



*Research article*

## **Catalytic hydrothermal liquefaction (HTL) of biomass for bio-crude production using Ni/HZSM-5 catalysts**

**Shouyun Cheng<sup>1</sup>, Lin Wei<sup>1\*</sup>, Mustafa Alsowij<sup>1</sup>, Fletcher Corbin<sup>2</sup>, Eric Boakye<sup>3</sup>, Zhengrong Gu<sup>1</sup> and Douglas Raynie<sup>3</sup>**

<sup>1</sup> Department of Agricultural & Biosystems Engineering, South Dakota State University, Brookings, SD 57007, USA

<sup>2</sup> Driftmier Engineering Center, University of Georgia, 597 DW Brooks Drive, Athens, GA 30602, USA

<sup>3</sup> Department of Chemistry & Biochemistry, South Dakota State University, Brookings, SD 57007, USA

\* **Correspondence:** Email: [lin.wei@sdstate.edu](mailto:lin.wei@sdstate.edu); Tel: +1-605-688-4179; Fax: +1-605-688-6764.

**Abstract:** Hydrothermal liquefaction (HTL) is an effective method that can convert biomass into bio-crude, but direct use of bio-crude derived from biomass HTL remains a challenge due to the lower quality. In this study, bifunctional Ni/HZSM-5 catalysts and zinc hydrolysis were combined to produce upgraded bio-crude in an in-situ HTL process. The K<sub>2</sub>CO<sub>3</sub> and HZSM-5 catalysts with different Ni loading ratios were tested. The effects of different catalysts on the yield and quality of bio-crude and gas were investigated. The results indicated that the catalysts improved bio-crude and gas yields, compared to pine sawdust liquefaction without catalyst. The catalysts reduced the contents of undesirable oxygenated compounds such as acids, ketones, phenols, alcohols and esters in bio-crude products while increased desirable hydrocarbons content. K<sub>2</sub>CO<sub>3</sub> produced highest bio-crude yield and lowest solid residue yield among all catalysts. Compared to parent HZSM-5 catalyst, bifunctional Ni/HZSM-5 catalysts exhibited higher catalyst activity to improve quality of upgraded bio-crude due to its integration of cracking and hydrodeoxygenation reactions. 6%Ni/HZSM-5 catalyst produced the bio-crude with the highest hydrocarbons content at 11.02%. This catalyst can be a candidate for bio-crude production from biomass HTL.

**Keywords:** bio-crude; hydrothermal liquefaction; Ni/HZSM-5; hydrocarbon; catalyst; HZSM-5; K<sub>2</sub>CO<sub>3</sub>

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## 1. Introduction

The exploitation of renewable energy has attracted great interest in responding to the depletion of fossil fuels and the growing greenhouse effect. Biomass has proven to be a potential and alternative energy resource due to its renewable and environmentally friendly properties [1]. Biomass conversion methods are mainly consisted of biochemical methods such as fermentation and thermochemical methods including combustion, pyrolysis, gasification and liquefaction [2]. Among these methods, thermochemical liquefaction is one efficient and promising method that converts biomass into liquid fuel (named bio-crude), gas and solid residue [3]. Hydrothermal liquefaction (HTL) is the thermochemical process treating wet biomass under high temperature (250–350 °C) and pressure (5–15 MPa) in the presence of solvent (water or alcohols) with or without using a catalyst [4].

Catalysts had a significant influence on bio-crude yield and quality during HTL process [5-8]. Acids catalyst such as sulfuric acid, hydrochloric acid and phosphoric acid and alkali catalysts such as  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , KOH, NaOH and  $\text{Ca}(\text{OH})_2$  were widely used in biomass liquefaction [6,9,10]. However, the use of homogeneous acid and alkali catalysts had a corrosion effects on liquefaction equipments [11]. Besides, additional separation steps with high cost and energy consumption are required for catalyst recovery when using the homogeneous catalysts [5]. Conventional catalysts were expected to be replaced by more environmentally friendly heterogeneous catalysts to improve bio-crude yield and quality in biomass liquefaction [12]. The heterogeneous Ni/HZSM-5 catalyst was a hydrothermally stable catalyst for pyrolysis bio-oil upgrading. Ni/HZSM-5 catalyst showed a high stability that can be used in reaction-regeneration cycles for hydrocarbons production [13]. The heterogeneous solid catalysts were almost fully separated and recovered from reaction products, and they were easy and safe to dispose of [11]. However, there is very little information of using bifunctional Ni/HZSM-5 catalyst in biomass HTL process in literature.

