Research article

Directly catalytic upgrading bio-oil vapor produced by prairie cordgrass pyrolysis over Ni/HZSM-5 using a two stage reactor

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Abstract: Catalytic cracking is one of the most promising processes for thermochemical conversion of biomass to advanced biofuels in recent years. However, current effectiveness of catalysts and conversion efficiency still remain challenges. An investigation of directly catalytic upgrading bio-oil vapors produced in prairie cordgrass (PCG) pyrolysis over Ni/HZSM-5 and HZSM-5 in a two stage packed-bed reactor was carried out. The Ni/HZSM-5 catalyst was synthesized using an impregnation method. Fresh and used catalysts were characterized by BET and XRD. The effects of catalysts on pyrolysis products yields and quality were examined. Both catalysts improved bio-oil product distribution compared to non-catalytic treatment. When PCG pyrolysis vapor was treated with absence of catalyst, the produced bio-oils contained higher alcohols (10.97%) and furans (10.14%). In contrast, the bio-oils contained the second highest hydrocarbons (34.97%）and the highest phenols (46.97%) when PCG pyrolysis vapor was treated with Ni/HZSM-5. Bio-oils containing less ketones and aldehydes were produced by both Ni/HZSM-5 and HZSM-5, but no ketones were found in Ni/HZSM-5 treatment compared to HZSM-5 (2.94%). The pyrolysis gas compositions were also affected by the presenting of HZSM-5 or Ni/HZSM-5 during the catalytic upgrading process. However, higher heating values and elemental compositions (C, H and N) of bio-chars produced in all treatments had no significant difference.

Keywords: Ni/HZSM-5; pyrolysis; prairie cordgrass; biofuel; hydrocarbon

1. Introduction

Biomass-derived fuels (called biofuel) have been proposed to partly reduce our heavy dependence on fossil fuels, because they are possible to be processed in the existing petroleum infrastructure for the production of more fuels with little modification [1]. The biofuel can be produced from renewable biomass feedstock (such as wood, grass and agricultural waste) [2]. Prairie cordgrass (PCG) is indigenous throughout most of the continental United States and is well suited to grow on marginal land, and it can be used for biomass source [3]. One of the ways to convert the solid biomass such as PCG into liquid pyrolysis oil (bio-oil) is using thermochemical conversion process such as pyrolysis.

Biomass pyrolysis is a thermochemical process in which biomass is heated to 400–600 °C in absence of air decomposing the biomass into three products: solid charcoal (called bio-char), liquid products (also called bio-oil), and a gas mixture (so called pyrolysis gas). Generally, the raw bio-oil has to be upgraded for further direct application in traditional refineries because of its high viscosity, high oxygen content and especially the thermal instability. There are various bio-oil upgrading processes, but catalytic cracking and hydrodeoxygenation methods show better potential [4]. Specifically, catalytic cracking has more advantages since it does not require addition of hydrogen and could be operated at the atmospheric pressure [5]. Nonetheless, conventional catalytic cracking is still complicated and energy consuming since it is conducted in a separate upgrading reactor using liquid raw bio-oil as feedstock. Before catalytic cracking, raw bio-oil should be produced from biomass pyrolysis first and then must be re-heated up to vapor and fed into the upgrading reactor. This two-step bio-oil upgrading process may lead to low conversion efficiency and high processing costs. In recent years, catalytic upgrading of pyrolysis vapor emerged as one of the most promising processes for thermochemical conversion of biomass to advanced biofuels. This approach combines biomass pyrolysis and catalytic cracking in one continuous process using a two-stage reactor. After biomass is pyrolyzed into bio-oil vapor in the first stage reactor, the bio-oil vapor is directly fed into the second stage reactor for catalytic cracking to hydrocarbon biofuels without condensation step. Because this process eliminates the condensation step and converts biomass to hydrocarbon biofuel in one continuous reaction system, it can improve bio-oil yield and quality, conversion efficiency, and production costs [6,7]. However, current effectiveness of catalysts and conversion efficiency of this process still remain challenges for commercial production. Traditional zeolites such as HZSM-5, HY, β-zeolite, silicate, FCC catalyst, SBA-15 and MCM-14 have been widely studied on many biomass feedstock (such as pine sawdust and maple wood), but very fewer studies of PCG were reported in literature [8–14]. HZSM-5 was found as one of effective catalysts for biomass pyrolysis vapor catalytic upgrading process [15]. Although traditional catalysts were effective to convert the highly oxygenated compounds to hydrocarbons, but many problems were encountered, such as low organic liquid yield, low selectivity, short lifetime, etc. [16]. Therefore, many metals, such as zinc, copper, cobalt, iron, molybdenum, magnesium, aluminum, gallium and cerium were tested to adjust the acidity of ZSM-5 catalysts to increase the yield of useful compounds in bio-oils [17–23]. However, the above metal modified catalysts were either expensive or unstable. Another cheap transition metal (nickel) was selected to modify HZSM-5 to upgrade pine sawdust bio-oil because it is considered to increase the yield of aromatic hydrocarbons and the hydrothermal stability of zeolite [24].

