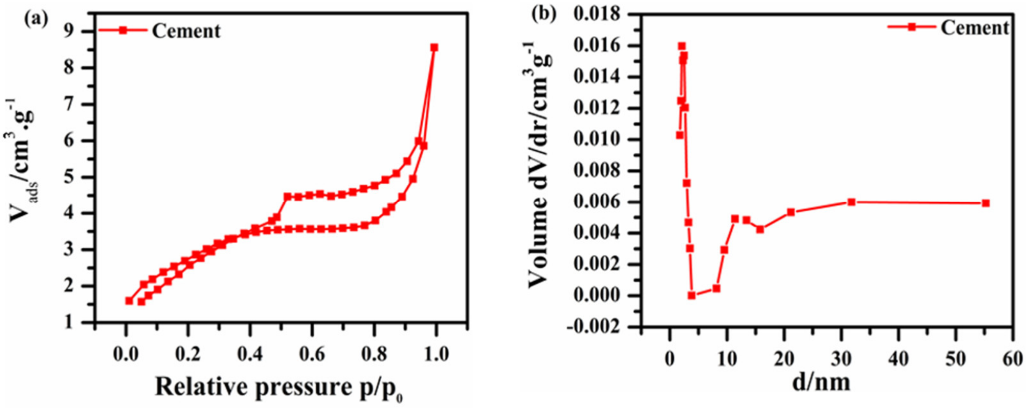

Figure 2. (**a**) The N_2 adsorption-desorption graphs at 77 K, and (**b**) the associated BJH pores diameter distribution rates for cement material.

ZETIUM PRO used XRF to determine the exact elemental constituents of cement (PANalytical). Most cement is made of silicon material and a reduced amount of oxide of an alkali earth metal. Premised on its mass, the cement had 38.14% O_2, 37.75% calcium, 12.81% silicon, 4.43% aluminum, 2.40% iron, 1.46% sulphur, 1.09% magnesium, 0.91% potassium, and 1.01% of other constituents. X'Pert PRO (PANalytical) XRD was used to determine the crystalline phase of the material (cement) and the diameter of its particulate. The appropriate investigational results are shown in Figure S2. Depending on the outcomes, it has been discovered that the mineral and oxide configuration has di- and tricalcium silicates, tri-calcium aluminate ferrite, silica, and calcium sulphoaluminate [28]. Table 1 shows several material states to 2 θ (°). Cement is a composite with a largely crystal pattern composed of many different minerals. Whereas each mineral has a unique form, molecular pores and catalytic activity occur in its crystalline framework.

Table 1. Different mineral phases to 2 θ (°).

2 θ (°)	Phase	d-Spacing (nm)
11.59	Gypsum (G) (100)	0.763
29.91	alite, (A) triclinic (25)	0.299
33.03	belite, (B) α form (100)	0.271
22.77	aluminate, cubic (12)	0.408
33.88	ferrite (100)	0.264
37.36	free lime (100)	0.241

The Portland cement micrograph has been previously illustrated [22,29]. It has been found that the cement morphology is irregular, and its particulate shape fluctuates greatly. These attributes are typically for cement consisting of clinker content, which is made in a rotary kiln by burning calcareous stone and grinding it in a ball mill [30]. The overall average diameter of the cement particulate was 2.74 "µm" as assessed by the FE-SEM microscopy. Conventional cement of this kind is defined by an access network and a permeable substructure, making the cement highly penetrable to gases and liquids that induce dehydration.