The objective of this study was to investigate the effect of heterogeneous Ni/HZSM-5 and homogeneous  $\text{K}_2\text{CO}_3$  catalyst on bio-crude production in pine sawdust HTL in the batch reactor. The catalytic effect of  $\text{K}_2\text{CO}_3$  and Ni/HZSM-5 catalysts with different Ni loading ratios on yields and properties of bio-crude and gas were determined.

## 2. Materials and methods

### 2.1. Materials

Pine sawdust (PSD) was provided by the Rushmore Forest Products company (Rapid City, South Dakota). Pine sawdust was further ground into powder with a particle size of less than 1 mm using a hammer mill (Thomas-wiley).

Zinc metal with zero valence was purchased from Fisher Scientific Inc. The HZSM-5 (Si/Al molar ratio = 30) was purchased from Zeolite International Company. Nickel (II) nitrate hexahydrate and  $\text{K}_2\text{CO}_3$  were purchased from Sigma-Aldrich. The Ni/HZSM-5 catalysts with different Ni loading (6 wt% and 12 wt%) were impregnated with aqueous solutions of nickel (II) nitrate hexahydrate. The prepared Ni/HZSM-5 and HZSM-5 catalysts were dried at 120 °C for 4 h and then calcined at 550 °C for 6 h.

## 2.2. Pine sawdust HTL

The pine sawdust HTL experiments were carried out in a 500 mL Parr 4575 autoclave reactor equipped with a stirrer. An electric heater was used to heat the reactor. 20.0 g pine sawdust, 4.0 g zinc metal, 4.0 g catalyst (HZSM-5, Ni/HZSM-5 or  $K_2CO_3$ ), 80.0 g ethanol and 30.0 g deionized water were loaded in the reactor for each test.

Ethanol can be produced from lignocellulosic biomass by hydrolysis and subsequent fermentation [14]. Ethanol was one promising solvent for biomass liquefaction [15], and it has been widely adopted as solvent for liquefaction of various biomasses such as lignocelluloses [16,17], microalgae [18], and sewage sludge [19]. Ethanol has several advantages in biomass liquefaction process including acting as hydrogen-donor to provide hydrogen, reacting with acidic compounds to form esters through esterification reactions and dissolving high-molecular weight products derived from biomass [15]. Besides, higher ethanol/biomass ratio has positive impacts to increase the bio-crude yield, since it can improve the stability and solubility of fragmented components [20,21]. Finally, the residual ethanol after reaction can be separated from bio-crude product through rotary evaporation at reduced pressure [15,22]. Therefore, ethanol/biomass ratio of 4 (80 g ethanol and 20 g PSD) was loaded as reactants for PSD liquefaction according to these factors and related reference [22].

However, a certain proportion of the added ethanol reacted with the decomposition fragments of PSD and formed more substituted compounds such as esters in PSD liquefaction [3,23]. Besides, some ethanol decomposed to gases such as  $C_2H_4$  and  $C_2H_6$  [22]. This resulted in the consumption of the added ethanol. Therefore, some of the added ethanol can be considered as a source that involved in liquefaction reactions that formed organic products [18]. The sources of organic products that were parts of bio-crude, solid residue and gas in the system resulted from both PSD and alcohol that was loaded.

Water-ethanol co-solvent is more efficient in biomass liquefaction reactions than either water or pure ethanol [24]. Similar low water to ethanol ratio (3:8) of this study was used in the liquefaction of woody biomass in the research of Cheng et al. [25], since the addition of water as a co-solvent into ethanol would enhance the liquefaction of biomass and improve bio-crude yield [25]. The biomass/ethanol loading ratio of 1:4 was determined according to our preliminary tests and referred to biomass liquefaction conducted by Brand et al. [22], because this biomass loading ratio was beneficial for improving bio-crude yield [22]. The biomass and total solvent loading ratio (biomass/total solvent ratio of 2:11) was determined according to the liquefaction of rice husk performed by Huang et al. [15,25]. This biomass loading ratio can increase the bio-crude yield and improve the stability and solubility of fragmented components derived from biomass [15].