The goal of this study was to develop effective Ni/HZSM-5 catalysts for catalytic upgrading

PCG bio-oil vapor into advanced biofuels. The tests of catalytic upgrading process were carried out in a two stage packed-bed reactor. The effects of Ni/HZSM-5 catalyst on products yields and quality were examined to verify its activity and selectivity.

2. Materials and Method

2.1. Feedstock preparation and characterizations

The prairie cordgrass was harvested from an agriculture extension farm nearby South Dakota State University as hay in fall 2013. Then it was dried in a swath before baling, and bales were stored indoors for three months. The baled grass was chopped into small pieces using a knife mill with a 25.4 mm screen before they were layered on floor and air-dried (moisture content was between 10% and 12%) for 2 months. The dried grass pieces were ground into powder by a hammer mill (M150, Winona Attrition Mill Co. MN 55987) with a 2 mm screen. After that, the prepared grass powder was stored in plastic bags for one month at room temperature (around 298.15 K). The grass powder was further ground into fine powder using a Thomas-wiley laboratory mill with a 1 mm screen before this study. The analysis of particle size and distribution for the fine powder was carried out using Nano-measurer 1.2 software.

The feedstock's moisture content was determined by following the ASABE standard (ASAE S358.2 DEC1988 (R2008)). The feedstock's elemental compositions（carbon, hydrogen and nitrogen）were analyzed by the CE-440 Elemental Analyzer. The higher heating value（HHV）of PCG samples was tested by the bomb calorimeter (Parr Instrument Company 1341).

2.2. Catalysts preparation and characterizations

The HZSM-5 (Si/Al molar ratio = 30) was purchased from Zeolite Company. The catalyst was further promoted with Ni (1wt.%) with via a wet impregnation method using aqueous solutions of nickel (II) nitrate hexahydrate (Sigma-Aldrich Inc.). The Ni-based catalysts were dried at 393.15 K for 3 h and then calcined at 823.15 K for 3 h before use. The same drying and calcinations were applied for the preparation of the pure HZSM-5 before use.

The BET specific surface area and porosity texture of each catalyst were determined by nitrogen adsorption measurements at 77.2 K using an automatic Micromeritics ASAP 2020 apparatus. The catalysts were first degassed at 573 K for around 6 h and then studied by a static volumetric technique. The specific surface area of catalysts was calculated according to the Brunauer–Emmett–Teller (BET) method, and the total pore volume was confirmed at a relative pressure $P/P_0 = 0.995$. Density functional theory (DFT) was utilized to determine the micropore, mesopore and pore size distribution.

XRD was used for catalyst phase identification and determination of the relative crystallinity. XRD measurements were conducted on a Rigaku Smartlab. The X-ray tube was operated at 40 kV and 44 mA. The X-ray pattern was accumulated in the range of 5–50° (2θ) each 0.02° (2θ) and the counting time was 1 s per step.

2.3. Experimental design and procedure

The biomass pyrolysis experiments were performed in a two stage reactor which consists of a pyrolysis fixed-bed reactor (ID 5.08 cm, height 45.72 cm), a catalytic fixed-bed reactor (ID 2.54 cm, height 40.64 cm) and the condenser. Both of the stainless steel reactors are heated by a temperature controlled furnace. Product vapors passed the condenser, and liquid product (bio-oil) was collected in a sample bottle. The gas product sample (pyrolysis gas) was collected and its composition was determined by a GC. The schematic diagram of the two-stage pyrolysis system is depicted in Figure 1. In each test, 100 g of PCG was inserted into the pyrolysis reactor, and 10 g of Ni/HZSM-5 or HZSM-5 was loaded as the bio-oil upgrading catalyst in catalytic reactor. Nitrogen was introduced into the system to remove air with flow rate of 15 ml/min for 30 min. The catalytic reactor was heated to 773.15 K at the beginning of the experiment. The nitrogen flow rate was set at 5 ml/min. Then the pyrolysis reactor furnace was heated at a rate of 25 K/min to 773.15 K. When the pyrolysis reactor reached 773.15 K, the reaction pyrolysis gas was collected and analyzed. The pyrolysis reactor temperature was kept at 773.15 K for 1 h, and then the furnaces were switched off.
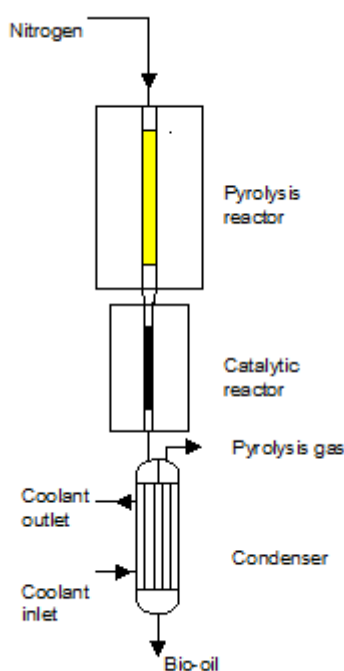

Figure 1.The schematic diagram of two-stage reactor system.