3. Results and Discussion

3.1. The Impact of Multiple Catalysts on Product Dispersion and Direct Pyrolysis of the Feedstock

The temperature for pyrolysis may vary according to the nature of the feedstock as well as the required product fraction (gas, liquid, solid). Rice straw has indeed been examined in fast pyrolysis at 600 °C. Previous studies have shown that this temperature is optimal for the rapid and efficient conversion of biomass from rice straw to bio-oil and gas [22]. All processes were conducted in a chamber with a constant bed. Herein, we mixed different catalysts such as cement and zeolite with the biomass via mechanical processes and investigated their effect on the product yield (Table 2). In some experiments, a dual catalytic chamber (cement and Zeolite) was used. Cement is a low-cost, commercially feasible feedstock for sintering catalysts, while ZSM-5 provides acidified locations inside the crystal lattices [31,32]. Fine silicon fiber was placed between the catalyzed bed cement and ZSM-5 catalyst. Every material was combined with 3 g of silicon to generate a cooling impact. The biomass was degraded at 600 °C, and volatile compounds were transferred across a dual catalytic surface that was flushed out of the reactors into the cooling region by N_2 as an inert atmosphere gas. The catalytic bed had a significant impact in increasing the gas production from 24.7 wt% to 29.9 wt%, whereas the biofuel output rose from 40.8 wt% to 42.1 wt%. The catalyzed efficiency of the two-reaction chamber was a result of the ionic locations of cement and complicated silicate minerals gaps, whereas the greater surface region and acidity areas of ZSM-5 may have converted volatiles into organic molecules and hydrocarbon. The catalytic bed boosted the total biomass-to-liquid and gas-transformation performance from 65.5 to 72.0 wt%.

Table 2. Impact of Catalyst Concentration on Product Dispersion at 600 °C.

Type of Catalyst	% Gas	% Liquid	% Char	Conversion Efficiency
CEM-ZSM-5 (bed)	29.9 ± 0.3	42.1 ± 0.3	28.0 ± 0.3	72.0 ± 0.3
Cement 10 wt.%	30.5 ± 0.2	40.4 ± 0.2	29.1 ± 0.2	70.9 ± 0.2
ZSM-5 10 wt.%	27.7 ± 0.2	42.8 ± 0.2	29.5 ± 0.2	70.5 ± 0.2
Without Catalyst	24.7 ± 0.4	40.8 ± 0.4	33.5 ± 0.4	66.5 ± 0.4

3.2. Carbon Balance Simulation of the Pyrolysis Process

Elementar Vario EL cubes were used to evaluate the elemental weights % of rice straw and bio-char before and after pyrolysis. Carbon balance ($C_{balance}$) was estimated for the quick pyrolysis process:

$$\text{Conversion of pyrolysis process (Conv, \%)} = \frac{m_{c,ricestaw} - m_{c,char}}{m_{c,ricestaw}} \times 100 \tag{15}$$

Carbon concentration of rice straw = 39.78%

$$\text{100 g of biomass, } m_{c,ricestaw} = 100 \times \frac{39.78}{100} = 39.78 \text{ g}$$

Carbon amount in bio-char = 43.0 wt.%

Char proportion at 600 °C = 33.5%

$$\text{Hence, } m_{c,char} = 100 \times \frac{33}{100} \times \frac{43}{100} = 14.41 \text{ g}$$

$$\text{Conv } (\%) = \frac{39.78 - 14.41}{39.78} \times 100$$

Conv = 63.78%

3.3. Constituents Evaluation of Pyrolysis Gas Products

The pyrolysis gases were examined employing an Agilent Technologies 7890B GC systems gas chromatograph. The output of the pyrolysis reaction chamber (biogas) was deposited into MS. To eliminate the effect of N_2 on the CO content, helium (He) was employed as the moving gas rather than nitrogen. The gaseous phase output consisted mostly of hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), ethane (C_2H_6), and ethylene (C_2H_4). At lower temperatures (<400 °C), CO and CO_2 evolved, while hydrogen gas was formed at higher temperatures (500–700 °C). The gaseous output was made up of several hydrocarbons generated by deoxygenation, demethylation, and dehydrogenation. CO and CO_2 were evolved due to the cleavage of carbonyl and carboxyl functional groups at 300 °C, whereas at 400 °C, the generation of CH_4 was due to the disintegration of the alkyl CH^- groups. The aromatic ring finally broke at 500 °C with the gradual evolution of H_2 gas [33]. At 600 °C, the material had a considerable influence on the output of all gaseous constituents, such as H_2, CH_4, C_2H_4, C_2H_6, CO, and CO_2 (Figure 3). For H_2 and CH_4, the impact of the dual catalyst had a big influence. The substantial output of H_2 in the gaseous output after pyrolysis could be attributed to interactions between water, carbon, and methane. The water–gas shift process, wherein CO combines with water to generate CO_2 and additional H_2, is also essential for the generation of H_2. CO_2 may be trapped by passing it via lime, which generates calcium carbonates, allowing H_2 to be isolated from CO_2. The improved efficiency of the dual catalyst may be related to the sintered character of cement with silicon pores, whereas the zeolite exhibits a high surface region and acidity locations that can boost the production of all gaseous molecules, as shown in Table S1.