The reactor was purged with 100 psig  $N_2$  for 6 times to remove the inside air. Then, the initial pressure for the reactor was charged to 10 psig with  $N_2$ . The reactor was heated to 300 °C at a heating rate of 5.0 °C  $min^{-1}$ . The reaction temperature was kept for 1 h at a stirring rate of 1000 rpm. There were some solvolysis reactions occurred at 300 °C that consumed ethanol in this study, but the solvolysis reactions at 300 °C were not significant. This is because solvolysis reactions were significant at temperatures above 350 °C in biomass liquefaction [26]. Besides, the low solvent/biomass ratio (11:2) in this study restricted solvolysis reactions [25]. Finally, the reactor was rapidly cooled to room temperature (20 °C) by an electric fan. The liquid-solid suspension in the reactor was poured out and filtered using a pre-weighed filter paper at a reduced pressure, and the solid product remaining on the filter paper was dried at 105 °C for 24 h in a drying oven and weighed [15]. The dried solid sample contained unreacted pine sawdust, ash, coke, generated ZnO and used catalyst is designated as mixed solid residue (SR1). The residual ethanol-water mixture was

evaporated from the liquid filtrate using a rotary evaporator at 90 °C in a reduced pressure [15,22]. The recovered ethanol can be reused for PSD liquefaction [27]. The resulted liquid product (bio-crude) was weighed. The yield of products ( $Y_{\text{product}}$ ) including solid residue and bio-crude were determined based on equation (2) and gas yield ( $Y_{\text{gas}}$ ) was calculated following equation (3):

$$M_{\text{solid residue}} = M_{\text{SR1}} - M_{\text{generated ZnO}} - M_{\text{used catalyst}} \quad (1)$$

$$Y_{\text{product}} = M_{\text{product}} / (M_{\text{pine sawdust}}) \times 100\% \quad (2)$$

$$Y_{\text{gas}} = (1 - Y_{\text{solid residue}} - Y_{\text{bio-crude}}) \times 100\% \quad (3)$$

where  $M_{\text{product}}$  represents the mass of solid residue and bio-crude, respectively.

### 2.3. Feedstock and products analysis

Moisture content of pine sawdust was determined following the ASABE standard (ASAES358.2 DEC1988 (R2008)) [28]. Ash content of pine sawdust was determined by heating samples at 575 °C until its weight remained constant in a muffle furnace according to NREL standard procedure [29]. High heating value (HHV) of pine sawdust samples was tested by the bomb calorimeter (IEA C2000) [30,31]. Elemental compositions (carbon, hydrogen and nitrogen) of pine sawdust and bio-crude were analyzed by CE-440 Elemental Analyzer [32]. Moisture content, ash content, elemental analysis and HHV properties of pine sawdust are presented in Table 1.

**Table 1. Properties of PSD.**

Analysis	Pine sawdust
Moisture content (wt%)	7.23 ± 0.12
Ash content (wt%)	0.56 ± 0.03
Elemental analysis (wt%)	
Carbon	47.64 ± 0.02
Hydrogen	6.25 ± 0.07
Nitrogen	1.24 ± 0.02
Oxygen <sup>a</sup>	44.87 ± 0.04
Higher heating value (MJ Kg <sup>-1</sup> )	19.19 ± 0.15
O/C (molar ratio)	0.71 ± 0.01
H/C (molar ratio)	1.57 ± 0.02

<sup>a</sup> Calculated by the difference

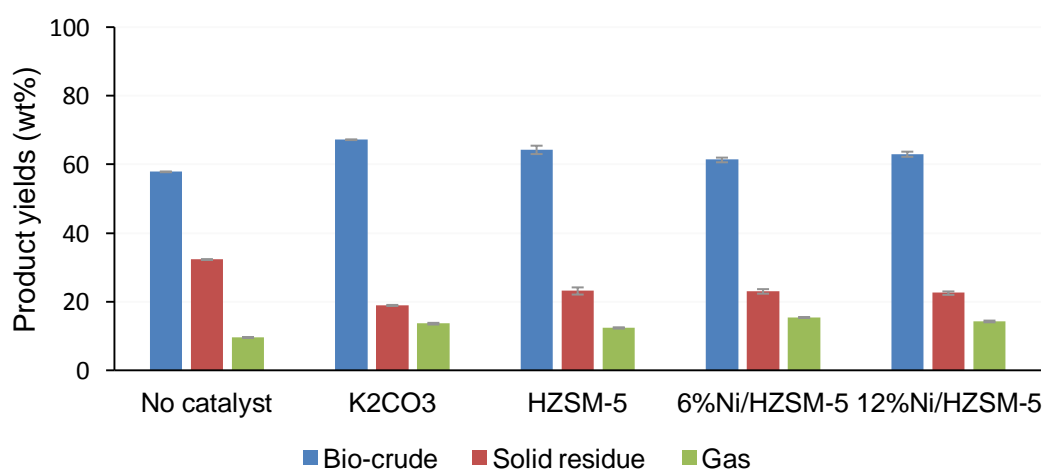
Gas chromatography (Agilent GC-7890A with a DB-5 column: 30 m × 0.25 mm × 0.25 μm) and mass spectrometry (MSD-5975C with electron ionization at 70 eV, mass range of 50–500 m z<sup>-1</sup>) was employed to determine chemical compositions of bio-crude samples [33,34]. The samples were dissolved in methanol before test. The injection temperature and injection volume were 300 °C and 1 μL respectively. An oven temperature program was firstly set at 60 °C and then increased following ramp 1 at 3 °C min<sup>-1</sup> to 140 °C, ramp 2 at 10 °C min<sup>-1</sup> to 180 °C, ramp 3 at 3 °C min<sup>-1</sup> to 260 °C and ramp 4 at 10 °C min<sup>-1</sup> to 300 °C. The main chemical compounds present in bio-crudes were identified from National Institute of Standards and Technology (NIST) mass spectral library and related literature [35].