For comparison purposes, three groups of reaction conditions were carried out in the two-stage catalytic pyrolysis reactor. The reaction conditions were pyrolysis reaction at 773.15 K and non-catalytic reaction at 773.15 K, pyrolysis reaction at 773.15 K and catalytic reaction at 773.15 K using HZSM-5, pyrolysis reaction at 773.15K and catalytic reaction at 773.15 K using Ni/HZSM-5. The system was allowed to cool for 1 h to collect bio-oil from the condenser after each test. Bio-char was obtained by disassembling the pyrolysis reactor. The pyrolysis gas was computed by subtracting the bio-char and bio-oil weights from original feedstock weight. In order to make experiment results

objective, each test was conducted in duplicate and average data values were utilized.

Pyrolysis gas analysis was using a GC (Agilent GC-7890A (Hp-5 column: 30 m × 0.25 mm × 0.25 μm)) with a combined TCD and FID. Standard gas mixtures were employed for calibration, and argon was utilized as the carrier gas. GC–MS (AgilentGC-7890A (DB-5 column: 30 m × 0.25 mm × 0.25 μm)) and MSD-5975C (electron ionization at 70 eV, mass range of 50–5000 m/z, semi-quantitation based on TIC, mass chromatograms) were utilized to analyze the chemical composition of bio-oils. The gas chromatograph was programmed at 333.15 K for 1 min, followed by ramp 1 at 2 K/min to 533.15 K and ramp 2 at 10 K/min to 553.15 K. The temperature was kept for an additional 5 min after each ramp. The injector temperature was 573.15 K, and the injection size was 1 μL. The flow rate of carrier gas (hydrogen) was 1 mL/min. The compositions were identified based on the NIST Mass Spectral Library and literatures [8]. The bio-chars' elemental compositions（carbon, hydrogen and nitrogen ）and higher heating value（HHV）were analyzed by the CE-440 Elemental Analyzer and the bomb calorimeter (Parr Instrument Company 1341) respectively.

3. Results and Discussion

3.1. Feedstock characterization

Moisture content, elemental analysis and higher heating value (HHV) of the PCG used for two-stage reaction are presented in Table1. With three times of particle size analysis tests, the results of particle size and distribution analysis of the PCG powder are shown in Figure 2. The mean particle size of PCG is 0.73 mm, and around 78% of particle sizes were less than 1.1 mm. This small size and distribution is beneficial for improving the heating transfer rate during pyrolysis, because it may have a large surface area with less diffusion resistance for the pyrolysis reaction [25].

Table1. PCG characterization.

Analysis	Result
Moisture content (wt.%)	7. 14 ± 0.18
Elemental analysis	
Carbon (wt.%)	44.27 ± 0.62
Hydrogen (wt.%)	5.82 ± 0.04
Nitrogen (wt.%)	4.13 ± 0.07
Rest[a] (wt.%)	45.77 ± 0.73
Higher heating value(MJ/kg)	17.42 ± 0.31

[a] Rest includes oxygen and traces of other elements.

3.2. Catalysts characterization

BET parameters of different catalysts are summarized in Table 2. The surface area of fresh HZSM-5 used in the study was 473.33 m^2/g and the total pore volume was 0.46 cm^3/g. However,