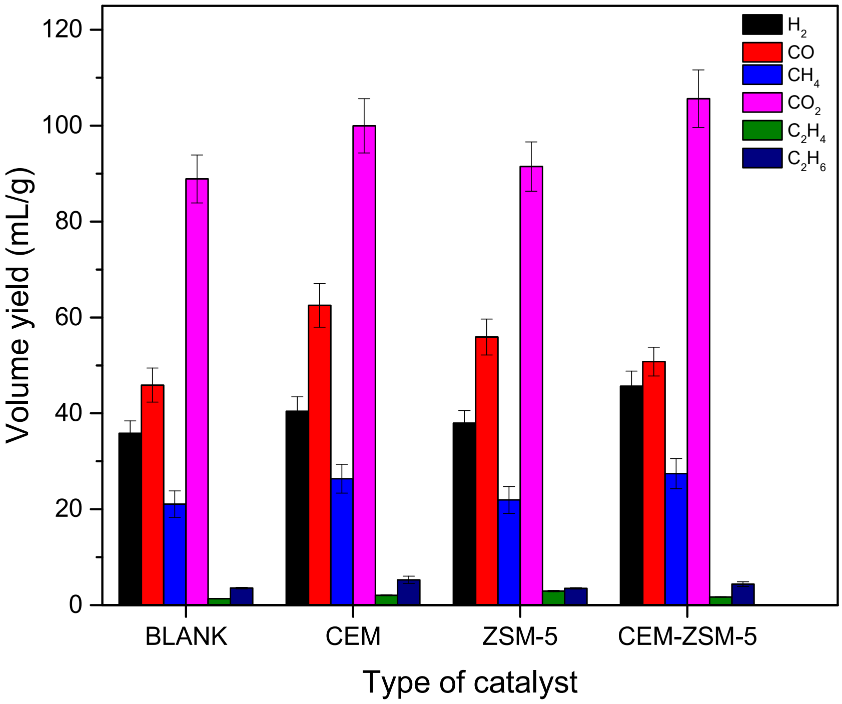

Figure 3. Impact of different catalysts on gas volume output at 600 °C taking the reaction blank as reference (Data collected in Table S1).