Gas compositions was analyzed by gas chromatography system (Agilent GC 7890A with a  $50\text{ m} \times 0.53\text{ mm} \times 15\text{ }\mu\text{m}$  19095P-S25 column) [36].  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{N}_2$  were identified by thermal conductivity detector (TCD) [37]. Light hydrocarbons (C1-C3) were determined by flame ionization detector (FID) [38]. The carrier gas used in GC was argon, and calibration was conducted by using standard gas mixtures [39].

### 3. Results and discussion

#### 3.1. Product yields

Pine sawdust HTL products were distributed in gas, liquid (bio-crude) and solid residue. Figure 1 summarizes the yields of bio-crude, solid residue and gas products of different treatments. Compared to non-catalytic treatment, the use of zeolite catalysts (HZSM-5 and Ni/HZSM-5) increased yields of bio-crude and gas, and decreased solid residue yields. This is consisted with the study of Wang and Saber et al. [6,8]. Ni/HZSM-5 induced a better catalytic effect than HZSM-5, which indicated that Ni modification not only maintained the role of zeolite-cracking, but also had the function of hydrocracking that increased conversion of large molecules compounds in bio-crude to gaseous low-carbon small-molecules [40,41]. This resulted in the higher yields of gas and lower yields of bio-crude for Ni/HZSM-5 catalysts in comparison with HZSM-5 catalyst. Lignin conversion was relatively unaffected by pH in the thermal process. Alkaline catalysts such as  $\text{K}_2\text{CO}_3$  was effective in biomass liquefaction to enhance the yield of bio-crude products and suppress the formation of char [42-49].  $\text{K}_2\text{CO}_3$  showed higher catalytic activity to improve biomass conversion and bio-crude yield than other alkaline catalyts such as  $\text{KOH}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  in biomass HTL process [47].  $\text{K}_2\text{CO}_3$  produced higher bio-crude yield and lower solid residue yield compared to HZSM-5 and Ni/HZSM-5 catalysts in this study.  $\text{K}_2\text{CO}_3$  can react with water to form the bases and bicarbonates which acted as a secondary catalyst to improve bio-crude yield during the liquefaction reactions [47,50]. The bio-crude yield of  $\text{K}_2\text{CO}_3$  in this study was higher than the study of Wang et al. [50]. This was due to the lower reaction temperature ( $300\text{ }^\circ\text{C}$ ) that led to lower degree of condensation and redecomposition reactions of bio-crude products compared to their study ( $375\text{ }^\circ\text{C}$ ) [51,52].



**Figure 1. Product yields of different treatments.**

The yields of solid residues of HZSM-5 based catalysts was higher than that obtained by  $K_2CO_3$  catalyst. This indicated that the acidity of zeolites enhanced coke formation that resulted in catalysts deactivation, which in turn caused lower PSD conversions to bio-crude and gas products compared to alkaline catalysts. Similar results were found in the batch PSD liquefaction study of Wang et al. [50].

Biomass decomposition reactions occurred to some extent due to the slow heating rate [22]. The slow heating rate had no effect on the individual compounds of bio-crude product [53]. The slow heating rate reduced bio-crude yield and improved gas yield compared to high heating rate [22,53]. The slow heating rate increased solid residue yield due to the increased coke formation compared to high heating rate [53,54]. The slow heating rate decreased the relative concentrations of chemical compounds present in bio-crudes in comparison with high heating rate [54].