after the catalytic reaction, the surface area of used HZSM-5 reduced by around 83 m^2/g and the pore volume also decreased. Impregnation of transition metal Ni on HZSM-5 reduced the surface area and pore volume of fresh HZSM-5. This is due to pore blocking by metal species dispersed in the channels or by the presence of metal oxide aggregates [8].
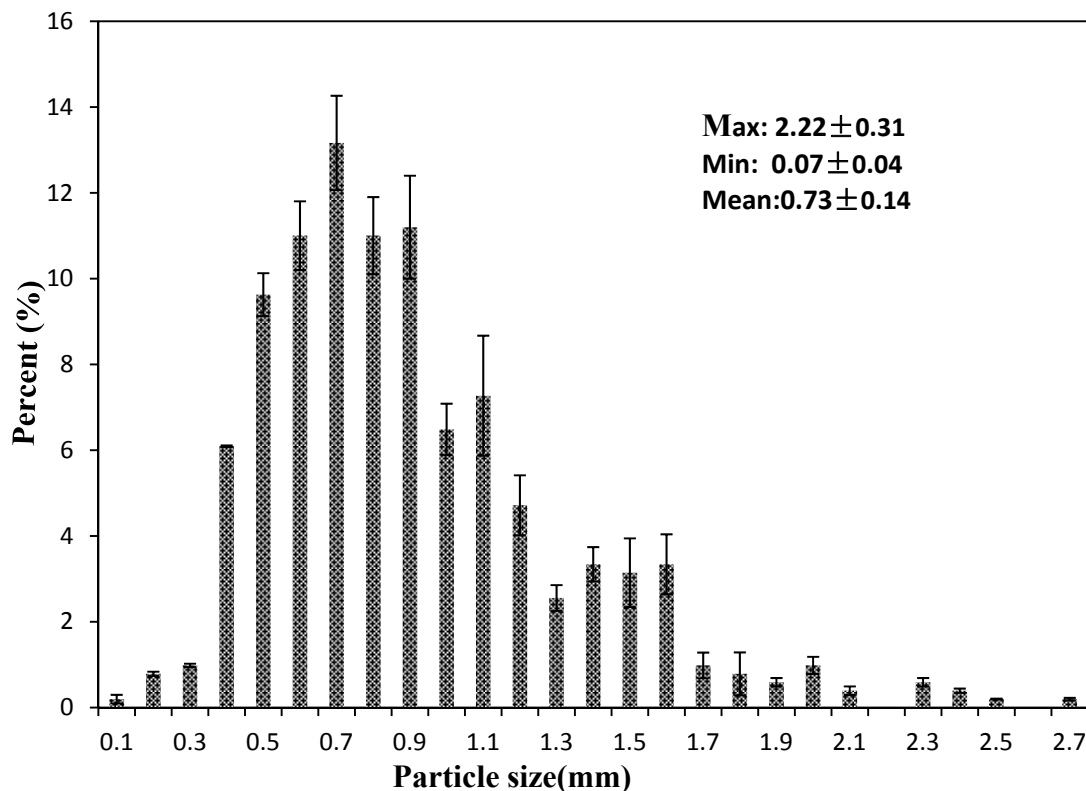

Figure 2. Particle size distribution of PCG.

Table 2. BET parameters of the different catalysts.

Catalyst	Surface area (m^2/g)		Pore Size (nm)		Pore volume (cm^3/g)		
	BET	Langmuir	Average	Total[a]	Micropores	Mesopores	
Fresh HZSM-5	473.33 ± 44.27	597.62 ± 79.71	4.22 ± 0.14	0.46 ± 0.09	0.09 ± 0.04	0.25 ± 0.07	
Used HZSM-5	390.27 ± 17.41	493.38 ± 22.24	4.40 ± 0.08	0.43 ± 0.01	0.05 ± 0.01	0.24 ± 0.01	
Fresh Ni/HZSM-5	451.41 ± 16.04	584.18 ± 32.29	3.92 ± 0.03	0.44 ± 0.02	0.07 ± 0.01	0.21 ± 0.01	
Used Ni/HZSM-5	429.90 ± 27.11	555.55 ± 45.30	4.16 ± 0.24	0.45 ± 0.05	0.06 ± 0.01	0.24 ± 0.05	

[a] Total pore volume, measured at $P/P_0 = 0.995$

The XRD patterns of the fresh and used catalysts in the angle region (5–50°) were measured, and the results are shown in Figure 3. The similarity of the XRD patterns between fresh HZSM-5 and other catalysts indicates that the framework of HZSM-5 was still kept after loading Ni or after reaction, because the presences of typical peaks of HZSM-5 (23–24°) are still maintained [26]. However, the intensities of diffraction peaks in used catalysts changed compared to fresh catalysts, and this is due to the distortion of the zeolite lattice caused by the deposition of carbonaceous materials within zeolite pores [27].
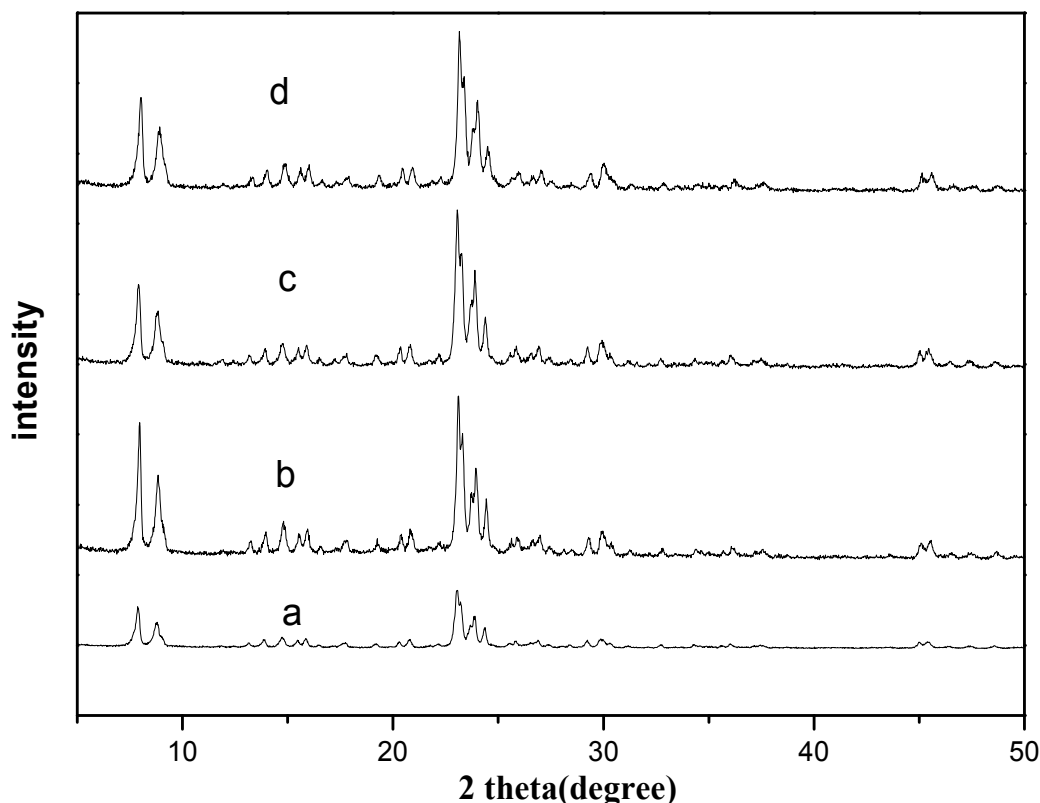
Figure 3. XRD patterns of fresh and used catalysts (a-fresh HZSM-5, b-used HZSM-5, c-fresh Ni/HZSM-5, d-used Ni/HZSM-5).

