EVALUATION OF ANAEROBICALLY DIGESTED BIOMASS IN CATALYTIC SUPERCRITICAL WATER GASIFICATION FOR BIOFUEL PRODUCTION

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ABSTRACT

Digested water hyacinth with waste sludge as inoculum were obtained after anaerobic digestion at 35 and 45°C. High organic content of digested biomass were evaluated through gasification at supercritical conditions of water in the absence and presence of catalysts (KOH, NaOH, LiOH and K_2CO_3) with 10 wt.% of volatile solid in feed. Supercritical water gasification of digested biomass was performed in batch reactor system at temperature and pressure ranges of 500–600°C and 35–45 MPa, respectively. The highest carbon gasification efficiency, hydrogen and methane yields were reached at 600°C (with samples digested at 45°C) in the absence of catalyst as 84.6 (g C in gaseous/g C in digestate), 53.0 (mol H_2%) and 14.2 (mol CH_4%), respectively. High organic content of digested biomass was converted by supercritical water gasification to methane and hydrogen rich gas, and aqueous products (aliphatic hydrocarbons, phenol, substituted phenols, N-heterocyclic, substituted N-heterocyclics, and substituted benzene) that can be evaluated as platform chemicals.

Keywords: Water hyacinth, Supercritical water gasification, Hydrogen, Methane

1. INTRODUCTION

Water hyacinth is an aquatic weed that spreads very rapidly and cause environmental problems for irrigation, navigation, aquatic life and crops. Utilization of waste plants is essential for energy production. Anaerobic digestion (AD) is a method for biological conversion of organic materials into biogas and digestate. Conversion of the volatile organic matter is between 40–60% in AD systems and the amount of digestate left is usually around 50% of the fed material [1]. After AD, digested biomass still has high organic content which was mostly evaluated as natural fertilizer or composting material [2]. The digestates were used as fertilizer due to their suitable contents of N, P, K and micronutrients. However, high variability and unbalanced contents of digestate makes their analysis necessary before they can be used as fertilizer [3]. Evaluation of digestate as fertilizer is not suitable because of low capacity for application in agriculture, different pollutions like heavy metals and organic compounds, danger of infection, legal problems and transportation distances. In addition, composting process produces mostly carbon dioxide which is not valuable for energy production and increase greenhouse gas emissions.

Digestate with high organic content can be converted to hydrogen and methane rich gas by supercritical water gasification (SCWG). The most important advantages of SCWG are gasification of biomass without drying, high reaction rates, formation of less coke and carbon monoxide [4]. AD has been used for many centuries, while SCWG is a much newer and more technologically advanced process. There are some comparisons between the two processes. Simultaneous production of methane and hydrogen rich gas with high yield can be accomplished in SCWG. Former application of AD provides physical consistency of digestate for handling of pumpable fluid that is one of main requirement in SCWG. AD is a biological process whereas SCWG is a thermochemical process. This allows SCWG to be more uniform, precisely controllable, and repeatable in its performance regardless of feedstock. A SCWG system will give higher gas yield than an AD system because the conversion is almost complete. Application of SCWG after AD provides conversion of volatile organic materials up

to 99% which cannot be succeeded by only AD system. Large volume of digestate left after AD was minimized by SCWG into water and inorganics that were almost clean and have no odor. AD systems are low-pressure systems (mostly atmospheric) while SCWG systems operate at a higher pressure (around 20 MPa) that is useful for gas cleanup processes such as pressure-swing adsorption and membrane separation both require a large pressure differential. Application of SCWG after AD also provides product gas under high pressure which is usually required for gas transfer and storage. Extra compression cost will emerge if AD process was applied alone.

Gas product composition changes with operating conditions and catalyst type used. Metallic, alkali, carbon-based catalysts are usually used in SCWG of biomass to enhance the gas yield and lower coke. While metallic catalysts such as Raney nickel, Ru/C and Ru/Al$_2$O$_3$ resulted in high methane yields [5], alkali catalysts such as NaOH, KOH, K$_2$CO$_3$ and Na$_2$CO$_3$ accelerate hydrogen production rate [6–8].

Model compounds such as cellulose [5, 6], hemicellulose [9, 10], lignin [4, 11, 12], pyrocatechol [13], and real biomass feedstocks such as agricultural wastes [14, 15], aquatic weed [16, 17], sewage sludge [18, 19] etc. have been gasified in supercritical water. There are only few studies present on supercritical water gasification of digested biomass in anaerobic digestion. Boukis et al. [20] were gasified digested sludge in the pilot plant using a Ru/C catalyst protected by a bed of ZnO to remove sulfur compounds and potassium hydrogen carbonate to catalyze the water-gas shift reaction. They obtained a gas product (CGE of 45.8%) with 16% H$_2$ and 60% CH$_4$ at 420°C and 280 bar. Series application of SCWG with anaerobic digestion was investigated by using zootechnical sludge. This hybrid process was thought as clean technology to produce electricity and biomethane, and also evaluated as treatment of wastewater [21]. Differing from aforementioned studies [20, 21], this study were mostly concentrated on conversion of digestates to hydrogen rich gas not to methane rich gas. Hydrogen is a clean energy carrier, not an energy source and can be used in fuel cells to generate electricity, or power and heat. It also provides reduction in greenhouse gas emissions compared to methane.