### 3.2. Elemental compositions and higher heating value of bio-crudes

Properties of the bio-crude products including elemental compositions (C, H, and N) and higher heating value (HHV) are presented in Table 2. Compared to PSD, all bio-crude samples obtained from PSD liquefaction had much higher contents of carbon and hydrogen, and much lower contents of oxygen, leading to a significantly increased HHV. Compared to no catalyst treatment, the use of catalyst improved the contents of carbon and hydrogen and reduced the oxygen content. This was due to deoxygenation activities of used catalysts that removed partial amount of oxygen in the bio-crude products [50]. HHV (26.78–27.93 MJ/kg) of  $K_2CO_3$  and HZSM-5 produced bio-crudes was in the range of biocrude produced in pure ethanol (25.8 MJ/kg) and pure water (30.8 MJ/kg) in pinewood sawdust  $K_2CO_3$  liquefaction of Wang et al. [50]. This was due to the mixed solvents (ethanol and water) used in this study. The oxygen content of catalytic bio-crudes (27.60–29.32 wt%) was in the range of the oxygen content of  $K_2CO_3$  produced bio-crude using ethanol and water (30.42 wt% and 23.38 wt% respectively) conducted by Wang et al. [50]. The molar ratios of O/C (0.32–0.35) and H/C (1.48–1.49) were in the range of the  $K_2CO_3$  liquefaction using ethanol and water (0.26–0.37 and 1.42–1.67 respectively) of Wang et al. [50]. However, there was no significant difference in the properties (elemental compositions and HHV) of  $K_2CO_3$  and Ni/HZSM-5 produced bio-crudes. The recovery ratio of carbon and hydrogen were 71.03–85.44 wt% and 61.26–80.36 wt% respectively. It was lower than the carbon recovery ratio of Yang et al. [55]. This was due to the loss of higher amount of some low boiling points organic compounds in rotary evaporation of bio-crude product at higher temperature (90 °C) than their study (50 °C). However, the carbon and hydrogen recovery ratio of  $K_2CO_3$  treatment were a bit lower than that of HZSM-5 and Ni/HZSM-5 treatments. The O/C (molar ratio) of bio-crude (0.32–0.44) decreased to some extent compared to that of PSD (0.71). However, the oxygen content of bio-crude products was still high (27.60–33.99 wt%) compared to PSD (44.87 wt%). This indicated that only small amount of oxygen was removed in the bio-crude product. These results indicated that the high bio-crude yields were due to high oxygen content in bio-crude products.

The ethanol consumption rate responding to different catalysts was ranging from 4.76 wt% to 6.03 wt%. This indicated that some ethanol was consumed in PSD HTL process which increased the cost of HTL process. However, the main objective of this study was to explore the application of heterogeneous Ni/HZSM-5 and alkaline  $K_2CO_3$  catalysts in biomass HTL process.

**Table 2. Elemental compositions and higher heating value of different bio-crudes.**

Relative content (%)	No catalyst	K <sub>2</sub> CO <sub>3</sub>	HZSM-5	6%Ni/HZSM-5	12%Ni/HZSM-5
Carbon (wt%)	58.42 ± 0.12	62.15 ± 0.14	63.29 ± 0.24	63.78 ± 0.12	63.13 ± 0.13
Hydrogen (wt%)	6.61 ± 0.10	7.71 ± 0.07	7.81 ± 0.06	7.92 ± 0.07	7.76 ± 0.14
Nitrogen (wt%)	0.98 ± 0.08	0.82 ± 0.06	0.72 ± 0.09	0.70 ± 0.08	0.73 ± 0.08
Oxygen <sup>a</sup> (wt%)	33.99 ± 0.14	29.32 ± 0.07	28.18 ± 0.07	27.60 ± 0.09	28.38 ± 0.05
HHV (MJ/kg)	23.12 ± 0.08	26.78 ± 0.19	27.51 ± 0.07	27.93 ± 0.16	27.35 ± 0.13
Carbon recovery ratio (wt%)	71.03 ± 0.12	81.24 ± 0.06	85.44 ± 0.08	82.17 ± 0.09	83.54 ± 0.12
Hydrogen recovery ratio (wt%)	61.26 ± 0.08	76.82 ± 0.04	80.36 ± 0.07	77.78 ± 0.07	78.27 ± 0.07
O/C (molar ratio)	0.44 ± 0.07	0.35 ± 0.02	0.33 ± 0.15	0.32 ± 0.12	0.34 ± 0.05
H/C (molar ratio)	1.36 ± 0.02	1.49 ± 0.01	1.48 ± 0.02	1.49 ± 0.01	1.48 ± 0.03
Ethanol consumption rate (wt%)	5.01 ± 0.14	4.76 ± 0.23	5.61 ± 0.34	4.89 ± 0.21	6.03 ± 0.18

<sup>a</sup> Calculated by the difference

### 3.3. Chemical compositions of bio-crude

In order to evaluate the change of chemical compositions of bio-crudes produced by different catalysts, bio-crude products derived from different treatments were determined by GC-MS. The main chemical components detected in bio-crudes are present in Table 3.