3.3. Evaluation of two-stage catalytic pyrolysis process

3.3.1.　Effect of different catalysts on products yields

The products yields of different catalysts and non-catalytic pyrolysis on the two-stage reactor system were summarized in Figure 4. Taking into the standard deviation, there is no significant difference in product yields（bio-oil and pyrolysis gas）among HZSM-5, Ni/HZSM-5 and non-catalytic treatment. The bio-char yields of all treatments also have no significant difference. However, both catalysts have great effect on the product distribution of bio-oil and pyrolysis gas compared to the treatment without catalyst, and their influence will be further discussed. The carbon balance of each treatment was calculated by dividing the total amount of carbon in products (bio-oil,

bio-char and pyrolysis gas) with the total amount of carbon in feedstock, and the carbon balance is $98.87 \pm 0.89\%$ in this work. The carbon loss might be due to little bio-char deposited on the inner wall of pyrolysis reactor which was difficult to be collected, and it caused measuring errors.
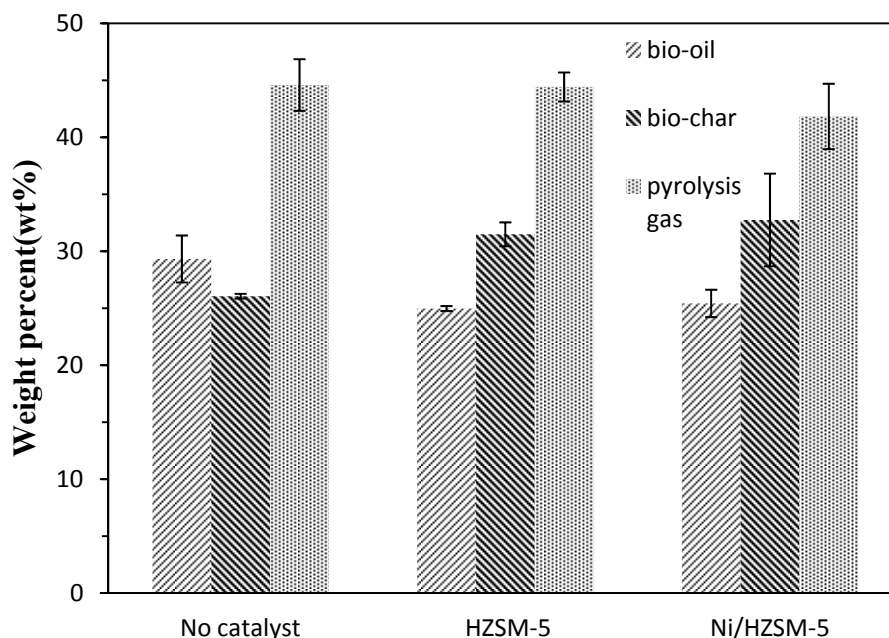

Figure 4. Product yields of non-catalytic pyrolysis and catalytic pyrolysis of PCG.

