



Research article

Influence of alkali catalysts on product yield and Si-containing products from hydrothermal liquefaction of corn stover

Godfrey Bryan D.A. Satiada, Rowena B. Carpio^{*}, Gino Apollo M. Guerrero, Monet Concepcion M. Detras, Manolito E. Bambase Jr.

Department of Chemical Engineering, University of the Philippines Los Baños, College, Laguna, 4031, Philippines

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ABSTRACT

This study investigated the effects of different alkali catalysts (K_2CO_3 , KOH, NaOH, and Na_2CO_3) on the yield and composition of biocrude oil and aqueous products obtained from hydrothermal liquefaction (HTL) of corn stover. HTL was performed in a laboratory-scale tubular reactor at 320 °C for 90 min and catalyst loading of 5.0 and 7.5 % (by weight of biomass). The composition of the biocrude oil and aqueous products was determined using GC-MS. Results revealed that hydroxide catalysts are more effective than carbonate catalysts in increasing biocrude oil yield. Notably, NaOH achieved a high conversion rate of 92–94 % daf (dry and ash-free basis), significantly surpassing the uncatalyzed HTL (69.4 % daf). The highest biocrude oil yield of 22.12–22.57 % daf was obtained using KOH. Si-containing compounds (e.g., silanes and siloxanes) were identified as the most abundant components in the biocrude oil, suggesting potential for further exploration in producing platform chemicals from these compounds.

1. Introduction

Lignocellulosic materials are promising feedstock, as renewable and natural resources, for producing various high-value products, including biofuels, platform, and fine chemicals. Agro-based industries generate considerable amounts of lignocellulosic biomass as waste. First-generation biofuels, made from biomass like starch and sugar, can help reduce carbon emissions and reliance on fossil fuels but they present a food vs. fuel dilemma. On the other hand, non-food biomass, such as lignocellulosic biomass, is used as a feedstock to create second-generation biofuels [1]. Lignocellulosic biomass is favored for its price, accessibility, and production speed [2]. It can be converted into an energy source through thermochemical processes and can take the form of crop or forestry residue, such as sawdust, rice straw, or maize husk. Biofuels derived from lignocellulosic biomass produce lower levels of SOx and NOx during combustion due to their low sulfur and nitrogen content. The composition and structural makeup of lignocellulosic biomass vary depending on the species. Lignocellulosic biomass generally comprises 40–50 % cellulose, 25–35 % hemicellulose, 10–30 % lignin, along with other compounds [2]. In this study, corn stover was selected as the representative lignocellulosic biomass feedstock. Corn is a major crop in the Philippines. According to the Philippine Statistics Authority (PSA), 1.81 million metric tons of corn were harvested between October and December 2018. The harvested corn includes various parts such as the grain, stalk, leaves, sheath, husks, shanks, cobs, tassels, and silks. While the corn grain is commonly consumed, the remaining parts, collectively referred to as corn stover, are generally treated as waste. Considering that the amount of corn stover generated is almost equal to that of the grain, its disposal poses a

^{*} Corresponding author.

E-mail address: rbcarpio@up.edu.ph (R.B. Carpio).

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considerable challenge.

Hydrothermal liquefaction (HTL) is a thermochemical process that lignocellulosic biomass can undergo, where the biomass is converted under high pressure (4–25 MPa) and elevated temperatures (250–375 °C) [3]. Unlike other thermochemical methods, HTL can process lignocellulosic biomass with high moisture content, reducing the need for drying. Various factors, such as residence time, reaction temperature, biomass-to-water ratio, catalyst type, and biomass composition, play a role in determining the HTL outcome [4]. Table 1 presents a comprehensive summary of related HTL studies conducted on various biomass types over the past decade and in recent years, detailing the different conditions applied, such as temperature, duration, and catalyst usage, along with their major findings.

When utilizing a water or alcohol medium for HTL of biomass, acid catalysts are generally considered inefficient [5]. In contrast, alkali catalysts have been shown in numerous HTL experiments involving various biomass types to enhance the HTL process. As presented in Table 1, commonly used alkali catalysts include K_2CO_3 , KOH, NaOH, and Na_2CO_3 . These catalysts are known to suppress char formation, improve biomass conversion, liquefaction yield and promote oil formation [6–9]. However, oil yields vary significantly depending on the biomass type, catalyst, and HTL conditions. The literature reveals extensive research on the application of different alkali catalysts to lignocellulosic biomass (such as wood biomass [6,7,9–13] and agricultural residue [8,14–21]), macroalgae [22], sewage sludge [23], carbohydrate-rich food waste [24], biopulp [25], and kenaf [26], with varying catalytic effects observed. The lignocellulosic composition of biomass (cellulose, hemicellulose, lignin content) influenced the outcome of HTL, with certain catalysts performing better depending on the specific biomass characteristics. Minowa et al. [17] is one of the early studies that used Na_2CO_3 as a catalyst in HTL using 18 different types of biomass residues. This research found a strong correlation between lignin content and the yield of solid residues (or biochar), indicating that higher lignin content led to an increase in biochar yield. Comparative studies of the reactivity of different alkali catalysts (based on oil yield) [8,10,20,22] showed varying trends depending on biomass type and HTL process conditions. For example, a catalyst activity order of $KOH > NaOH > K_2CO_3$ was reported for the HTL of rice straw using a water-ethanol co-solvent [20]. Meanwhile, in the HTL of two species of red macroalgae—*Kappaphycus alvarezii* (KA) and *Eucheuma denticulatum* (ED)—subjected to same process condition, the following reactivity order was observed for KA: $Na_2CO_3 > CaCO_3 \approx KOH > Na_2SO_4 > NaOH > K_2CO_3$; for ED, $KOH > NaOH > CaCO_3 > Na_2SO_4 > K_2CO_3 > Na_2CO_3$ [22]. Recent studies [14,16,25] have also examined the effects of recycling aqueous phases with alkali catalysts in HTL, demonstrating significant improvements in oil yield and energy recovery, underscoring the potential for enhanced efficiency through process optimization. Additionally, a synergistic effect on biocrude oil yield and energy recovery has recently been reported when using a combination of metallic Fe and alkali catalysts in the HTL of pinewood sawdust [12].

The pH of the reaction medium significantly influences the reaction pathway of the biomass conversion. According to Yin et al. [27], the main compounds for the acidic condition are 5-(Hydroxymethyl)furfural (5-HMF) and levulinic acids while for alkaline condition, lactic acid and acetic acid are prevalent. On the other hand, the neutral condition may follow either an acidic or alkaline pathway. The acid-catalyzed HTL of biomass is prone to polymerization reaction, leading to the production of a solid phase, whereas alkali-catalyzed HTL favors condensation reaction that produce aromatic oils [28]. The addition of an alkali catalyst enhances liquid phase production by promoting the water-gas shift reaction. By raising the pH of the medium, alkali catalyst prevents further dehydration of the biomass which could lead to the formation of unsaturated compounds. These compounds are susceptible to polymerize, leading to char formation [29].

The existing literatures on the HTL of corn stover are still scarce and covers a range of topics. Ankit et al. [3] investigated HTL of corn stover within a temperature range of 250–375 °C, reaction times from 0 to 60 min, and initial pressures of 300 and 600 psi. They observed a decrease in oil yield with increasing temperature or reaction time, regardless of the initial pressure. On the other hand, Carpio et al. [16] explored HTL of corn stover at 300–340 °C, with reaction times of 30–90 min and catalyst loading of 0–10 % using K_2CO_3 . They found that the interaction of reaction temperature and time significantly affects oil yield, with a synergistic effect observed at high temperatures (e.g., 340 °C) and longer reaction times (e.g., 90 min). Ankit et al. [3] also noted that pressure has a more pronounced impact on the heavy oil fraction at lower temperatures (250–300 °C), with no significant effect at higher temperatures (350–375 °C). They highlighted that under all tested conditions, the heavy oil fraction was predominantly composed of phenol derivatives, with some presence of ketones, linear saturated and unsaturated hydrocarbons, and phenyl groups, while fatty acids and fatty acid alkyl ester derivatives were mainly observed at 250 and 300 °C. Carpio et al. [16] also reported that the addition of an appropriate amount of K_2CO_3 could improve oil production. At lower temperatures (e.g., 300 °C), a higher catalyst load is recommended to offset the effects of low temperature and boost oil production, while at higher temperatures (e.g., 320 °C), a moderately high catalyst load is sufficient. Their analysis of the biocrude oil obtain at 320 °C, 90 min, with or without 5 % K_2CO_3 , revealed a high abundance of aromatics and Si-containing compounds.