Reaction time is another parameter in SCWG process. Sınag et al. [22] was studied the catalytic hydropyrolysis of glucose at 500°C, 30 MPa, and 1 h reaction time in a batch reactor. They found that after a reaction time of 1 h, the system is very close to equilibrium. The researchers [23] found that hydrogen yield increased from 7 to 14 (mol/kg of biomass feeding) when reaction time increased from 10 to 40 minutes during experiments with rice husk at 650°C, 30 MPa and 2 wt% of biomass concentration in a batch reactor. No further increase was noted when the reaction time increased to 60 minutes. As it is understood from the studies in the literature, the reason why the reaction time is chosen for one hour is the optimum period in which the gas production and the gas composition do not change any more.

In this study, supercritical water gasification of digested water hyacinth with waste sludge (at 35 and 45°C) was investigated in the absence and presence of alkali catalyst (KOH, NaOH, LiOH and K$_2$CO$_3$) at temperature and pressure ranges of 500–600°C and 35–45 MPa, respectively. Series application of AD with SCWG was used to evaluate high organic content of digested biomass to produce methane and hydrogen rich gas, and aqueous products to use as platform chemicals.

2. EXPERIMENTAL

2.1. Materials

Potassium hydroxide (KOH, purity of ≥95 wt%), sodium hydroxide (NaOH, purity of ≥95 wt%), lithium hydroxide (LiOH, purity of ≥98 wt%) and sodium carbonate (K$_2$CO$_3$, purity of ≥95 wt%) were supplied by Merck (St. Louis, MO, USA). Helium, nitrogen, air and hydrogen gases (purity of ≥99.9%) were purchased from Erma Gaz A.S. (Izmir, Turkey). Distilled and deionized (DDI) water was prepared using a Milli-Q Ultrapure water purification system with a 0.22 μm filter (Billerica, MA, USA).

2.2. Experimental Procedure

Anaerobically digested water hyacinths (50 g/L) with waste sludge (50 g/L) at different temperatures (35 and 45°C) were used as feedstock for SCWG studies. Proximate analysis of biomass solution after anaerobic digestion was given in Table 1. SCWG studies were performed in a batch reactor with a volume of 100 mL. Batch reactor is made of stainless steel (SS316) and constructed to endure 50 MPa at 650°C. Detailed information on batch reactor system was given in a previous study [24].

Table 1. Proximate analysis of digested biomass solution after anaerobic digestion.

Run Code	D35	D45
Digestion Temperature (°C)	35	45
Total Solids (TS, wt.%)	2.16	2.16
Volatile Solids (VS, wt.%)	65.9	67.2
Total Carbon (TC, wt.%)	29.2	30.1

In a previous study [25], anaerobic digestion of water hyacinths (50 g/L) with waste sludge (50 g/L) was performed at different temperatures (35 and 45°C). These high organic content digestates were conducted to SCWG after completion of biogas production in anaerobic digestion. Digested biomass solution with a volume of 15 mL was used in SCWG at 500 and 600°C (pressure range of 35-45 MPa). Catalyzed studies were performed with KOH, NaOH, LiOH and K_2CO_3 with 10 wt.% of volatile solid in feed. Experimental conditions for SCWG of digested biomass were given in Table 2.

Table 2. Experimental conditions for SCWG of digested biomass.

Run Code	D35T5/D35T6	D45T5/D45T6
SCWG Temperature (°C)	500/600	500/600
Volume of feed (mL)	15	15
Mass of TS in feed (g)	0.325	0.323
Mass of VS in feed (g)	0.214	0.217
Mass of catalyst (g)	0.0214	0.0217

Inside of the reactor was purged with nitrogen for 15 min. to obtain oxygen-free medium. Reactor is heated with an electrical heater with a constant heating rate of 6 K min^{-1}. Reaction time was selected as one hour that was not including heating period. At the end of reaction time, batch reactor was rapidly cooled down by using fans and then placed in cooled water. The volume of gaseous products was measured by using gasometer and gaseous samples were collected in gas tight syringes and analyzed in gas chromatography. Since all experiments were performed in triplicate, deviation in the volume of gaseous product was calculated as ±10% by using standard deviation formula. The inside of the reactor was washed with water and then filtered to separate aqueous product and solid residue. Aqueous products were stored in a refrigerator at 4°C. Detailed explanation on analysis of the gaseous and aqueous products was given in the section 2.3.

2.3. Analysis

2.3.1. Feed Characterization

Digested biomasses are subjected to analysis of total solids, volatile solids and total carbon contents. The total solids content includes both the suspended solids and dissolved salts, and used to determine dry weight of digested biomass. The volatile solids represent the organic content of the sample and

total carbon content is the sum of the organic and inorganic carbon present in the sample. The total solids, volatile solids and total carbon contents were determined by methods of ASTM E1756, ASTM E872 and ASTM E777, respectively.

2.3.2. Gaseous Product Analysis

Composition of the gaseous products (H_2, CO_2, CO and C_1-C_4 hydrocarbons) was analyzed by Agilent HP 7890A gas chromatography (GC) equipped with 3 detectors (FID-TCD-TCD) and serially connected 7 columns. Technical features and operating conditions of gas chromatography were given in previous work [26]. The standard deviation for the results of gas composition was calculated to be ±2%.

2.3.3. Aqueous Product Analysis

Total organic carbon (TOC) content of aqueous phase was analyzed by a TOC analyzer (Shimadzu TOC-V_{CPH}, Japan). Organic compounds in the aqueous phase were isolated by solid-phase extraction (SPE) technique and qualitatively analyzed by GC-MS (Agilent Technologies, HP 7890A-5975 VL MSD). Helium was used as carrier gas with a flowrate of 1.2 ml/min. HP-5MS (30 m x 250 µm x 0.25 µm) column was used and oven program was; 40°C for 8.5 min., then 22°C/min to 48°C for 5 min., then 5°C/min to 141°C for 1 min., and then 5°C/min to 270°C for 2 min. Injection, MS source and MS quadrupole temperatures were 260°C, 230°C and 150°C, respectively. Mass spectroscopy library of the National Institute of Standards and Technology (NIST) was used to identify compounds.