3.4. Analysis of Bio-Oil Composition by GC/MS

The constituents of biofuel derived from pyrolysis are depicted in Tables S2–S4. Changing the catalyst exhibits a profound effect on the composition of the bio-oil. In the non-catalytic pyrolysis of rice straw, the bio-oil contains mainly oxy-compounds, for example, phenol, aldehyde, ketones, acids, alcohol, and esters. Aromatic concentrations (especially toluene, p-xylene, and mesitylene), cyclic ketones, furans, and cyclic alkanes are relatively low. The incorporation of cement has a significant influence on the quantities of aromatics, cyclic ketones, cyclic alkanes, and polycyclic hydrocarbons. The catalyst reduces the amount of phenols from 31.16 to 26.17% while raising the amount of ketones, especially cyclopentanones-2-Methyl, which contributed to 8.43% of the total increase in ketones from 16.17 to 18.17% (CaO) [34]. The high quantity of aromatic compounds owing to the entrapped features of cement may be related to the acidic and basic behaviour of Lux-flood. The incorporation of ZSM-5 into pyrolyzed biofuel oils has been demonstrated by summarizing the comprehensive experimental results. The biofuel is composed of phenols, hydrocarbons, aromatic, ketones, and furans. The quantities of phenols increased from 26.17% to 29.54%, and hydrocarbons increased from 9.16% to 33.67%, while aromatics (toluene and p-xylene) increased from 6.36% to 10.43%. The high yield of different compounds in the bio-oil sample is due to the high catalytic activity of zeolite. The catalyst offers an acidic site, and a high surface area exhibits a significant role in increasing the quantities of different compounds. We can find that the volatiles over the dual catalytic chamber (CEM/ZSM-5) display a significant effect in increasing phenols, hydrocarbons, aromatics (toluene and o-xylene), and cyclic ketones and furans. The phenols increased from 31.16% to 37.78%, and cyclic ketones decreased from 16.17% to 11.35%, while furans and hydrocarbons increased from 9.70 and 9.16% to 10.71 and 19.40%, respectively. The non-catalytic bio-oil sample contains aromatics such as benzene, 1-ethyl-4-methyl and styrene while the catalytic pyrolysis bio-oil sample contains toluene and o-xylene as aromatics compounds. The aromatic yield was increased from 6.36% to 13.51%. The catalyst generally increased the yield of different value-added compounds, except that the ketones were decreased. In the catalytic bio-oil sample, heterocyclic compounds were also noticed. The description of liquid materials was determined by aggregating the experimental data. The dual catalytic CEM/ZSM-5 reduced the quantity of oxygen-based molecules in the generated biofuel. The drop in oxygen content from 19.09 to 5.40 suggests enhanced catalytic efficiency. The production of aromatics compounds from 6.36 to 13.51% owing to the entrapped quality of cement is caused by the acidic and basic behaviour of Lux-flood [17]. In contrast to aromatic hydrocarbons and phenolic compounds, several kinds of value-added chemicals were found in biofuel. In addition, it was found that the biofuel generated via a dual pyrolysis process of rice straw has no water, whereas that generated by the thermal technique includes 27% water. This biofuel also included alkanes, cycloalkanes, PAHs, heterocyclic, furans, and ketones. The better performance of the catalytic bed (CEM-ZSM-5) is due to the clinker nature of cement and acid zeolite, which offers sites that improve the quantity of different value-added compounds. The resulting bio-oil in the presence of a catalyst enriches with a different class of hydrocarbons.

4. Conclusions

The biomass conversion investigations of rice straw were performed using a dual catalytic bed of an inexpensive and readily available cement and acid zeolite material. The effects of the dual catalytic bed on two-phase product distribution at an optimum temperature was demonstrated. The experimental findings revealed that catalytic beds had a significant influence on output efficiency when contrasted to a manually combined catalyst with the biomass. The significant productivity of cement in the catalytic bed is owing to its acidic and basic behavior, as well as its durability at elevated temperatures, while the acidic zeolite exhibits a high surface area. The catalytic bed improved aromatics quantity from 6.36% to 13.51%, while hydrocarbons increased from 9.16% to 19.40%. The output of the gaseous constituent in the gas phase was increased. The quantity of value-added constituents in biofuel, including aromatic and cyclic chemicals, was enhanced. Furthermore, the biofuel content was considerably enhanced by reducing oxygen-containing chemicals, and water was eliminated during pyrolysis aided by the cement catalyst in the dual catalytic bed.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su151411057/s1, Figure S1: X.R.D and SEM images of "ZSM-5(50)" represents the SiO_2:Al_2O_3 = 50; Figure S2: X.R.D pattern of ordinary cement; Table S1: Effect of different catalysts on product gas yield; Table S2: Constituents of biofuel derived from pyrolysis using cement catalyst; Table S3: Constituents of biofuel derived from pyrolysis using ZSM-5 catalyst; Table S4: Constituents of biofuel derived from pyrolysis using dual catalytic bed (CEM/ZSM-5).

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