Few studies focused on pretreatment of corn stover alongside other lignocellulosic biomass to improve oil production. Recently, Gu et al. [30] conducted a pretreatment experiment using a white-rot fungus and found it highly effective in delignifying corn stover and poplar wood chips while preventing cellulose loss. The subsequent two-stage HTL process (first stage at 180 °C, second stage at 220 °C) was reported to enhance the production of hydrolyzed sugars and value-added derivatives, resulting in a 163.6 % increase in hemicellulose sugar recovery from poplar and a 75.2 % improvement from corn stover, compared to untreated samples during the first stage of the HTL process. Halleraker et al. [31] studied different delignification methods and reported that the outcome of HTL of lignin derived from corn stover and other biomass sources is also influenced by these methods, impacting both the yield and composition of the oil.

Water is generally used as the solvent in HTL. Recently, Das et al. [32] investigated the HTL of corn stover and wheat straw using different alcohols (methanol, ethanol, and 2-propanol) as co-solvent and found that a water-alcohol co-solvent system enhances the quality of the heavy oil more significantly than it affects the yield. Co-HTL has emerged as a promising method in converting biomass

Table 1
Comprehensive summary of related HTL studies.

Biomass	HTL condition	Catalyst/Buffering agent	Lignocellulose component (%dw)			Major findings	Ref.
			C	H	L		
Corn stover	250–375 °C 300 & 600 psi 0–60 min	None	NA	NA	NA	Quantitative optimum condition: Max. yield of heavy oil (29.25 wt%) and highest conversion rate (82.62 %) both obtained at 300 °C, 600 psi and 0 min retention time; with a C content of 65.7 wt% and HHV of 28.22 MJ/kg. Qualitative optimum condition: Highest C content (76.32 wt%) and HHV (35.13 MJ/kg) obtained at 375 °C, 600 psi, 15 min. Across all conditions, the heavy oil primarily consisted of phenol derivatives, with some ketones, linear saturated and unsaturated hydrocarbon, and phenyl groups. At 250 and 300 °C fatty acids and fatty acid alkyl ester derivatives were also detected.	[3]
Wood biomass (sawdust from pine)	280 °C 15 min	0.235, 0.47 & 0.94 M K ₂ CO ₃	NA	NA	NA	Max. conversion (96 %) and oil yield (33.7 %) was obtained with 0.94 M K ₂ CO ₃ . Biomass to water ratio impacts product distribution and composition of oil product; distribution of oxygenated hydrocarbons vary according to the biomass to water ratio and concentration of K ₂ CO ₃ solution.	[6]
Birch wood sawdust	300 °C 30 min	5 % KOH, FeSO ₄ ·7H ₂ O, K ₂ CO ₃ , MgO, synthetic hydrotalcite (HT) & ground colemanite (GC)	NA	NA	NA	The alkaline catalysts (KOH, K ₂ CO ₃ , and GC) demonstrated superior performance in terms of oil yield and solid residue yield. The highest biocrude oil yield (40 %), lowest solid yield (12 %) obtained with KOH. In contrast, the uncatalyzed process yielded 18 % oil and 33 % solid. The presence of catalysts, particularly the alkaline ones, significantly increased the occurrence of phenol derivatives (primarily 2-methoxy-phenol) and aliphatic compounds in the oil.	[7]
Empty Palm Fruit Bunch	270 °C 20 min 20 bars	1.0 M NaOH, KOH, & K ₂ CO ₃	44.20	33.50	20.40	The catalytic performance and optimal biomass-to-water ratio significantly enhanced the conversion. The highest liquid yield of 68 wt% was achieved with a 72.4 wt% mass conversion and 65.6 wt% lignin degradation using 1.0 M K ₂ CO ₃ and a 2:10 biomass-to-water ratio (B/W). B/W > 2:10 resulted in reduced conversion and lower liquid hydrocarbon yields. The liquid products were primarily composed of phenols and esters. The reactivity order, based on biomass conversion and liquid yield, was as follows: K ₂ CO ₃ > KOH > NaOH.	[8]

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Table 1 (continued)

Biomass	HTL condition	Catalyst/Buffering agent	Lignocellulose component (%dw)			Major findings	Ref.
			C	H	L		
Paulownia wood	280–360 °C 10 min	10 % (w/w) Fe 5 % (w/w) Na ₂ CO ₃	42.35	25.22	23.44	Both catalysts effectively enhanced the biocrude oil yield. The maximum heavy oil yield (36.34 wt%) was obtained with Fe at 340 °C, while minimum solid residue yield (8.12 wt%) was obtained using Na ₂ CO ₃ at 320 °C. The oils were predominantly composed of phenol derivatives, ketones, carboxylic acids/esters, benzene derivatives, long-chain alkanes, aldehydes, and their derivatives. The use of different catalysts could alter the distribution and relative abundance of these produced compounds.	[9]
Furniture saw dust	280 °C 15 min	1.0 M NaOH, Na ₂ CO ₃ , KOH, & K ₂ CO ₃	32.63	37.23	22.16	The highest biocrude oil yield (34.9 wt%) and lowest solid residue yield (6.8 wt%) were obtained using 1.0 M K ₂ CO ₃ . The reactivity order, based on biomass conversion and liquid yield, was K ₂ CO ₃ > KOH > Na ₂ CO ₃ > NaOH. With or without a catalyst, the heavy oil fraction contained both low and high boiling oxygenated hydrocarbons, while the light oil fraction only consisted of low boiling oxygenated hydrocarbons. The heavy oil in all catalytic experiments mainly contained tarry compounds. The concentration of K ₂ CO ₃ significantly influenced the elemental composition and HHVs of the bio-oils.	[10]
Larch (softwood) & Mongolian oak (hardwood)	300 °C 30 min	0–1% (w/w) K ₂ CO ₃	NA	NA	26.1-29.9	The highest oil yields from Larch (25.7 %) and Mongolian Oak (27.7 %), along with the greatest carbon conversion, were achieved using 0.5 % K ₂ CO ₃ . The presence of a catalyst significantly reduced the formation of hydrochar. The oil's organic compound content also increased, particularly for lignin-derived compounds like catechol and hydroquinone in the presence of a catalyst. Adding an appropriate amount of alkali catalyst can enhance both the production efficiency and the quality of biocrude oil.	[11]
Pinewood sawdust	300 °C 30 min	10 % Metallic Fe + other catalyst (10 % w/w Na ₂ CO ₃ , NaOH, FeSO ₄ , MgO, Ru/C, FeS)	NA	NA	30.29	Using a combination of Fe and other catalysts resulted in synergistic effects that enhanced the yield and quality of bio-oil. The maximum bio-oil yield of 48.24 wt% and energy recovery of 81 % were achieved with the Fe + Na ₂ CO ₃	[12]

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Table 1 (continued)