3. RESULTS AND DISCUSSION

Carbon gasification efficiency (g C in gaseous/g C in digestate) and carbon liquefaction efficiency (g C in liquid/g C in digestate) were expressed by using following formulas;

Carbon gasification efficiency: (CGE, wt.%) $= \dfrac{\sum_i n_i C_i \frac{PV}{RT} M}{wm} \times 100$

Carbon liquefaction efficiency: (CLE, wt.%) $= \dfrac{TOC_{aq}\overline{V}}{wm} \times 100$

Reactor pressure was stabilized at desired value with a precision of ±0.5 MPa. Carbon balance of products (gaseous and aqueous) closed within 57.2-93.6%. Remaining part in carbon balance was coke, tar and loss. All experiments were performed in triplicate with an approximately 5% resulting precision of product efficiency.

3.1. Product Yields

Variations of product efficiencies (CGE and CLE) with temperature (500 and 600°C) were given in the absence and presence of catalyst in Figures 1 and 2 for samples digested at 35 and 45°C, respectively. CGE considerably increased with increasing temperature while slightly decreased with the addition of alkali catalysts. In general, temperature is the most dominant factor in SCWG. High reaction temperature accelerates free-radical reactions towards formation of low-molecular weight compounds and higher yield of gaseous products [27]. Moreover, alkali catalysts prove high reaction rate and provide high conversion at lower reaction temperatures compared to uncatalyzed ones [28].

When digested water hyacinth at 35°C was used in SCWG, the highest CGE (79.2 wt.%) and lowest CLE (9.8 wt.%) yields were reached at 600°C with KOH. Other catalysts (NaOH, LiOH and K_2CO_3) give lower CGE than uncatalyzed one. Complete conversion to products (that means total of CGE and CLE) was found lower with these aforementioned catalysts (Figures 1 and 2). Addition of alkali catalysts may be caused increased formation of sticky tar products which were not recovered from the inside of reactor wall.
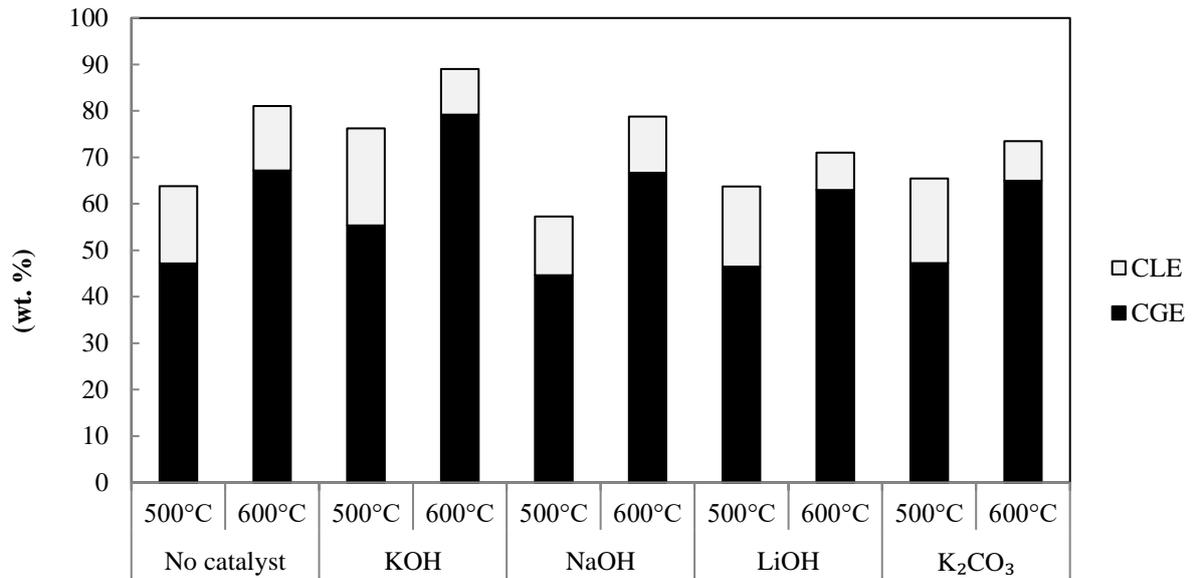
Figure 1. Effects of temperature and alkali catalyst on product yield for SCWG of digested water hyacinth at 35°C.