**Table 3. Chemical composition of different bio-crudes.**

Relative content (%)	No catalyst	K <sub>2</sub> CO <sub>3</sub>	HZSM-5	6%Ni/HZSM-5	12%Ni/HZSM-5
Phenols	10.8	9.84	9.94	8.64	8.93
Furans	2.63	1.25	0.43	0.57	2.46
Ethers	4.9	5.4	6.31	4.17	1.1
Aldehydes	0.2	3.76	2.16	0.12	2.9
Ketones	15.91	7.23	8.9	12.09	13.84
Esters	35.74	21.06	28.35	26.39	26.52
Alcohols	8.28	5.74	2.07	5.28	6.77
Acids	5.57	0	1.95	0.88	1.27
Hydrocarbons	3.04	6.63	8.26	11.02	6.49
Others	12.93	39.09	31.63	30.84	29.72

The main components detected in the bio-crude produced from no catalyst treatment were undesirable oxygenated compounds including esters (35.74%), ketones (15.91%), phenols (10.80%), alcohols (8.28%) and acids (5.57%). These oxygenated compounds resulted in the corrosiveness and low heating value of bio-crude products. Only minor amounts of desirable hydrocarbons (3.04%) was observed in non-catalytic bio-crude.

For the produced bio-crudes in the presence of catalysts, the chemical compositions of bio-crude products changed deeply in comparison with non-catalytic bio-crude. The contents of acids in bio-crudes produced by catalysts were significantly decreased. One reason is that some acidic compounds were converted to esters through esterification reactions with alcohols [56]. Another reason was that some acidic compounds were transformed to hydrocarbons through decarboxylation reactions [56]. There were no acid compounds detected in the bio-crude produced by K<sub>2</sub>CO<sub>3</sub>

treatment [55]. The contents of ketones in bio-crudes were also decreased by tested catalysts. This is consistent with the research results of Iliopoulou et al. [57]. Ketones were transformed to hydrocarbons through decarbonylation, cracking and aromatization reactions [58].

The alcohols content in bio-crudes decreased in all catalytic treatments. Some alcohols were transformed to hydrocarbons through dehydration, cracking and aromatization reactions [48,58], and some alcohols were converted to esters through esterification reactions [46,56]. The contents of phenols decreased in catalytic bio-crude products, because they were transformed into hydrocarbons through dehydration, dehydroaromatization, hydrogenolysis and hydrogenation reactions in the presence of zeolite catalysts [59]. Similar decrease of phenols content in upgraded bio-crudes from biomass liquefaction using HZSM-5 catalyst was observed by Torri et al. [60]. The contents of esters in the bio-crude of catalytic treatments reduced compared to no catalyst treatment. This was due to the transformation of esters to hydrocarbons due to dehydration, cracking and oligomerization reactions that occurred over HZSM-5 and Ni/HZSM-5 catalysts [28].

The content of desirable hydrocarbons in biofuel produced by all catalysts increased significantly in comparison with non-catalytic bio-crude. This was due to the catalytic reactions of cracking, decarbonylation, decarboxylation, hydrocracking, hydrodeoxygenation and hydrogenation that transformed oxygenated organic compounds to hydrocarbons over HZSM-5 based catalysts [50,61,62]. Compared to bio-crude produced from HZSM-5 catalyst, 6%Ni/HZSM-5 catalyst produced bio-crude with the higher hydrocarbons content at 11.02%. This increase was due to the Ni promoted hydrogenation and dehydro-aromatization reactions [63]. Compared to the 6%Ni/HZSM-5 treatment, 12%Ni/HZSM-5 catalyst produced lower hydrocarbons content in the bio-crude product. When more NiO was loaded on the HZSM-5, the Ni reduced from NiO preferentially aggregated and replaced the Brønsted acid sites that were responsible for catalyst activity [64]. This led to the lower formation of hydrocarbons over higher Ni loading HZSM-5 catalyst [65]. The hydrocarbons content of 6%Ni/HZSM-5 and HZSM-5 produced bio-crude were higher than bio-crude produced by  $K_2CO_3$  catalyst. This indicated the enhanced deoxygenation reactions on HZSM-5 based catalysts than  $K_2CO_3$ .