Biomass	HTL condition	Catalyst/Buffering agent	Lignocellulose component (%dw)			Major findings	Ref.
			C	H	L		
Waste bamboo stick	290–380 °C 30 min	20 % (w/w) K ₂ CO ₃	46.5	26.8	25.5	combination. The relative content of phenols, aromatics, and hydrocarbons in the bio-oils increased, while the oxygenated compounds decreased when Fe was used alone. Among the Fe mixed additives, the highest phenol content was obtained with Fe + Na ₂ CO ₃ , while relatively lower oxygenated compounds and higher hydrocarbon contents were achieved with Fe + FeS or Fe + Ru/C. The maximum biocrude oil yield of 21.2 % was achieved at 290 °C with the addition of a catalyst, in contrast to just 3.8 % without a catalyst. The heating value increased slightly from 30.9 MJ/kg to 31.6 MJ/kg with the catalyst. Simulated distillation of the bio-oil indicated that its characteristics are similar to diesel and superior to heavy oil and boat oil.	[13]
Barley straw	Without aqueous phase (AP) recycling: 280–400 °C 15 min; With AP recycling: 300 °C 15 min	10 % (w/w) K ₂ CO ₃	46	23	15	Without AP recycling, the highest oil yield (34.9 %) was achieved at 300 °C, while the solid residue yield increased from 8.1 % to 13.2 % as the temperature rose from 300 °C to 400 °C. At higher temperatures, the biocrude oil exhibited improved quality with lower oxygen content and HHVs. The biocrude oil primarily consisted of phenolics, carboxylic acids, aldehydes, and alcohols, with the relative contents of phenolics and carboxylic acids decreasing as the temperature increased. AP recycling led to a progressive increase in biocrude oil yield, from 34.9 % to 38.4 % after three cycles, without the addition of fresh catalyst. The HHVs of biocrude oil produced through HTL with recycled AP (28.4–29.4 MJ/kg) were slightly higher than those obtained using fresh water.	[14]
Barley straw	300 °C 15 min	10 % (w/w) K ₂ CO ₃	46	23	15	The yield of biocrude oil increased from 17.88 wt% to 34.85 wt% with the addition of K ₂ CO ₃ , improving both quality and reducing solid residue. The carbon and energy recovery with K ₂ CO ₃ was twice higher compared to without a catalyst. Carboxylic acids, phenolic compounds, and ketones were the primary compounds in the biocrude regardless of catalyst use, but distribution and relative amounts varied. The	[15]

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Table 1 (continued)

Biomass	HTL condition	Catalyst/Buffering agent	Lignocellulose component (%dw)			Major findings	Ref.
			C	H	L		
Corn stover	Without recycling: 300–340 °C 30–90 min	0–10 % (w/w) K ₂ CO ₃	26.10	29.05	25.32	catalytic process resulted in a higher concentration of phenolic compounds and a lower concentration of carboxylic acids. The maximum oil yield of 14.54 % was obtained at 340 °C and 90 min without a catalyst. With 7.5 % K ₂ CO ₃ , the maximum oil yield of 10.52 % was obtained at 320 °C for 60 min. At low reaction temperatures (e.g., 300 °C), a higher amount of catalyst should be used to offset the effects of the low temperature and enhance oil production. At higher temperatures (e.g., 320 °C), a moderately high catalyst load is sufficient. Recycling AP led to a gradual increase in biocrude oil yield (from 9.21 to 11.63 %) and energy recovery (10.55–21.37 %) while there is a decrease in solid residue after three cycles. Nitrogenates and O&N heterocycles decreased, while Si-containing compounds increased after the 3rd cycle.	[16]
	With aqueous phase (AP) recycling: 320 °C 90 min	5 % (w/w) K ₂ CO ₃					
18 different biomass residues (Acacia mangium, Bagasse, Bagasse pith, Banana stem, Coconut husk, Coconut shell, Corn stalk, Kenaf Metroxylon sp. petioles, Metroxylon sp. stem, Oil-palm empty fruit bunch, Oil-palm husk, Oil-palm petioles, Oil-palm shell, Pineapple leaf, Rice husk, Rice straw, Rubber tree)	300 °C 30 min	5 % (w/w) Na ₂ CO ₃	26.49–52.13	NA	10.31–48.91	The oil yield range between 21 and 36 wt% (on an organic basis). The highest oil yield was obtained from oil-palm shell while the lowest was from banana stem. A high correlation between lignin and residue was observed - residue yield increased with the lignin content. The oils exhibited similar properties, including about 70 wt% carbon, 7 wt% hydrogen, less than 1 wt% nitrogen, an HHV of 30 kJ/g, and a viscosity greater than 10 ⁵ mPa s.	[17]
Paddy straw	275 °C 10 MPa 40 min	1 % (w/w) K ₂ CO ₃	>25	NA	NA	Without a catalyst, the product yields were 70 ml of biocrude oil, 600 ml of aqueous phase, and 38 g of char. With a catalyst, the yields were 120 ml of biocrude oil, 430 ml of aqueous phase, and 52 g of char. The biocrude oil produced with the catalyst had fuel properties similar to those of biodiesel standards, including heating value, flash point, and fire point.	[18]
Sugarcane bagasse	200–330 °C 5–90 min	Solid alkali catalyst of MgMOx (M = Mn, Ni, Fe, Cr, Zn and Al)	46.47	33.35	18.96	The highest liquefaction degree of 93.7 % was achieved with MgMnO ₂ at 250 °C for 15 min. The MgMnO ₂ catalyst demonstrated excellent reusability, maintaining its activity even after five consecutive uses. The HHV of	[19]

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Table 1 (continued)

Biomass	HTL condition	Catalyst/Buffering agent	Lignocellulose component (%dw)			Major findings	Ref.
			C	H	L		
Rice straw	300-350 °C 30 & 60 min	5 % NaOH, KOH & K ₂ CO ₃	NA	NA	NA	the THF-soluble product from bagasse liquefaction increased from 27.44 to 32.61 MJ/kg with the MgMnO ₂ catalyst. Under optimal conditions (300 °C, 60 min, a rice-straw-to-water ratio of 1:10, and a final pressure of 18 MPa), the biocrude oil yield was 12.3 wt % with an energy recovery of 36 %. When methanol was used as a co-solvent with water in a 50:50 (v/v) ratio, the oil yield increased to 31.7 wt%. The addition of KOH further boosted the oil yield to 39.9 % and improved energy recovery to 82.9 %. The reactivity order based on oil yield was KOH (39.9 %) > NaOH (34.5 %) > K ₂ CO ₃ (33.8 %). The main product groups in the biocrude oil without a catalyst were esters, phenolics, and cyclo-oxygenates. The addition of a catalyst significantly reduced the ester content, following the trend: K ₂ CO ₃ > KOH > NaOH. Selectivity towards phenolic compounds in the biocrude oil was observed with the use of KOH and K ₂ CO ₃ .	[20]
Wheat husk	280 °C 15 min	500 mol/m ³ KOH & K ₂ CO ₃	36	18	16	Total bio-oil yield: K ₂ CO ₃ (31 %) > KOH (30 %); Light hydrocarbon yield: K ₂ CO ₃ (22 %) > KOH (14 %); Heavy hydrocarbon yield: KOH (16 %) > K ₂ CO ₃ (9 %); Solid residue yield: K ₂ CO ₃ (22 %) > KOH (16 %)	[21]
<i>Kappaphycus alvarezii</i> (KA) & <i>Euचेuma denticulatum</i> (ED) (red macroalgae)	350 °C 30 min	5 % (w/w) Na ₂ CO ₃ , K ₂ CO ₃ , CaCO ₃ , Na ₂ SO ₄ , NaOH & KOH	NA	NA	NA	The reactivity order based on biocrude oil yield using KA was as follows: Na ₂ CO ₃ (16.6 %) > KOH (16.2 %) ≈ CaCO ₃ > Na ₂ SO ₄ (16.1 %) > NaOH (15.7 %) > K ₂ CO ₃ (14.2 %). Without a catalyst, the oil yield was 12 %. Using ED, the order was KOH (15.8 %) > NaOH (15.1 %) > CaCO ₃ (12.1 %) > Na ₂ SO ₄ (11.8 %) > K ₂ CO ₃ (11.3 %) > Na ₂ CO ₃ (11 %). Without a catalyst, the oil yield was 10 %. The oils from both feedstocks were mainly composed of cyclic oxygenates. Carbonated salts (Na ₂ CO ₃ , K ₂ CO ₃ , and CaCO ₃) showed significantly higher selectivity towards cyclic oxygenated compounds compared to other treatments. A high degree of deoxygenation (64.2 %) was observed in biocrude oil from KA with Na ₂ SO ₄ , while the maximum energy recovery (99 %) was achieved with Na ₂ CO ₃ treatment of ED.	[22]

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Table 1 (continued)