When digested water hyacinth at 45°C was used in SCWG, the highest CGE (84.6 wt.%) and lowest CLE (8.4 wt.%) yields were reached at 600°C in the absence of catalyst. Addition of catalysts affects CGE negatively and CLE was improved as the digested biomass converted to intermediates in the aqueous products. Higher CGE and CLE were obtained in SCWG of samples digested at 45°C compared to 35°C. As the biomass samples was better hydrolyzed and degraded into biogas and digestate during anaerobic digestion at 45°C, SCWG reactions progress more easily with heavily degraded biomass into gaseous and aqueous products (Figure 2).
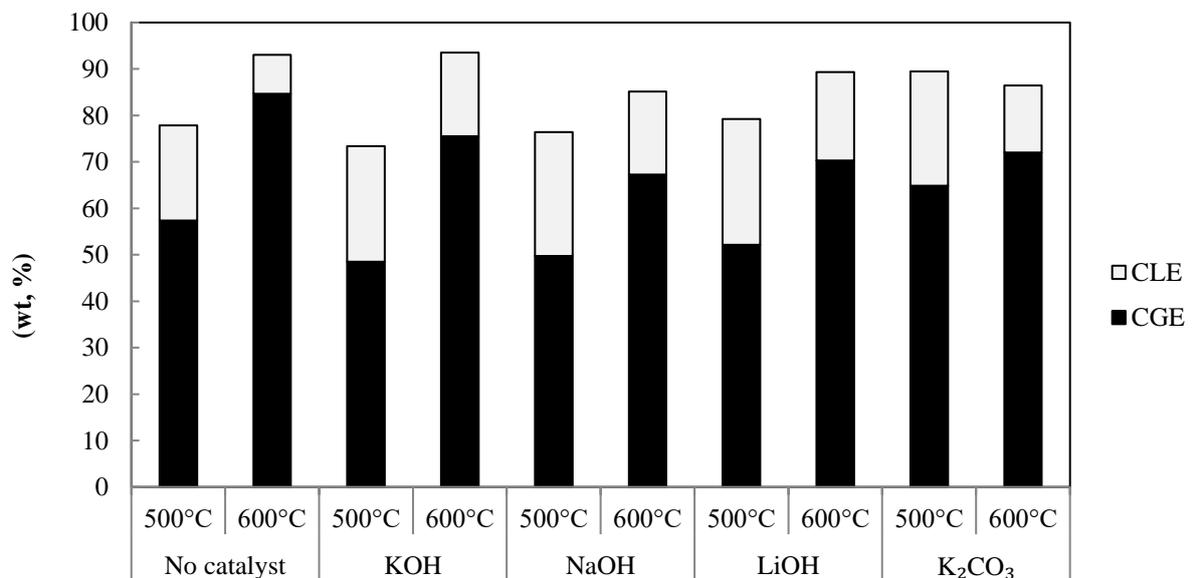
Figure 2. Effects of temperature and alkali catalyst on product yield for SCWG of digested water hyacinth at 45°C.

3.2. Gaseous Products

Figures 3 and 4 shows the variations of gaseous product composition with temperature in the absence and presence of catalyst for samples digested at 35 and 45°C, respectively. Gaseous products were mainly composed of CO_2, H_2, CH_4, and C_2-C_4 hydrocarbons as minors. It is found that gaseous product yield (mol gas/kg digestate) increased with increasing SCWG temperature. As the SCWG temperature increased from 500 to 600°C in the absence of catalyst, hydrogen yield increased from 6.7 to 11.9 mol/kg, while mole fraction of hydrogen increased from 39.4% to 44% for samples digested at 35°C. Hydrogen yields were found higher when SCWG was applied for samples digested at 45°C. Hydrogen yield increased from 8.5 to 22.9 mol/kg, while mole fraction of hydrogen increased from 39.8% to 53.0% for samples digested at 45°C, as the SCWG temperature increased from 500 to 600°C in the absence of catalyst.

When the SCWG temperature increased from 500 to 600°C in the absence of catalyst, methane yield increased from 2.6 to 4.5 mol/kg, while mole fraction of methane increased from 15.5% to 16.7% for samples digested at 35°C. Also, methane yields were found higher when SCWG was applied for samples digested at 45°C. Methane yield increased from 3.1 to 5.4 mol/kg, while mole fraction of methane increased from 12.5% to 14.2% for samples digested at 45°C, as the SCWG temperature increased from 500 to 600°C in the absence of catalyst.

In terms of total of hydrogen and methane yields, NaOH was found to be effective at 500°C and KOH was found to be effective at 600°C in SCWG of samples digested at 35°C. For this sample, effectiveness of catalysts at 600°C can be ordered as KOH>NaOH>K_2CO_3>LiOH. Total yields of hydrogen and methane were found higher in the presence of K_2CO_3 at 500°C and in the absence of catalyst at 600°C in SCWG of samples digested at 45°C.