3.3.2.   Effect of different catalysts on bio-oil

Due to the interaction of high temperature and zeolite catalysts, various reactions occurred, such as decarbonylation, decarboxylation, dehydration, polymerization, aromatization cracking and hydrodeoxygenation [29,30]. There are many types of organic compounds which generated from above reactions, including hydrocarbons, alcohols, phenols, furans, esters, ethers, aldehydes and ketones. These functional groups can be divided into two groups which were desired compounds and undesired compounds. Desired compounds include hydrocarbons, alcohols, phenols and furans, which can be used as alternatives for fossil fuel or high valued chemicals. On the other hands, bio-oils also contain undesired compounds such as esters, ethers, aldehydes and ketones, which results in the low heating value and low stability of bio-oils.

In order to characterize the bio-oil composition of different treatments, GC-MS was utilized to analyze bio-oil. Typical GC-MS spectroscopy of bio-oil characterization is shown in Figure 5. It indicated that the separation of different organic compounds in bio-oils was successful.

The detailed compositions of non-catalytic and catalytic bio-oils are shown in Figure 6 and Figure 7. Compared to non-catalytic treatment (2.37%), both catalysts induced a significant increase in hydrocarbons in bio-oil. The increase of hydrocarbons is due to the rise of aromatic hydrocarbons which results from the aromatization reaction on zeolites. In contrast, Ni/HZSM-5 generated the second highest hydrocarbons at 34.91% which is a little lower than HZSM-5 (39.07%). Similarly, an obvious improvement was observed for phenols in Ni/HZSM-5 and HZSM-5 and the highest

proportion of phenols was from Ni/HZSM-5 (46.97%). This could be related with the decrease of Bronsted sites which are masked by the nickel ions [31]. On the other hand, more alcohols (10.97%) and furans (10.14%) can be obtained from non-catalytic treatment. However, alcohols (3.52%) and furans (3.63%) of bio-oils from Ni/HZSM-5 were higher than they are from HZSM-5 (0.67% and 0.36% respectively).
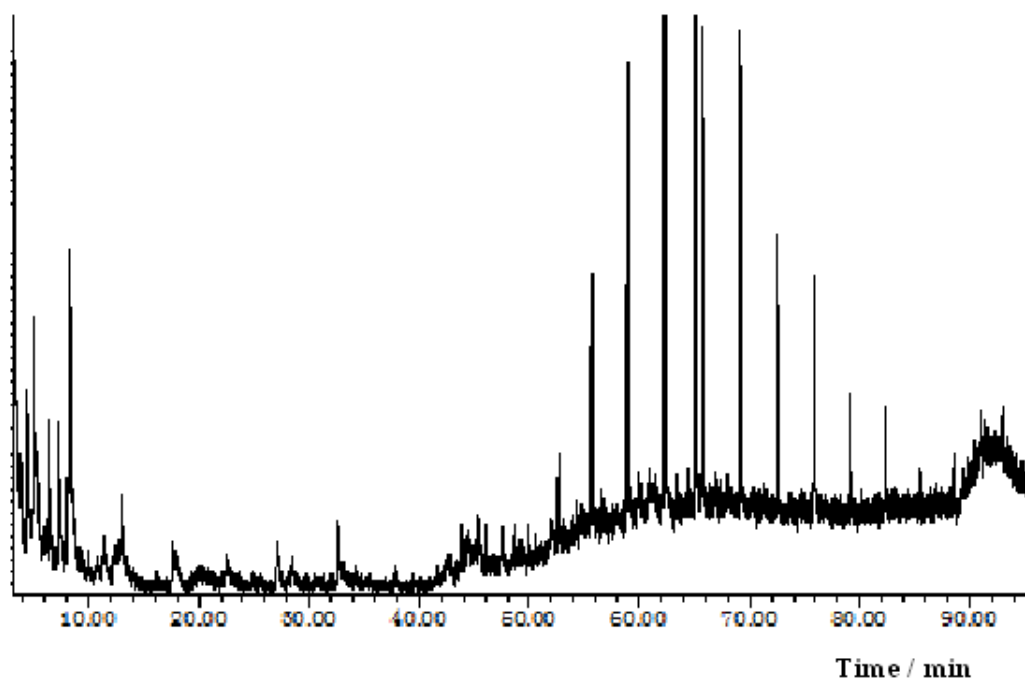

Figure 5. GC-MS spectroscopy of bio-oil by HZSM-5 treatment.