### 3.4. Mechanism of liquefaction reactions on HZSM and Ni/HZSM-5 catalysts

The XRD characterization of fresh catalysts (HZSM-5 and Ni/HZSM-5) has been conducted in our published paper [66]. The XRD characterization of spent catalysts in bio-oil upgrading was performed in other published papers [35,57].

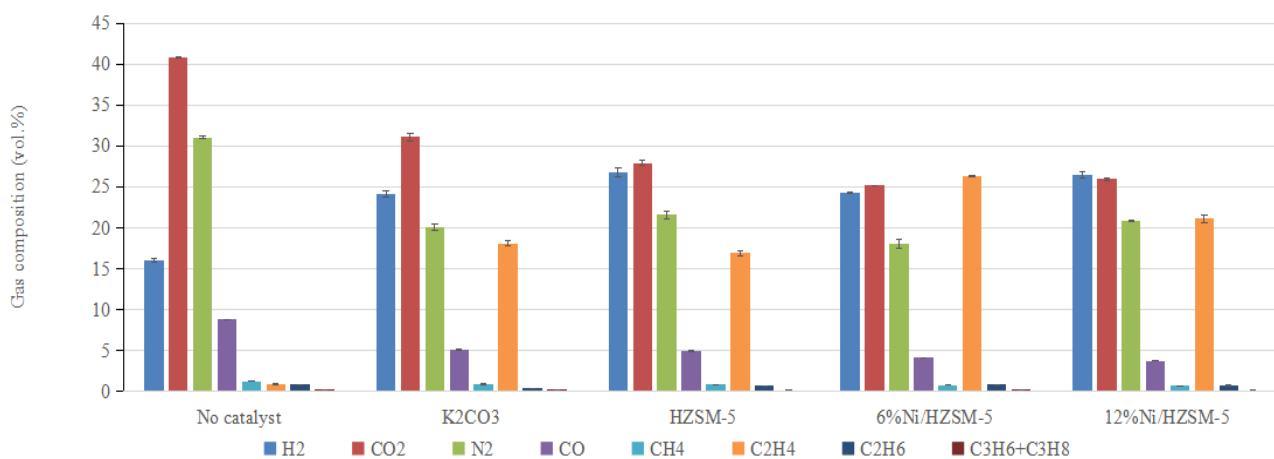
HZSM-5 contained mainly Brønsted acid sites with high acidic strength and few Lewis acid sites [57]. Brønsted acid sites catalyzed different hydrocarbon conversion reactions such as cracking, dehydrogenation, cyclization and aromatization [67]. This resulted in the increased hydrocarbons content in the bio-crudes produced by HZSM-5 based catalysts. NiO particles were formed in the fresh Ni/HZSM-5 catalysts in this study [66,68]. The loading of NiO reduced the number of Brønsted acid sites on Ni/HZSM-5 [57]. In contrast to the Brønsted acid sites, the formation of nickel oxides functioned as Lewis acidic centers that increased the number of Lewis acid sites on Ni/HZSM-5 [57]. The following reaction pathway on Ni/HZSM-5 was proposed from the PSD liquefaction results. Firstly, the de-oxygenation of bio-crude was conducted through decarboxylation reactions, and the in situ produced hydrogen from zinc hydrolysis was saved in the reactor [57]. Secondly, the saved hydrogen atoms promoted hydrogen transfer reactions on the Ni metals through carbenium ion intermediates formed on zeolitic acid sites. This resulted in increased formation of hydrocarbons through hydro-deoxygenation reactions on Ni/HZSM-5 catalyst [57]. The Ni particles



were reduced from NiO on Ni/HZSM-5 catalysts in the reductive atmosphere at high reaction temperature in bio-crude upgrading reactions [57,68].

### 3.5. Effectiveness of catalysts on PSD liquefaction

The yields of bio-crudes produced by catalysts (HZSM-5, Ni/HZSM-5 and  $K_2CO_3$ ) improved compared to no catalyst treatment.  $K_2CO_3$  produced higher bio-crude yield compared to other catalysts. The oxygen content of catalytic bio-crudes was lower than non-catalytic bio-crude. The heating value of catalytic bio-crude was higher than non-catalytic bio-crude. The undesirable contents of acids in catalytic bio-crudes decreased compared to non-catalytic bio-crude. This is beneficial to decrease the acidity and corrosiveness of catalytic bio-crudes [67]. The valuable hydrocarbons content of catalytic bio-crude improved compared to that of non-catalytic bio-crude. 6%Ni/HZSM-5 catalyst produced bio-crude with higher hydrocarbons content in comparison with other catalysts. Therefore, these results indicated that the use of catalysts (especially 6%Ni/HZSM-5 and  $K_2CO_3$ ) was effective for improving bio-crude yield and properties in PSD liquefaction.