Biomass	HTL condition	Catalyst/Buffering agent	Lignocellulose component (%dw)			Major findings	Ref.
			C	H	L		
Sewage sludge	350 & 400 °C 15 min	2.5 % (w/w) K ₂ CO ₃ & CH ₃ COOH	NA	NA	NA	The addition of K ₂ CO ₃ or CH ₃ COOH did not result in a notable increase in biocrude yield. Alkali catalysts are unsuitable for converting high-protein feedstocks, such as sewage sludge, which contains 43 % protein. In the absence of a catalyst, energy recovery as biocrude improved by 50 % through aqueous phase recirculation, but the nitrogen content in the biocrude nearly doubled after eight recycling cycles. Additionally, successive rounds of recycling led to a higher accumulation of potassium and sodium in the aqueous phase.	[23]
Manure digestate & carbohydrate-rich food waste	300 °C 60 min	5.0 M H ₃ PO ₄ 1 M NaOH	NA	NA	NA	Oil yields from manure digestate reached 58 % with H ₃ PO ₄ , 42 % with NaOH, and about 36.5 % without a catalyst. For food waste, the yields were 43 % with H ₃ PO ₄ , 33 % with NaOH, and approximately 36.4 % without a catalyst. Acid addition had a more significant effect on HTL reactions for manure than for food waste. In manure, acid addition shifted HTL oil products toward straight fatty acids and amides, while base addition had a lesser impact on the oil composition. In food waste, acid addition directed the biocrude oil composition toward furan compounds, whereas base addition promoted the formation of phenols and straight fatty acids.	[24]
Biopulp (org fraction of municipal solid waste)	Without aqueous phase (AP) recycling: 350 & 400 °C 15 min With AP recycling: 350 °C 15 min	2 % (w/w) K ₂ CO ₃	NA	NA	NA	Without AP recycling, both oil yield and energy recovery were enhanced with the use of a catalyst at both temperatures. Whether a catalyst was used or not, higher oil yield and energy recovery were observed at 350 °C compared to 400 °C. When the concentrated AP is recycled over four consecutive cycles in the catalytic experiment at 350 °C, the biocrude oil yield increased from 36.6 % to 49.3 %, and the energy recovery improved from 61.7 % to 84.3 %. The catalyst level with recirculation was maintained by adding fresh K ₂ CO ₃ . Carboxylic acids were the most abundant chemical group in the biocrude oils, throughout recirculation their level gradually decreased while the N-containing	[25]

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Table 1 (continued)

Biomass	HTL condition	Catalyst/Buffering agent	Lignocellulose component (%dw)			Major findings	Ref.
			C	H	L		
Korean native kenaf	250–350 °C 15–120 min	0–5 % (w/w) NaOH	39.95	15.04	19.99	compounds significantly increased. The highest biocrude oil yield (23.74 %) with energy recovery of 51.52 % was obtained at 350 °C, 30 min, using 1 % (w/w) NaOH. Benzene compounds were the most abundant in this oil, followed by ketones, phenols, hydrocarbons, and carboxylic acids. A high catalyst loading greater than 3 % has adverse effect on oil yield at temperature near critical point (370 °C).	[26]
Corn stover, poplar, & wheat straw	1st stage: 180 °C 2nd stage: 220 °C 30 & 60 min	None	39.5–43.2	18.1–27.1	18–27.8	Two-stage HTL of fungal-pretreated biomass led to significant results. Fungal pretreatment enhanced delignification, reducing the initial degradation temperatures by 11–36 °C. In the first stage of HTL, the recovery of hemicellulose sugars increased by 163.6 % from poplar and by 75.2 % from corn stover compared to untreated samples.	[30]
Lignin derived Soft wood, spruce, beechwood, corn stover, rice straw	320 & 360 °C 2 h	None	NA	NA	42–95.4	Lignin derived from different source using different delignification methods (including Kraft pulping, Organosolv processing, acetone/water oxidation, Milox pulping, deacetylation and acid precipitation) were subjected to HTL. The study highlights that although the origin of lignin does influence the composition of bio-oil, its impact is not as significant as the methods used for biomass fractionation (e.g., delignification method), the way biomass is pretreated has a more profound effect on both the yield and the molecular composition of the resulting bio-oil.	[31]
Corn stover & wheat straw	300 °C, initial reactor pressure of 600 psi 0 min	None	37.4–38.1	25.3–35.6	20.2–20.4	The co-solvents used include methanol, ethanol, and 2-propanol. A 50:50 (v/v) water-co-solvent mixture impacts the quality of heavy oil more than its yield. The composition of biomass (cellulose, hemicellulose, lignin, etc.) influences the heavy oil yield. The water–2-propanol mixture significantly improved the quality of heavy oil, resulting in the lowest oxygen content, HHV, lowest total acid number (TAN), and compounds similar to diesel.	[32]
Corn stover (CS) + cow manure (CM)	375–450 °C 12–30 min	None	NA	NA	NA	The highest biocrude yield of approximately 24 wt%, with an	[33]

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Table 1 (continued)

Biomass	HTL condition	Catalyst/Buffering agent	Lignocellulose component (%dw)			Major findings	Ref.
			C	H	L		
	1:1, 1:2, & 2:1 CS to CM mass ratio					HHV of 34 MJ/kg, was achieved under moderate conditions of 400 °C, 16 min, and a mass ratio of 1:1. The selectivity for phenol in the biocrude oil of up to 43 % was sustained for a reaction time of up to 30 min. Additionally, co-HTL produced a hydrochar with an HHV as high as 27.31 MJ/kg.	
Corn stover & loblolly pine	350 °C	1 % (w/w) Na ₂ CO ₃	NA	NA	NA	Na ₂ CO ₃ was employed as a buffering agent to maintain the pH above 4. In a bench-scale continuous HTL process, the aqueous phase product was characterized and found to contain acids, which made up nearly half of the carbon content. Alcohols and ketones were also identified. Significantly high levels of potassium, sulfur, and both alkali and alkaline earth metals were also detected, raising concerns about potential challenges in catalyst performance during downstream upgrading or reforming processes.	[34]

C: cellulose, H: hemicellulose, L: lignin; NA: not available.

mixtures into biocrude oils with enhanced yields and quality. Liu et al. [33] investigated the fast co-HTL of corn stover and cow manure, achieving the highest biocrude oil of over 24 % with HHV around 34 MJ/kg at 400 °C and 16 min, using a 1:1 mass ratio. Although interest in the aqueous phase fraction from HTL of lignocellulosic feedstock has grown, only a few studies have focused on corn stover [16,34]. The interest on the aqueous phase arises from the need to make biocrude oil production via HTL more sustainable. By reusing aqueous phase as an aqueous medium, the process can reduce fresh water consumption, minimize wastewater streams, and enable the recovery of organic materials during subsequent HTL cycles, potentially enhancing both the yield and quality of the oil. Additionally, the aqueous phase was also studied as a potential substrate in hydrothermal gasification to recover energy in the form of methane for process integration. Panisko et al. [34] characterized the aqueous phase from the HTL of corn stover and found that acids accounted for nearly half of the carbon content in this fraction. They also detected high levels of potassium, sulfur, and both alkali and alkaline earth metals, raising concerns about potential issues with catalyst use in downstream upgrading or reforming processes. Carpio et al. [16] studied K₂CO₃-catalyzed HTL of corn stover with recycled aqueous phase and reported an increase in oil yield and energy recovery, with the oil being enriched with Si-containing compounds after the 3rd round of recycling.

Several studies have proposed biorefinery models and carried out techno-economic and sustainability performance analyses of the HTL process using corn stover. Collett et al. [35] demonstrate a proof-of-concept and presented a techno-economic analysis for an innovative hybrid biorefinery model that uses corn stover, lipid-producing oleaginous yeast and continuous hydrothermal liquefaction process, achieving a 40 % biocrude oil yield with a carbon yield of 55 %. The subsequent hydrotreatment of the biocrude oil produced a hydrocarbon fuel blendstock, with majority of the product boiling in the distillate range. Huang et al. [36] evaluated the sustainability performance of three major technologies: alcohol-to-jet (ATJ), Fischer-Tropsch (FT) and HTL to convert corn stover to jet fuel using the mixed-integer linear programming model that incorporate spatial, agricultural, techno-economical, and environmental data for multi-objective optimization. The results show that HTL is the most cost-effective with a cost of \$4.64/gal while FT is most environmental-friendly, producing 0.10 kg CO₂/gal.