Based on results of our previous study dealing with anaerobic digestion of water hyacinth with waste sludge [25], the higher biogas and methane yields were reached at 45°C compared to 35°C. In the first phase of anaerobic digestion, complex biopolymer structure (cellulose, hemicellulose and lignin) of the feed was hydrolyzed into monomers and oligomers. In the next phases, these fractions were converted to methane through acidogenesis, acetogenesis and methanogenesis. These reaction steps occurred with higher extent at 45°C (thermophilic condition) than 35°C (mesophilic condition) that is why methane yield was high at 45°C. This means that anaerobic digestion at 45°C were better fractionated biomass into intermediates that were further easily converted to H_2 and CH_4 through SCWG. As the compositions of digested water hyacinth were different at 35 and 45°C, its degradation product composition and yield were found different after SCWG. In addition, this variation affects the effectiveness of catalysts in SCWG. Digested water hyacinth with waste sludge is a complex mixture of degradation products (intermediates) of cellulose, hemicellulose, lignin etc. that can further undergo hydrolysis, pyrolysis, decomposition, steam forming and polymerization reactions in SCWG [29]. Addition of alkali catalyst increased formation of tars and coke amount at elevated temperatures [30] and resulting in lower gaseous product yield at catalyzed condition. Low gaseous product yield in catalyzed condition directly affects gas product distribution. Even though mole fraction of gaseous products was enhanced, it does not reflect on individual gas yields because gaseous product yields found lower at catalyzed condition. As a surplus, the highest carbon gasification efficiency, hydrogen and methane yields were reached at 600°C (with samples digested at 45°C) in the absence of catalyst as 84.6 (g C in gaseous/g C in digestate), 53.0 (mol H_2%) and 14.2 (mol CH_4%), respectively.
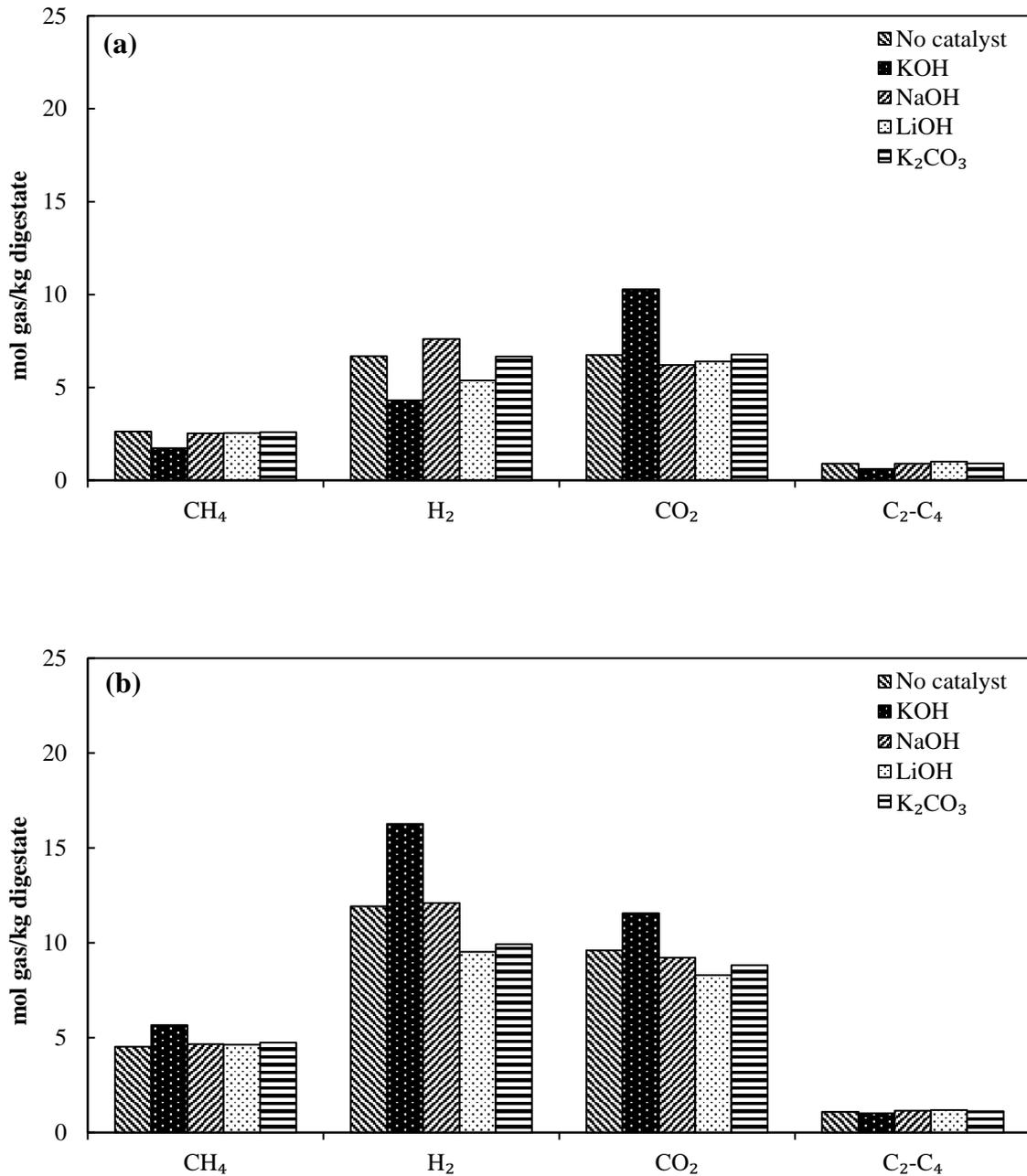
Figure 3. Effect of alkali catalyst on gaseous product composition for SCWG at (a) 500°C and (b) 600°C of digested water hyacinth at 35°C.

Total yield of H_2 and CH_4 was found to be higher than CO_2. It is known that presence of alkali salts leads to the formation of formates, which subsequently degrades to hydrogen and carbon dioxide during SCWG [31]. As the mole fraction of CO was found very low in gaseous products, its yield was not given. This situation may be caused by acceleration of water-gas shift reaction and, resulted in decrease in CO yield and increase in H_2 yield. Low yield of CO also confirms that system reached equilibrium