Regarding undesired compounds, esters were improved with the use of zeolite catalysts compared to the non-catalytic treatment. However, bio-oils generated by Ni/HZSM-5 contained less esters (12.44%) than HZSM-5 bio-oil (23.31%). In contrast, ketones were decreased with both catalysts, but no ketones were found in Ni/HZSM-5 treatment compared to HZSM-5 (2.94%). Zeolites also reduced the relative content of aldehydes and no aldehydes were identified by GC-MS in both Ni/HZSM-5 and HZSM-5 treatments. The decrease of ketones and aldehydes in both catalysts compared to non-catalytic treatment is consistent with the research results of Iliopoulou EF [31].
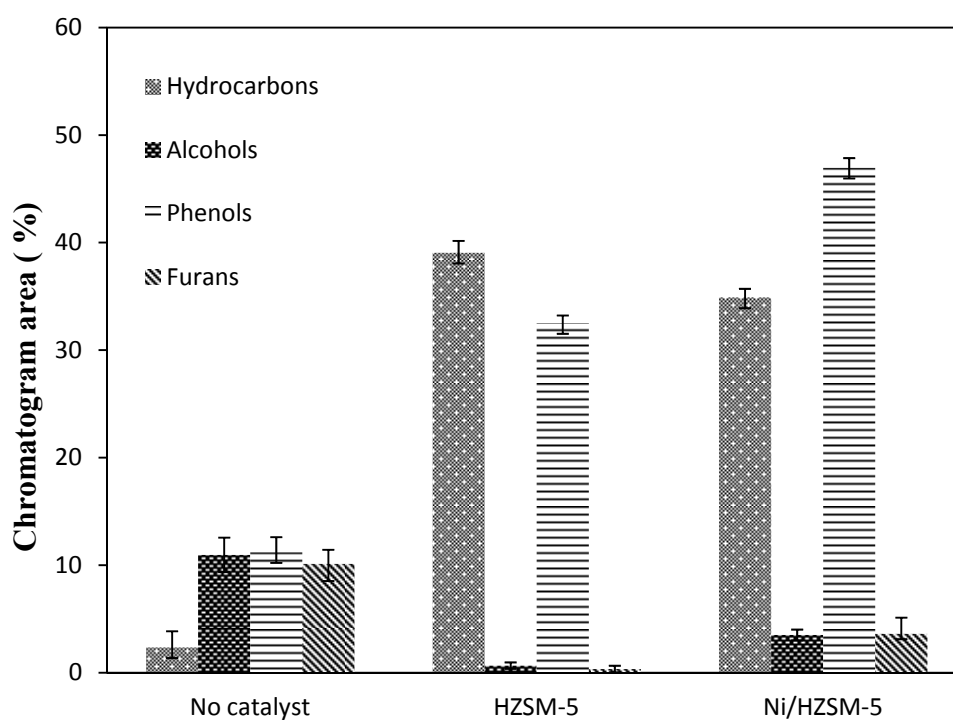
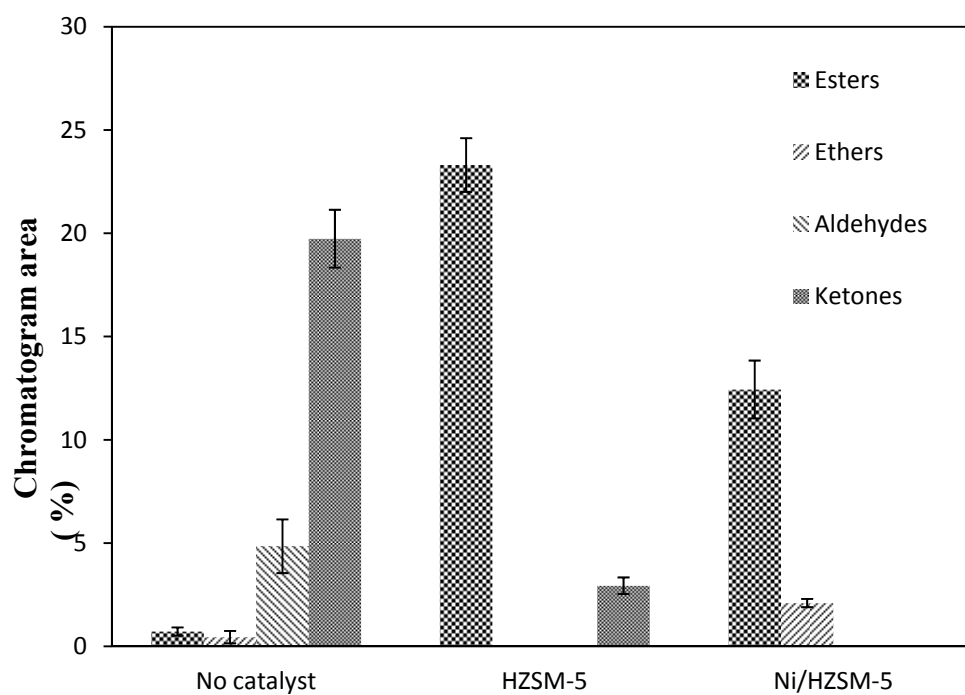**Figure 6. Composition of desired compounds in non-catalytic and catalytic bio-oils.**

Figure 7. Composition of undesired compounds in non-catalytic and catalytic bio-oils.