The objective of this study is to evaluate the impact of different alkali catalysts (K₂CO₃, KOH, NaOH, and Na₂CO₃) on oil production from the hydrothermal liquefaction of corn stover. The oil produced was analyzed by bomb calorimetry and gas chromatography mass-spectroscopy (GC-MS). Although HTL of corn stover has been previously studied, variations in corn plant characteristics, influenced by ecotype and planting origin, can impact oil production and catalyst effectiveness. This study further investigates the impact of different alkali catalysts on the generation of Si-containing compounds in the HTL products. The results of this work underscore the importance of selecting appropriate catalysts and optimizing process parameters based on the specific characteristics of the biomass used, as these choices directly impact the quality and composition of the end products. This research contributes to the development of HTL as a viable method for producing valuable products from lignocellulosic biomass, particularly for industrially important Si-containing

compounds.

2. Materials and methods

2.1. Materials

Powdered corn stover was prepared according to the same procedure in an earlier study by Carpio et al. [16]. The corn plant used in this study was provided by the National Seed Foundation, Institute of Plant Breeding at the University of the Philippines Los Baños. The corn plant harvest method was based on the study by Paul et al. [37]. The different components of the corn stover sample (leaves, stalks, husks, cobs, hairs, and flowers) were separated and weighed to determine the proportion of each part. The samples were then dried in a convection oven at 60 °C for 24 h to ensure the removal of excess moisture. The samples were then reduced in size using a blender and screened using Tyler mesh no. 24 to obtain a particle size of less than 0.71 mm. Each component of the dried corn stover was weighed and mixed according to the proportion of the dried corn stover composition.

The alkali catalysts sodium carbonate (Na₂CO₃), sodium hydroxide (NaOH), potassium carbonate (K₂CO₃), and potassium hydroxide (KOH) and dichloromethane (DCM) were procured from Sigma-Aldrich. Alkaline solutions were prepared by adding weighed pellets/powder and a calculated amount of water to achieve the catalyst's desired concentration (5 or 7.5 % w/w catalyst per biomass).

2.2. Experiment set-up and procedure

The HTL process was performed in a tubular bomb-type reactor constructed using a ¼ inch 316 stainless steel Swagelok union, cap, and plug. The reactor had approximately 8.5 mL capacity. In a typical run, the furnace was preheated to 320 °C while preparing the feedstock. The feedstock consisted of 0.45 g of corn stover powder and 7 mL of alkaline solution, which was then loaded inside the reactor. The reactor was then sealed, weighed, and placed inside the furnace. Once the furnace reached 320 °C, the temperature was maintained for 90 min. The reaction parameters used were based on the study by Carpio et al. [16]. After the reaction, the reactor was manually removed from the furnace using heat-resistant gloves and tongs. Then the reactor was quenched in a water bath to cool off the reactor back to room temperature.

2.3. Product separation and recovery

After cooling the reactor, the gaseous product was released by venting under the fume hood. The remaining reaction mixture was washed with 30 mL organic solvent DCM. Vacuum filtration was then performed to separate the liquid and solid components. The solid residue was washed further using DCM and then dried in a convection oven at 105 °C for 4 h. The resulting oven-dried mass gives the biochar product. The filtrate, consisting of the aqueous product, biocrude oil, and DCM, was separated using a separatory funnel. The aqueous phase product was collected in a pre-weighed container and stored in a refrigerator, while the organic phase, which consists of biocrude oil-DCM mixture, was transferred to a pre-weighed foil cup. The DCM was released under a fume hood for at least 8 h to obtain the biocrude oil product. Then, the biocrude oil sample was weighed. The constant weight of the sample in the analytical balance ensures the biocrude oil is DCM-free.

The product yield was estimated by gravimetry in dry, ash-free weight percentage (% daf), using equations (1)–(3). The biomass conversion was calculated using equation (4).

$$\text{Biocrude oil (\%daf)} = \frac{M_{oil}}{M_{FS}(1-m-a)} \quad (1)$$

Table 2
Characterization of corn stover sample [16].

Properties	Value
Moisture (%) (fresh)	62.51 ± 5.02
Moisture (%) (prepared)	12.52 ± 0.36
Chemical composition (% dry weight)	
Ash	7.22 ± 0.33
Crude Protein	7.17 ± 0.06
Crude Fiber	32.47 ± 0.51
Crude Fat	0.64 ± 0.05
Cellulose	26.10 ± 0.07
Hemicellulose	29.05 ± 0.07
Lignin	25.32 ± 2.69
Elemental Composition (% dry weight)	
Carbon	40.8
Hydrogen	6.53
Nitrogen	0.762
Sulfur	0.156
Oxygen (by diff.)	44.8
HHV (MJ/kg of dry weight)	16.66

$$\text{Biochar (\%daf)} = \frac{M_S - M_{FS} * a}{M_{FS}(1-m-a)} \quad (2)$$

$$\text{Aqueous + gas phases (\%daf)} = 100\% - \% \text{Biocrudeoil} - \% \text{Solid residue} \quad (3)$$

$$\text{Biomass conversion (\%daf)} = 100\% - \% \text{Solid residue} \quad (4)$$

where M_{oil} is the mass of the biocrude oil, M_{FS} is the mass of the feedstock, M_S is the mass of the solid after HTL, m and a are mass fraction of moisture and ash, respectively, in the biomass feedstock.

2.4. Characterization

The characteristic of the corn stover powder used in the present study was previously reported in a study by Carpio et al. [16], shown in Table 2. The higher heating value (HHV) of the oil was determined using Model 6200 Isoperibol Calorimeter (Parr Instrument Company). The chemical constituents of the biocrude oil and aqueous phase samples were analyzed using GC-MS TQ8049 (Shimadzu) with DB-5MS GC column (60 m × 0.25 mm I.D., 0.25 mm film thickness) and AOC-20i auto-injector (Shimadzu). The analyses were performed following the method described by Carpio et al. [38]. The spectra of all chromatogram peaks were evaluated using the GCMSsolution software (Shimadzu, Japan), and compared with electron impact mass spectrum from NIST Mass Spectral Database (NIST08) and W8N08 library (John Wiley & Sons, Inc., USA). The composition of the oil and aqueous samples is presented as % relative abundance. This is calculated by dividing the total ion chromatogram (TIC) peak area of a compound by the TIC total area of compounds identified in the sample, then multiplied by 100 %.

2.5. Statistical analysis

The experiment results were tested using Analysis of Variance (ANOVA) at $\alpha = 0.05$. The interaction between catalyst and concentration and their corresponding main effects were examined using Design Expert ® version 11.0.3.0 (Stat-Ease, 2018).

2.6. Literature search

The following search string in Scopus was used to find relevant studies that specifically mention hydrothermal liquefaction or HTL, corn stover, and biocrude oil or oil production in the title, abstract, or keywords: TITLE-ABS-KEY ("hydrothermal *liquefaction" OR "*HTL") AND TITLE-ABS-KEY ("corn stover") AND TITLE-ABS-KEY ("oil production" OR "bio-crude" OR "biocrude" OR "bio-oil" OR "bio oil") AND (LIMIT-TO (DOCTYPE, "ar") OR LIMIT-TO (DOCTYPE, "cp")) AND (EXCLUDE (EXACTKEYWORD, "Asymmetric Supercapacitor") OR EXCLUDE (EXACTKEYWORD, "Cellulosic Ethanol") OR EXCLUDE (EXACTKEYWORD, "Supercapacitor") OR EXCLUDE (EXACTKEYWORD, "Capacitance")). The asterisk (*) was used to capture any variations of the terms "liquefaction" (e.g., "co-liquefaction") and "HTL" (e.g., "co-HTL"). The search was limited to document type "ar" (article) and "cp" (conference paper). The search was further refined by excluding the keywords "Asymmetric Supercapacitor", "Cellulosic Ethanol", "Supercapacitor", and "Capacitance" using the keyword filtering option.