after reaction time of one hour. The high yield of hydrogen and methane shows that digested biomass with high organic content can be utilized in SCWG to high energy carriers (H_2 and CH_4).
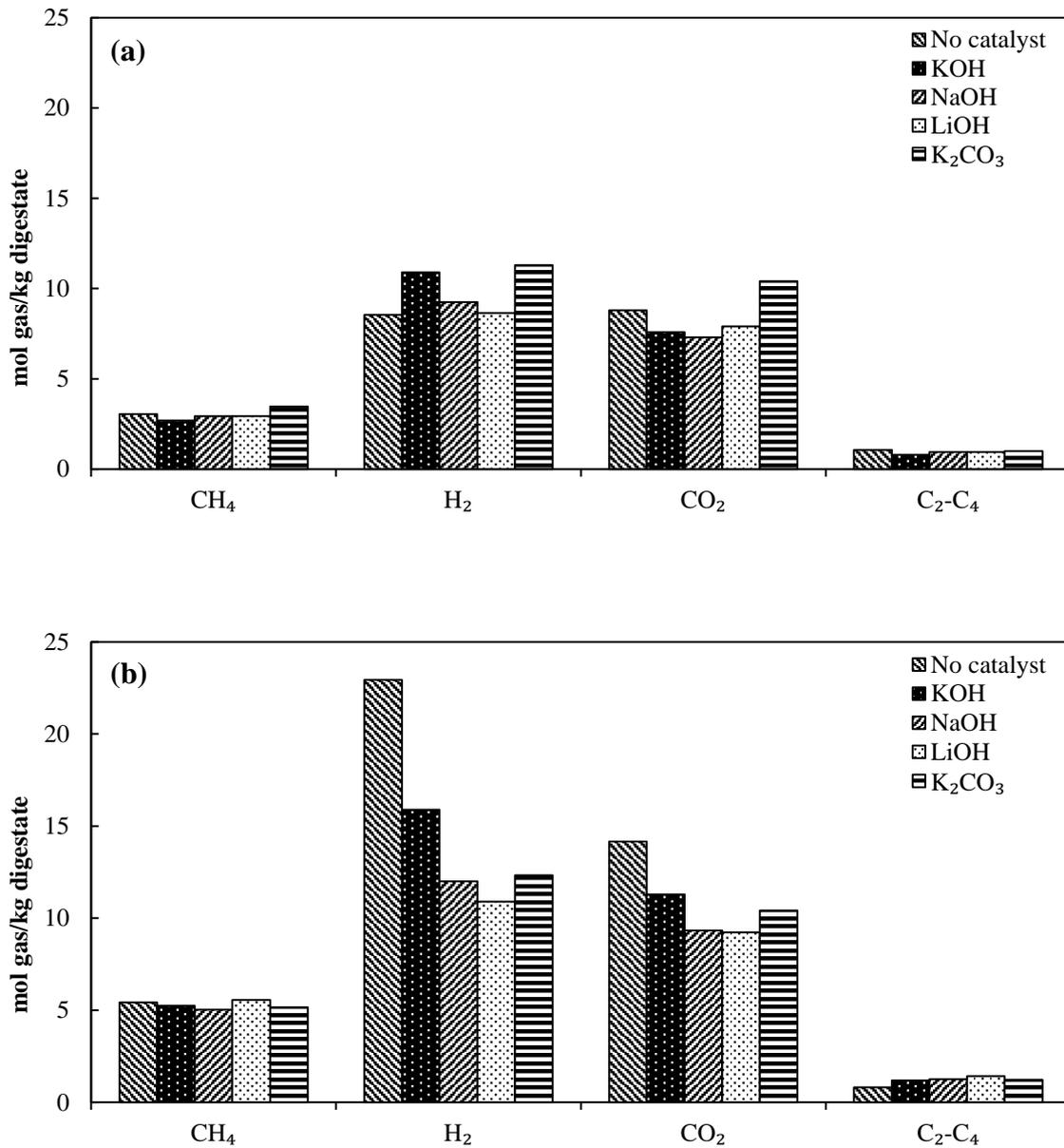
Figure 4. Effect of alkali catalyst on gaseous product composition for SCWG at (a) 500°C and (b) 600°C of digested water hyacinth at 45°C.

Table 3 shows CGE and gaseous product composition of different biomasses in SCWG. Hydrogen yield of this study was found higher than these compared studies. Pyrocatechol [13] is a model compound for aromatic compounds in wastewater and lignin in biomass which are both present in digested water hyacinth with waste sludge (from municipal wastewater treatment plant). Cellulose and water hyacinth [32] were gasified in the presence of metal catalyst with high yield of methane. Model compounds are easily degraded in SCW than real biomass feedstock and give high CGE with high H_2

and CH_4 yields. The main component of gaseous product changes depending on the catalyst type. While metallic catalysts give high CH_4 yield [20,32], alkali catalysts give high H_2 yield [13].

Table 3. Comparison of SCWG results of different biomasses.

Feedstock	Reactor type	T (°C)	Catalyst	CGE (%)	H_2 (mol%)	CH_4 (mol%)	Reference
Digested water hyacinth	Batch autoclave	600	None	84.6	53.0	14.2	This study
Pyrocatechol	Tumbling batch	500	KOH	n.d.	52.4	9.0	[13]
Pyrocatechol	Tumbling batch	500	LiOH	n.d.	40.4	n.d.	[13]
Sewage sludge	Continuous flow	500	None	57.0	15.0	25.0	[19]
Sewage sludge	Continuous flow	600	None	73.0	22.0	35.0	[19]
Digestate sludge	Pilot plant-continuous	420	Ru/C	45.8	16.0	60.0	[20]
Cellulose	Batch autoclave	400	Nickel	97.6	3.9	43.2	[28]
Water hyacinth	Batch autoclave	400	Nickel	73.1	11.3	35.9	[28]

n.d.: not determined

3.3. Aqueous Products

The effects of temperature and alkali catalyst on TOC of aqueous products for SCWG of digested water hyacinth at 35 and 45°C were given in Figure 5. Total organic carbon (TOC) is one of the most important parameters in the assessment of the organic pollution in aqueous phase. The TOC removal rate can be defined as the ratio of TOC removed from aqueous products to TOC of fed digested biomass solution. The TOCs of fed digested biomass solutions at 35 and 45°C were 14,266.67 and 14,466.67 mg/L, respectively. The minimum TOC of aqueous products in SCWG (at 600°C) of digested water hyacinth at 35°C was found as 149.4 mg/L in the presence of LiOH. Additionally, the minimum TOC of aqueous products in SCWG (at 600°C) of digested water hyacinth at 45°C was found as 126.5 mg/L in the absence of catalyst. For all runs, TOC removal rate was calculated between 97-98% for SCWG at 500°C and 98-99% for SCWG at 600°C. Reduction in TOC of aqueous solution with increasing temperature was in agreement with gaseous product formation.