3.3.3. Effect of different catalysts on pyrolysis gas

The main components of pyrolysis gas produced from non-catalytic and catalytic processes were carbon dioxide, carbon monoxide, methane and small quantity of C2-5 compounds. Pyrolysis gas distributions of different treatments are depicted in Figure 8. Pyrolysis gas compositions varied with different treatments. Compared to non-catalytic treatment, both Ni/HZSM-5 and HZSM-5 increased the total amount of carbon dioxide and carbon monoxide. This is due to the decarboxylation and decarbonylation reactions that occurred on zeolite catalysts respectively [30,32–33]. The production of CO_2 by Ni/HZSM-5 was higher compared to that with the non-catalytic and the HZSM-5 experiments, while the yield of CO was higher in HZSM-5 treatment. These changes in CO_2/CO yields are indicative of the different decarbonylation/decarboxylation mechanism that applies for NiO (generated on Ni/HZSM-5 after calcined at 823.15 K) compared to HZSM-5 due to the differences in their acidic properties (number, strength and mainly type of acid sites). Besides, the increased production of CO_2 may be associated with the oxygen atoms that are offered by NiO when it is reduced to metallic Ni during the reaction [31].
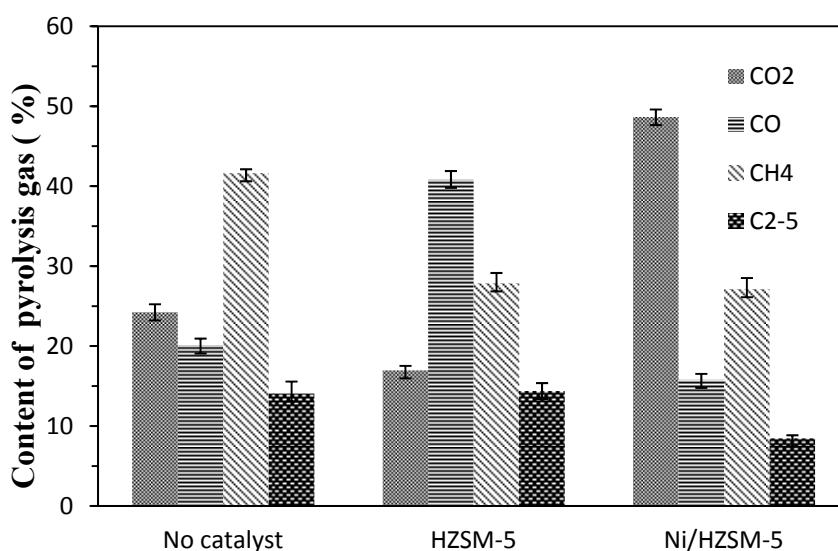

Figure 8. Pyrolysis gas distribution of different treatments.

3.3.4. Effect of different catalysts on bio-chars

Bio-char is a pyrolysis byproduct along with bio-oil and pyrolysis gas, and it is a solid product obtained from the carbonization of biomass [34]. The char may be used as soil enhancer, solid fuel or activated carbon [35–36]. The physical properties of different bio-chars are shown in Table 3. Because all bio-chars were obtained under the same pyrolysis conditions in the first stage reactor, there is no significant difference in HHV and elemental compositions.

Table 3. Physical properties of different bio-chars.

Treatment	No catalyst	HZSM-5	Ni/HZSM-5
HHV(MJ/Kg)	28.48 ± 0.20	26.92 ± 0.13	27.94 ± 0.25
Carbon (wt.%)	74.75 ± 0.75	69.42 ± 0.05	71.34 ± 0.62
Hydrogen (wt.%)	2.61 ± 0.40	3.18 ± 0.05	2.99 ± 0.13
Nitrogen (wt.%)	3.17 ± 0.17	3.14 ± 0.12	3.42 ± 0.38

4. Conclusion

Prairie cordgrass is firstly used as biomass feedstock to produce upgraded bio-oil through catalytic upgrading of bio-oil vapor in a two stage fixed-bed reactor. Catalytic effects of both Ni/HZSM-5 and HZSM-5 on products yields（bio-oil and pyrolysis gas）have no significant difference from product yields in the absence of catalyst. However, both catalysts have great effect on bio-oil and pyrolysis gas product distributions. Ni/HZSM-5 generated the second highest hydrocarbons at 34.91% and highest phenols in bio-oils (46.97%). In contrast, higher yields of alcohols (10.97%) and furans (10.14%) can be obtained from non-catalytic treatment. Both HZSM-5 and Ni/HZSM-5 reduced ketones and aldehydes which are responsible for low heating value and low stability of bio-oils, but no ketones were found in Ni/HZSM-5 treatment compared to HZSM-5 (2.94%). Bio-oils generated by Ni/HZSM-5 contained less esters (12.44%) than HZSM-5 bio-oil (23.31%). Both catalysts increased the total amount of carbon monoxide and carbon dioxide in pyrolysis gas compared to PCG pyrolysis without catalyst. Higher heating values and elemental compositions (C, H and N) of bio-chars produced in all treatments have no significant difference.

Conflict of Interest

The authors declare that there are no conflicts of interest related to this study.

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