A broader search on the hydrothermal liquefaction of biomass or lignocellulosic biomass using alkali catalyst employed the following search string in Scopus: (TITLE-ABS-KEY ("alkali catalyst*" OR "homogenous catalyst*") AND TITLE-ABS-KEY ("biomass" OR "lignocellulos*") AND TITLE-ABS-KEY ("hydrothermal *liquefaction" OR "*HTL")). Similarly, the asterisk (*) was used to capture any variations of the terms "catalyst" (e.g., "catalysts"), "lignocellulose" (e.g., "lignocellulosic"), "liquefaction" (e.g., "co-liquefaction"), and "HTL" (e.g., "co-HTL").

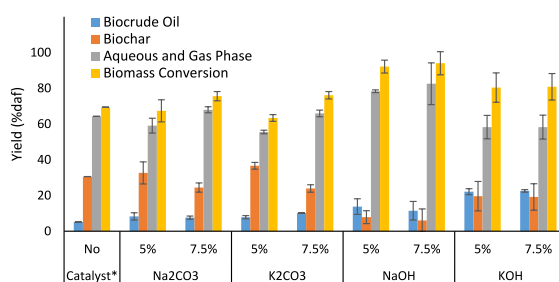


Fig. 1. Product yield from the HTL of corn stover at 320 °C and 90 min without and with different types of alkali catalyst. *Data adapted from previous work [16] conducted using the same batch of corn stover biomass and process conditions used in the present study.

3. Results and discussion

3.1. Effect of different alkali catalyst

Fig. 1 shows the product yield and biomass conversion from the HTL of corn stover with different alkali catalysts (Na_2CO_3 , K_2CO_3 , NaOH , and KOH) at two levels of concentration (5 % and 7.5 % w/w). The data for the non-catalytic run at the same reaction condition (320 °C, 90 min) was adapted from previous work by Carpio et al. [16] for comparison. The results showed a variation in the amount of biocrude oil produced using the different catalysts. Compared to the non-catalytic run (5.12 % daf), the oil yield increased to 7.61–22.57 % daf depending on the alkali catalyst used. Compared to the biochar yield without a catalyst (30.60 % daf), the addition of an alkali catalyst decreases the formation of biochar to 6–24 % daf, except at both 5 % Na_2CO_3 and 5 % K_2CO_3 where a slight increase in biochar was observed.

The ANOVA results revealed that only the type of catalyst had a significant effect ($p < 0.05$) on the oil yield and biochar yield. The catalyst concentration levels used were probably too narrow to show any notable effect. Therefore, it is recommended that future research should explore the effect of catalyst concentration using broader range of values.

The highest biocrude oil yield was obtained with KOH (22.12–22.57 % daf) followed by NaOH (11.46–13.79 % daf), K_2CO_3 (7.84–10.17 % daf), and Na_2CO_3 (7.61–8.29 % daf). The lowest biochar yield was obtained with NaOH (6.01–7.88 % daf) followed by KOH (19.17–19.62 % daf), Na_2CO_3 (24.44–32.63 % daf), and K_2CO_3 (23.92–36.63 % daf). Overall, the alkali hydroxides perform better than the alkali carbonates in terms of the biocrude oil yield, the desired product, compared to the biochar yield. It also appeared that KOH promoted biomass conversion to biocrude oil, while NaOH effectively suppressed biochar formation or improved biomass conversion efficiency to as high as 94 %.

The initial pH of the feedstock slurries using alkali hydroxides was all higher than those with alkali carbonates at the same % w/w concentration, as shown in Table 3. It was reported that a high initial pH value promotes the hydrolysis of cellulose and hemicellulose by breaking the glycosidic bonds and the hydrolysis of lignin by cleavage of ester and ether bonds [39]. The result is also consistent with the observation by Jindal and Jha [10], which reported that during HTL of waste furniture sawdust, a reaction medium with higher initial pH inhibited the dehydration of biomass monomers and suppressed the char formation. Between KOH and K_2CO_3 at the same concentration (5 or 7.5 % w/w), the result is inconsistent with the study by Nazari et al. [7], which reported a comparable performance of KOH and K_2CO_3 (both at 5 % w/w) on the biocrude oil and biochar yield using woody biomass. In the present study, the oil yield with KOH is more than double of what was obtained with K_2CO_3 .

Since the levels of weight concentration of catalysts used in the study were the same for each type, the molar concentration varies depending on the catalyst. At a catalyst concentration of 5–7.5 % w/w, the equivalent molar concentration for each of these catalysts is presented in Table 3. It can be verified that alkali hydroxides are 2–3 times higher in molar concentrations than alkali carbonates which could explain the better catalytic performance of the alkali hydroxides.

To illustrate the possible effects of K^+ , Na^+ , OH^- and CO_3^{2-} ions from the alkali catalyst on product yields, the equivalent number of moles of these ions were calculated and correlated with the biocrude oil and biochar yields as presented in Fig. 2. As the Na^+ ion increases, the biochar yield decreases, converting more solids to other phases. Therefore, it can be speculated that higher concentrations of Na-containing catalysts could enhance the degradation and conversion of biomass. Meanwhile, there is a weak correlation between the oil yield and the amount of Na^+ ions, the same is true for the biocrude oil and biochar yields with K^+ ions. While it should be noted that the amount of Na^+ ions (0.33–0.84 mmol) is present in a broader range than K^+ ions (0.42–0.64 mmol), this range is probably too narrow to establish any correlation. Future study should investigate a wider range of alkali catalyst concentrations to provide a more comprehensive understanding of their impact on product yields. Expanding this range will help establish more robust correlations between catalyst ion concentrations and HTL outcomes, facilitating optimization for both cost-effectiveness and performance. Future study should also consider standardizing molar concentrations across different catalysts or adjusting the concentrations to achieve comparable molarities for a more accurate comparison of catalyst performance.

The presence of metal ions (e.g., Na^+ and K^+) in the reaction medium may weaken the linkages that bind the lignin, cellulose, and hemicellulose chains. Roberts et al. [40] reported that Na^+ catalyzes the cleavage of the ether bonds by forming cation adducts with

Table 3

The pH of the reaction medium and aqueous phase product at varying types of catalyst and concentration.

Catalyst	Concentration		pH	
	(% w/w) ^a	mol/L	Initial ^b	Final ^c
Na_2CO_3	5	0.02	11.34	4.15
	7.5	0.04	11.43	4.73
K_2CO_3	5	0.03	11.4	4.4
	7.5	0.05	11.49	4.61
NaOH	5	0.08	12.91	4.85
	7.5	0.12	13.08	5.25
KOH	5	0.06	12.76	5.01
	7.5	0.09	12.93	5.58

^a Weight of catalyst/weight of biomass feedstock.

^b pH of the reaction medium before the reaction.

^c pH of the aqueous phase after the reaction.