The organic fraction of aqueous products before (D35/D45) and after (D35T5/D45T5) SCWG were analyzed by GC-MS. As stated by other researchers [33,34], area percentage of each compound was calculated by fraction of total ion chromatogram of each detected compound to total peak area and relative content of the compounds were found qualitatively. Based on GC/MS library search reports, range of the quality for the detected compounds was found between 70-96%. Compounds were not taken into account when quality was below 70%.
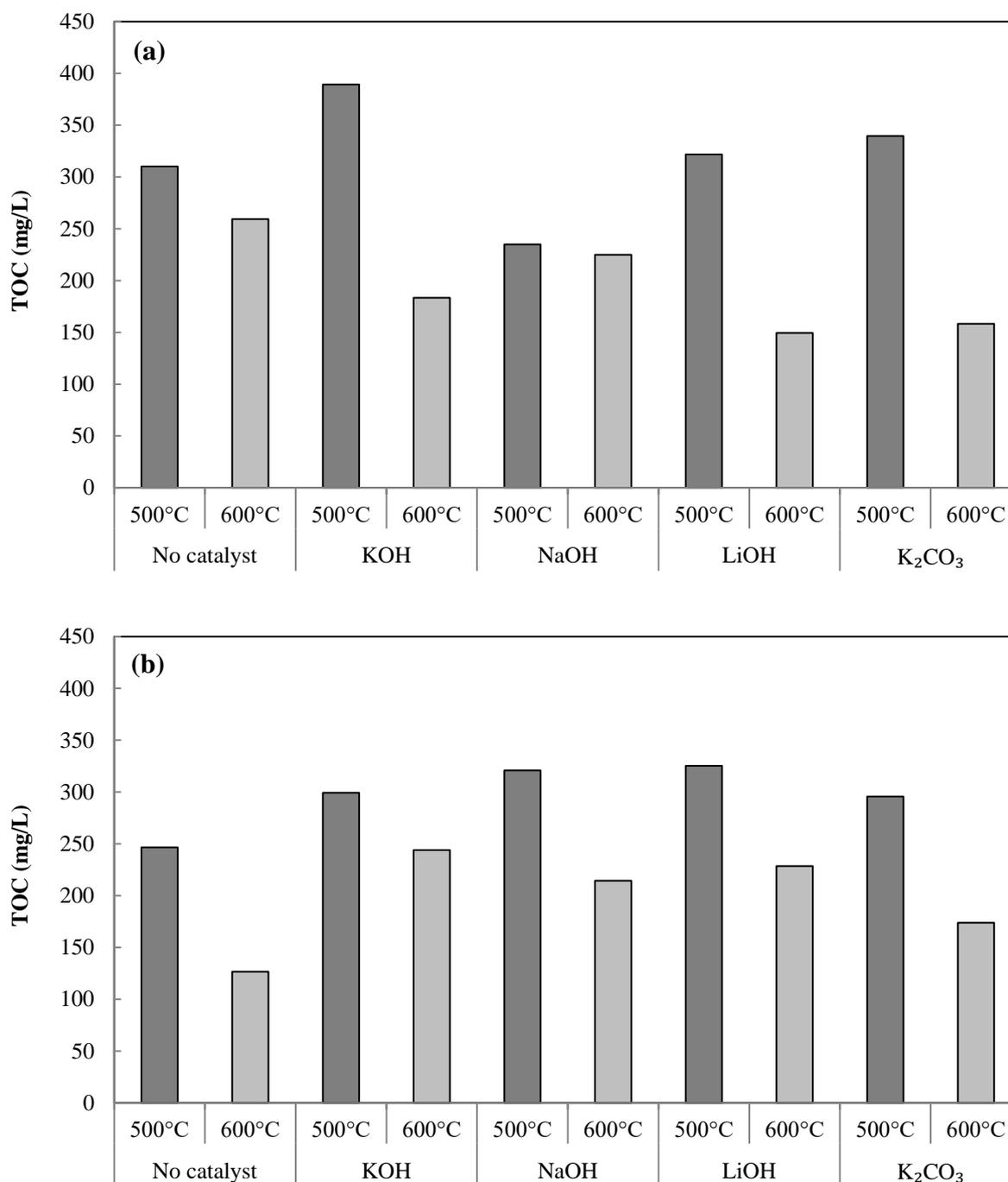
Figure 5. Effects of temperature and alkali catalyst on TOC of aqueous products for SCWG of digested water hyacinth at (a) 35°C and (b) 45°C.

According to GC-MS analysis, organic fraction of aqueous products was identified only at 500°C, because carbon liquefaction efficiency and total organic content of aqueous products were found lower at 600°C. As given in Table 4, organic fraction of aqueous products was mainly composed of aliphatic hydrocarbons, phenol, substituted phenols, N-heterocyclic (indole), substituted N-heterocyclics, and substituted benzene (p-xylene) that can be used as platform chemicals for pharmacy, dye industry, pesticide and polymer processes. P-xylene is widely used as a feedstock to produce industrial

chemicals such as terephthalic acid (TPA), purified terephthalic acid (PTA) and dimethyl-terephthalate (DMT). TPA, PTA and DMT are used to manufacture polyethylene terephthalate (PET) polyesters. N-hexadecane is used as a substrate for the bacterial production of biosurfactants [35].