**Figure 2. Gas distributions of different treatments.**

### 3.6. Gas distributions

After HTL, the gas products were collected and determined by GC. The compositions of produced gases are shown in Figure 2. Nine gas compounds ( $H_2$ ,  $N_2$ ,  $CO_2$ ,  $CO$ ,  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ ,  $C_3H_8$ ) were observed in the gas product. One main gas product was hydrogen that was produced from zinc hydrolysis reaction [69], and the existence of unreacted hydrogen indicated that the generated hydrogen was abundant for the HTL reactions. Another main component in gas product was  $CO_2$ , and this indicated that the oxygen in oxygenated compounds in bio-crude was predominantly removed in the form of  $CO_2$  through decarboxylation [70]. The presence of  $CO$  indicated decarbonylation of oxygenated compounds or reaction intermediates ( $C=O$ ,  $C-O-C$ ,  $COOH$ , etc.) in HTL processes [6,22]. The formation of  $CH_4$  was due to the decomposition of methoxyl groups ( $-O-CH_3$ ) during liquefaction process [22].  $C_2$ - $C_3$  hydrocarbons were also observed in the gas product, and they were produced from secondary cracking of reaction intermediates and/or decompositions of alcohols in the presence of  $H_2$  in PSD liquefaction process [22].

### 3.7. Reactor pressure

Reactor pressures of different treatments are listed in Table 4. Although the initial pressure of all treatments was the same, the maximum and final pressures for bifunctional Ni/HZSM-5 and  $K_2CO_3$  catalysts was higher than no catalyst or HZSM-5 treatments. The enhanced cracking performance of catalysts resulted in higher gas production that increased reactor pressure. This indicated that the Ni/HZSM-5 and  $K_2CO_3$  catalysts led to the promoted conversion of oxygenated compounds to light gases such as CO,  $CO_2$  and C1-C3 hydrocarbons.

The  $N_2$  partial pressure in final gas (25–28 psi, absolute pressure) is slightly higher than the initial  $N_2$  pressure (25 psi, absolute pressure). The increase of  $N_2$  between final  $N_2$  and initial  $N_2$  in the reactor was only 0–0.0049 moles compared to the initial total  $N_2$  amount of 0.0349 moles. The slightly increased amount of  $N_2$  formed from nitrogen atoms in PSD after PSD liquefaction process [71].

**Table 4. Reactor pressures of different treatments.**

Catalysts	No catalyst	$K_2CO_3$	HZSM-5	6%Ni/HZSM-5	12%Ni/HZSM-5
Initial (psig)	$10 \pm 0$	$10 \pm 0$	$10 \pm 0$	$10 \pm 0$	$10 \pm 0$
Maximum (psig)	$1680 \pm 20$	$1945 \pm 10$	$1875 \pm 15$	$1925 \pm 25$	$1900 \pm 20$
Final (psig)	$65 \pm 5$	$120 \pm 5$	$110 \pm 0$	$130 \pm 0$	$120 \pm 0$

## 4. Conclusions

HTL of pine sawdust on HZSM-5,  $K_2CO_3$  and Ni/HZSM-5 catalysts were carried out in the batch autoclave reactor at 300 °C. The catalytic effects of different catalysts are investigated in products (bio-crude and gas) yield and quality.  $K_2CO_3$  produced higher bio-crude yield and lower solid residue yield compared to other catalysts. The use of catalysts improved bio-crude and gas yields in comparison with no catalyst treatment. The catalysts reduced the contents of undesirable acids, ketones, phenols, esters and alcohols of bio-crudes, and increased the desirable hydrocarbons contents. Bifunctional Ni/HZSM-5 catalysts exhibited higher catalyst activities to improve bio-crude quality compared to parent HZSM-5 catalyst. Ni/HZSM-5 was more effective to convert oxygenated compounds to hydrocarbons due to the integrated cracking and hydrodeoxygenation reactions. Compared to HZSM-5, 6%Ni/HZSM-5 catalyst produced the bio-crude product with the highest hydrocarbon content at 11.02%.

Although the 6% Ni loading HZSM-5 catalyst was initial determined in this research, different Ni loading levels near 6% still need to be tested to identify optimized Ni loading level Ni/HZSM-5 catalyst for improving hydrocarbons selectivity in bio-crude product in the future studies.

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## Conflict of interest

All authors declare no conflict of interest in this paper.

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