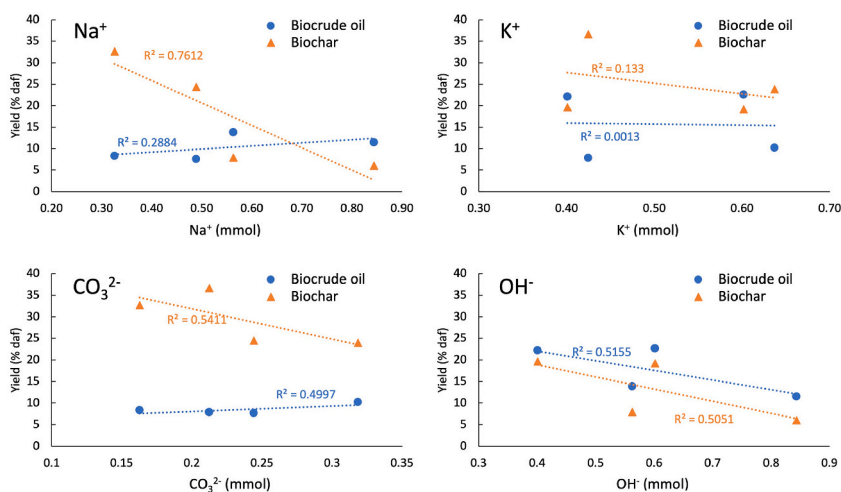


Fig. 2. Correlation of the amounts of Na⁺, K⁺, CO₃²⁻, and OH⁻ ions to the biocrude oil and biochar yield.

lignin that could cause the ether bonds to polarize. This result in an increased negative partial charge of the oxygen atom and reduces the energy required for bond cleavage. A similar effect could occur in the case of cellulose and hemicellulose. Saddawi et al. [41] suggested that the interaction of the metal ions (e.g., Na⁺ and K⁺) with the hydroxyl and ether bonds of cellulose changes the geometry of its structure; this enables certain ring conformation that improves the degradation. The electronegativity of Na and K are 0.93 and 0.82, respectively. This means that Na⁺ ions interact with ether bonds and OH⁻ groups better than K⁺ ions. Also, the amount of Na⁺ ions is higher than K⁺. This may explain the decreasing trend in biochar yield obtained with increasing levels of Na⁺ ions compared to that of K⁺, which showed no distinct trend. However, future study is necessary to confirm these effects, as there could be possible interaction between catalyst-derived ions (such as Na⁺ and K⁺) and naturally occurring inorganic elements in the biomass may occur. Such studies could reveal synergistic effects or identify potential co-catalysts that enhance the efficiency of the HTL process.

A study by Reza et al. [42] reported the presence of K (23,097 ppm) and Na (6,434 ppm) along with other inorganic elements (Si, Ca, Al, Mg, Fe, P, etc.) in raw corn stover. Patel et al. [43] reported that 38–59% of Na⁺ and K⁺ ions originally present in the microalgal biomass partition in the aqueous phase during HTL. Hence, a similar effect may also be speculated in the present study. Some inorganic elements or ions may also act as co-catalyst during the HTL process. Furthermore, the relative proportion of different inorganic elements may also influence the possible catalytic effect. For example, Belkheiri et al. [44] reported that when the ratio of Na⁺/(Na⁺ + K⁺) increased from 0.8 to 1.0, the amount of heavy oil obtained from the HTL of Kraft lignin increased from 22.4 to 37.6%. Furthermore, there could be a possible different interaction effect between the combinations of cations and anions that are not explored in this study. Hence, further study is recommended to investigate the effect of the interaction of cations and anions on product yield.

With increasing amounts of CO₃²⁻ ion (0.16–0.32 mmol), there is a decreasing trend in the biochar yield and a slightly increasing trend in oil yield. This result is probably because of the increasing formation of bicarbonates which may act as a secondary catalyst to enhance the yield of biocrude oils and suppress the char formation [10,45]. On the other hand, both the biochar and biocrude oil yield decrease with increasing OH⁻ ions (0.40–0.84 mmol). However, despite these results, the biomass conversion and oil yield obtained with OH⁻ ions are still higher than with CO₃²⁻ ions at any given concentration. The observed trend with OH⁻ ions is consistent with the effect of pH, as discussed earlier. The decrease in biochar and biocrude oil yield with increasing OH⁻ ions is attributed to the enhanced gasification of biomass or secondary decomposition of oil. Ding et al. [46] reported the high alkalinity from KOH promoted the production of H₂ from cellulose and pinewood in supercritical water (400–500 °C). For the present study conducted at a lower temperature (320 °C), it is speculated that a certain high alkalinity level could also promote gasification under subcritical water.

In general, the application of the catalyst on a w/w basis showed a catalyst activity in the order of KOH > NaOH > Na₂CO₃ > K₂CO₃ for biocrude oil and NaOH > KOH > Na₂CO₃ > K₂CO₃ for biochar. Considering the pH of NaOH (12.91–13.08) and KOH (12.76–12.93) are about in the same range, the oil yield obtained with KOH is twice as much as with NaOH even though NaOH (0.08–0.12 M) is present in higher molar concentrations than KOH (0.06–0.09 M). With this result, it is speculated that the presence of K⁺ positively affects oil production. Similar to Na⁺, K⁺ also aid in the collapse of biomass structures and fragmentation of biomass components that can be converted to organic product. A previous study [11] reported that potassium suppressed char formation reaction through repolymerization by the potassium by hindering the reaction between the unsaturated bonds of the decomposed compounds, such as by the removal of the acetate group from hemicelluloses, thereby improving the efficiency of oil production of the HTL process. Studies [47,48] also suggest that the presence of K⁺ lowers the degradation temperature of biomass and could also enhance the oil conversion process. Lundqvist [48] reported that K⁺ from K₂CO₃ acts as a catalyst that transcends the hydrothermal liquefaction into the gasification area.

The low activity by the carbonate catalysts is probably due to its relatively low molar concentration (Na₂CO₃: 0.02–0.04 M and K₂CO₃: 0.03–0.05 M). Compared to studies by Jindal and Jha [10] and Akhtar et al. [8], which generally reported the superior catalytic

performance of K_2CO_3 than KOH, NaOH and Na_2CO_3 used a much higher molar concentration in the range of 0.1–1.0 M, which is equivalent to 20–83 % w/w catalyst concentration.

A more systematic study is suggested for future work. The integration of alkali catalyst may be optimized to ensure cost-effectiveness while maintaining high biocrude oil yield and quality considering the following: catalyst selection and optimized loading to balance the cost and performance; optimizing reaction temperature, pressure and reaction time to balance yield, quality and energy consumption; development of efficient methods to recover and reuse the alkali catalyst; feedstock selection and pretreatment to improve reactivity with the catalyst. Due to funding limitation, the HTL experiments were conducted using a basic 8.5 ml batch reactor, which lacks a stirring mechanisms, provisions for purging oxygen or residual air, and the ability to charge initial pressure—all of which could affect the HTL outcome. Future studies should aim to secure funding for more advanced reactor systems. A reactor equipped with integrated stirring, purging, and pressure management features will provide a more controlled environment for the HTL process. This will lead in more reliable and reproducible results, thereby enhancing the understanding of process dynamics and improving the overall effectiveness of HTL experiments.

3.2. Compositional analysis of biocrude oil and aqueous products

The chemical constituents in the biocrude oil and aqueous phase products as determined by GC–MS were classified into several chemical groups: hydrocarbons, oxygenates, nitrogenates, aromatics, Si-containing compounds, and others. Only the compounds with a relative abundance area >1 % were considered in the group. These compound groups account for 67–86 % and 58–85 % of the total ion chromatogram peak area for biocrude oil and aqueous phase, respectively. The results are reported in Fig. 3. It is to be noted that the GC oven used has a maximum temperature of 310 °C; hence, only compounds with a boiling point below or at this temperature were detected by the GC-MS.

As can be observed, Si-containing and aromatic compounds are the main groups in biocrude oil without a catalyst. The addition of a catalyst remarkably decreased the aromatics, while the Si-containing group (mainly siloxanes and silanes), in most cases increased and remained the leading compound group. It is also noted that the compound groups in oils with alkali catalysts are more varied than those without a catalyst, except with 5 % KOH which is almost composed only of Si-containing compounds. On the other hand, the Si-containing compounds, a major compound group in the aqueous phase in the non-catalyzed reaction markedly decreased and, in some cases, disappeared in the presence of a catalyst. Si-containing compounds such as siloxanes decrease their solubility in water with increasing molecular weight, and they may or may not be volatile. It appeared that the Si-containing compounds were partitioned to the organic solvent used (DCM) during the separation of the biocrude oil and aqueous phase products, thus increasing the abundance of the Si-containing compounds in the biocrude oil, which consequently, improved the oil yield. Siloxanes are common impurities in biogas [49] and were recently reported in trace amounts in the biocrude oil produced by the pyrolysis of residual sewage sludge [50]. Siloxane was reported as a product of the adverse reaction of transesterification of oil from *Chlorella vulgaris* with CuO/Zeolite catalyst [51].