Table 4. Identification of organic compounds in aqueous product before (D35/D45) and after (D35T5/ D45T5) SCWG of digested biomass.

No	Formula	Compounds	Area Percentage, %			
			D35	D45	D35T5	D45T5
1	C_8H_{10}	p-xylene	19.69	46.88	4.39	27.37
2	C_6H_6O	Phenol			16.67	
3	C_7H_8O	4-methyl-phenol			13.16	
4	$C_8H_{10}O$	3-ethyl-phenol			18.42	
5	$C_8H_{10}O$	2,4-dimethyl-phenol				2.80
6	$C_9H_{12}O$	2-ethyl-4-methyl-phenol			10.53	
7	$C_8H_{10}O$	3,4-dimethyl-phenol			3.51	
8	$C_9H_{12}O$	2-ethyl-6-methyl-phenol				15.02
9	C_9H_8O	2,3-dihydro-1H-inden-1-one			1.75	
10	C_6H_{10}	1-methyl-cyclopentene			17.54	
11	$C_{10}H_{12}$	1,2,3,4-tetrahydro-naphthalene		7.29	4.39	4.13
12	$C_8H_{10}O_2$	2-phenoxy-ethanol	4.06			
13	$C_{11}H_{10}$	1-methyl-naphthalene	2.15	1.92		
14	$C_{12}H_{12}$	2-ethenyl-naphthalene	0.69			
15	$C_{14}H_{30}$	Tetradecane	3.14	2.36		
16	C_8H_7N	1H-indole	4.37		7.02	9.38
17	C_9H_9N	6-methyl-1H-indole				12.82
18	C_9H_9N	2-methyl-1H-indole				5.12
19	C_9H_9N	3-methyl-1H-indole			1.75	
20	$C_{10}H_{11}N$	5,7-dimethyl-1H-indole				6.28
21	$C_{16}H_{34}$	Hexadecane	31.80	17.82		
22	$C_{14}H_{10}$	Phenanthrene	7.20	5.21		2.07
23	$C_{18}H_{38}$	Octadecane		18.53	0.88	7.62
24	$C_{20}H_{42}$	Eicosane	26.90			7.40

Main compounds in organic fraction of aqueous products before SCWG (D35/D45) were p-xylene and long-chain aliphatic hydrocarbons (hexadecane, octadecane and eicosane), and this fraction was mostly consisting of phenolic and N-heterocyclic compounds after SCWG (D35T5/D45T5) of digested biomass. The most prominent compounds in D35T5 were phenol and substituted phenols, while p-xylene, substituted phenols, N-heterocyclic (indole), and substituted N-heterocyclics were mostly present in D45T5.

Digested water hyacinth with waste sludge was a complex mixture of cellulose, hemicellulose, lignin, protein, fats and inorganics that have different degradation behavior in supercritical water and provides production of numerous compounds [36]. Lignin can be degraded in hydrothermal conditions to low molecular weight products, mainly phenolic compounds that also show antioxidant properties [37]. Origin of identified N-heterocyclic compounds can be products of hydrolysis of proteinaceous

fraction and reaction of amino acids and sugars [38]. Anaerobic digestion process proceeds dissolution of cellulose and hemicellulose integration from lignin structure and further facilitating degradation of these fractions in SCWG. Successive application of AD with SCWG can be a potential method for production of chemical feedstock from biomasses.

4. CONCLUSION

Lignocellulosic biomasses can be subjected to anaerobic digestion for biogas production, but evaluation of high organic content digestate for energy production is better, instead of composting or using as fertilizer. Water hyacinth is renewable waste that does not have food value and abundantly present in nature. SCWG of anaerobically digested water hyacinth with waste sludge was investigated at different reaction temperatures and alkali catalysts in this study. Application of AD before SCWG created a pretreatment effect and facilitated degradation of digestate to products with high conversion and yield. Series application of AD with SCWG provides conversion of digested high organic content biomass to high energy carrier gaseous products (H_2 and CH_4), and aqueous products (aliphatic hydrocarbons, phenol, substituted phenols, N-heterocyclic, substituted N-heterocyclics, and substituted benzene) that can be evaluated as chemical feedstock. This hybrid process may be applied for organic wastes to produce electricity, biomethane and biohydrogen.

NOMENCLATURE

TS	Total solid (wt.%)
VS	Volatile solid (wt.%)
TC	Total carbon (wt.%)
AD	Anaerobic digestion
SCWG	Supercritical water gasification
TOC	Total organic carbon
SPE	Solid-phase extraction
CGE	Carbon gasification efficiency (wt.%)
CLE	Carbon liquefaction efficiency (wt.%)
C_i	Concentration of component 'i' in the gas product (vol. %)
n_i	Number of carbon atoms of component 'i' in the gas product
m	Weight of digested biomass in feed (g)
M	Molar mass of carbon (g mol^{-1})
P	Pressure (MPa)
R	Universal gas constant, 8.3143 J mol^{-1} K^{-1}
T	Temperature (K)
V	Volume of gas product under ambient conditions (L)
$\bar{V}$	Volume of aqueous product under ambient conditions (L)
w	Carbon content of digested biomass (wt.%)
TOC_{aq}	Total organic carbon content of the aqueous product (g L^{-1})

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