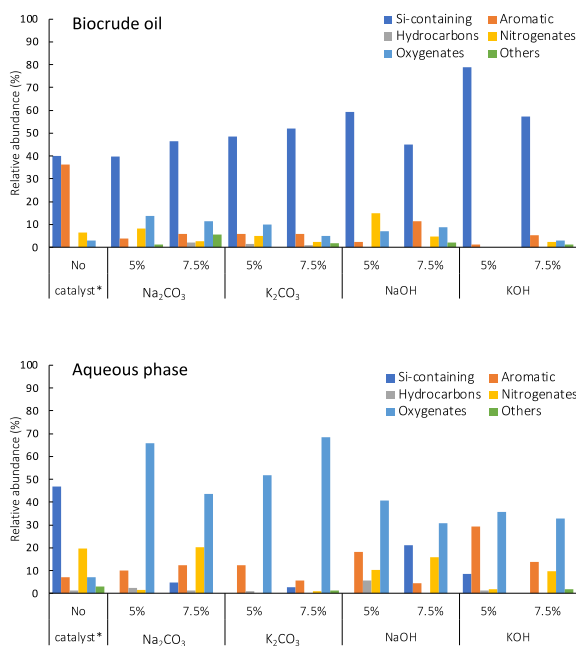


Fig. 3. Major compound groups in the biocrude oil and aqueous phase products.

The corn plant is a natural silicon accumulator and is believed to be the source of silicon in oil and aqueous phase products. Silicon accumulation in plants, including corn, is part of the plants' mechanism against environmental stress. Research indicates that silicon is involved in activating multiple physiological and biochemical mechanisms. These include the activation of antioxidant systems which mitigate oxidative stress and the stimulation of gene expression and defense responses, bolstering the plant's resilience and protecting its structures and functions under drought conditions [52,53], such as those experienced in the tropical climate of the Philippines. Silicon is deposited throughout the plant as phytoliths which are composed mainly of hydrated silica, $\text{SiO}_2 \cdot n(\text{H}_2\text{O})$ [54]. A study by Reza et al. [42], also reported Si was also the most abundant inorganic element in raw corn stover.

A recent study [55] reported the unexpected formation of organic siloxanes from catalytic hydrogenation of waste enzymatic lignin from corn stover using ethanol as solvent and Ru/SBA-15 as a catalyst. The study confirms the formation of the siloxane precursors, tetraethyl orthosilicate (TEOS, formally named tetraethoxysilane) and diethyl dimethyl orthosilicate (EMOS), from the depolymerization process of lignin and silicon from the lignin and reported the highest yield of siloxanes of 61.63 % at 280 °C reaction temperature and 4 h reaction time. A similar mechanism may explain the presence and abundance of Si-containing compounds produced from the HTL of corn stover biomass in the present study. The abundance of Si-containing compounds in the liquid product is attributed to the high lignin content and presumably high-silica content present in the corn stover biomass used and the high reaction condition employed in the process.

The lists of Si-containing compounds present in the aqueous phase and biocrude oil are available in the **Supplemental Data**. This compound group is dominated by a linear siloxane (Heptasiloxane, hexadecamethyl-) in the biocrude oil and phenyl-rich siloxane (1,3,5,7-Tetramethyl-3,5,7-triphenyl-1-[2-(1,3,3,5,5-pentamethyl-2,4,6-trioxo-trisilacyclohexyl)ethyl]-2,4,6,8-tetraoxa-1,3,5,7- and bis [di (trimethylsiloxy)phenylsiloxy]trimethylsiloxyphenylsiloxane) in the aqueous phase from the uncatalyzed reaction. Notably, these compounds disappeared or were detected in trace abundance in the catalyzed reactions, wherein new and diverse species of cyclosiloxanes emerged. Further, the oxygenates group, which appeared markedly low in the aqueous phase without a catalyst, is the most abundant group with a catalyst. The oxygenates in the aqueous phase products, which include carboxylic acids, alcohol, esters, aldehydes, and ketone are decomposition products of carbohydrates, cellulose and hemicellulose [56]. These compounds are important precursors in oil formation. The high abundance of oxygenates with a catalyst suggests an enhanced biomass decomposition.

When dissolved in water, silicon exists as orthosilicic acid ($\text{Si}(\text{OH})_4$), also commonly called silicic acid (H_4SiO_4). However, $\text{Si}(\text{OH})_4$ is rarely observed because it is highly unstable and readily condenses to polysilicic acid (PSA) (such as TMOS, TEOS), solid silica, and other siliceous material. The rate of condensation depends on pH. This condensation is a reversible process [57]. The derivatives compound of silicic acid is a candidate precursor to the formation of the Si-containing groups found in both aqueous phase and biocrude oil. The biomass polymers, lignin, cellulose, and hemicellulose, under hydrothermal liquefaction are converted to intermediate and final products such as phenol, catechol, C2-C5 alcohols [56,58]. These products probably reacted with PSA and its derivatives via substitution reaction which form the linear siloxanes [55,57]. The cyclosiloxanes probably emerged as a thermodegradation products of siloxane [59] which is catalyzed by the reduction of the threshold degradation temperature in the presence of the alkali catalyst. However, further study is recommended to understand the formation of Si-containing compounds which dominates the biocrude oil produced.

In this study, Si-containing compounds detected are in the form of siloxanes and silanes, which are known to have many industrial uses, such as in coatings/paints, adhesives, sealants, and fire retardants [60,61] and household products such as detergents, shampoos, and cosmetics. Hence, the Si-containing compounds-rich oil obtained from HTL of biomass residue of our local-corn plant could provide a potential renewable source. The oil production can be improved, and Si-containing compounds may be further enriched using KOH as a catalyst.

Table 4 shows the HHV of biocrude oils produced with Na_2CO_3 , NaOH, and K_2CO_3 catalyst in the range of 18.98–23.79 MJ/kg, which are higher than that of the original corn stover biomass (16.66 MJ/kg). The value for KOH was not included due to the mishandling of oil samples. The HHV of the oil obtained is within range or somewhat lower than the value reported in a similar study by Jindal and Jha [10] using waste furniture sawdust (20–32 MJ/kg) and Nazari et al. [7] using woody biomass (22–27 MJ/kg). The relatively low calorific value of biocrude oil obtained in this study is probably due to the abundant oxygen molecules in Si-containing compounds such as siloxane, which has an oxygen-silicon backbone, and in some silane species. This limitation highlights the need for additional work to develop further deoxygenation processes to make the oil suitable for fuel applications.

4. Conclusion

Using an alkali catalyst significantly improved the biocrude oil yield from the HTL of corn stover. KOH increased the oil yield from

Table 4
Higher heating values of biocrude oil for all catalysts at 5 % concentration.

CATALYST	HHV (MJ/kg)
KOH ^a	–
Na_2CO_3	23.08
NaOH	18.98
K_2CO_3	23.79

^a Not available due to mishandling of oil sample.

the non-catalytic run to the highest level (22.12–22.57 % daf), while NaOH produced the least biochar (6.01–7.88 % daf). In general, the catalytic activity indicates the following trends: KOH > NaOH > K₂CO₃ > Na₂CO₃ for biocrude oil production and NaOH > KOH > Na₂CO₃ > K₂CO₃ for biochar reduction. GC-MS analysis of the biocrude oil and aqueous phase showed that Si-containing compounds produced during HTL tend to distribute themselves in the biocrude oil when an alkali catalyst is used. When KOH is employed, the compound groups are less varied and the Si-containing compounds become the predominant group. In the future, additional work is needed to investigate the effect of the combinations of cations and anions resulting from both the catalyst and those leached from the biomass and to gain deeper insights into the formation of Si-containing compounds that dominate the biocrude oil produced.

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Data availability statement

Data included in article/supp. material/referenced in article.

CRediT authorship contribution statement

Godfrey Bryan D.A. Satiada: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **Rowena B. Carpio:** Writing – review & editing, Supervision, Methodology, Formal analysis, Conceptualization. **Gino Apollo M. Guerrero:** Writing – review & editing, Formal analysis. **Monet Concepcion M. Detras:** Writing – review & editing, Formal analysis. **Manolito E. Bambase:** Writing – review & editing, Formal analysis.

Declaration of competing interest

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e37520>.

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