



Research Article

EFFECT OF REACTION TEMPERATURE AND ETHANOL-TO-WATER RATIO ON BIO-OIL YIELD FROM CATALYTIC HYDROTHERMAL LIQUEFACTION OF SUGARCANE LEAVES

T. Nonchana¹
K. Pianthong^{1,*}
B.E. Milton²
K. Takayama³

¹ Department of Mechanical Engineering, Faculty of Engineering, Ubon Ratchathani University, Warin Chamrap, Ubon Ratchathani 34190, Thailand

² School of Mechanical and Manufacturing Engineering, The University of New South Wales, Sydney 2052, NSW, Australia

³ Institute of Fluid Science, Tohoku University, Sendai, Japan

Received 15 September 2021
Revised 18 November 2021
Accepted 19 November 2021

ABSTRACT:

This study investigates the effects of reaction temperature and ethanol per water ratio (EPW) on bio-oil yields from the hydrothermal liquefaction (HTL) of sugarcane leaves. Experiments were performed in a high-pressure 100 mL Ni-alloy batch reactor at different EPWs (0:1, 1:10, 1:5, 1:2.5, and 1:1). The HTL process was conducted with 5 g. sugarcane leaves and 1 wt.% Na₂CO₃ as a catalyst. The reaction temperatures ranged from 250-350 °C with a reaction time of 60 min. A maximum yield of 34.8% was obtained with an EPW of 1:5 at a reaction temperature of 300 °C. The maximum conversion of 89.36% was obtained at an EPW of 350 °C. Gas chromatography-mass spectrometry results indicated that the main bio-oil component was the fatty acid methyl ester group, of which the oleic acid methyl ester was the largest component. Finally, the WSP from the HTL process was weakly acidic and had high conductivity.

Keywords: Bio-oil, Co-solvent, Hydrothermal liquefaction, Reaction temperature, Sugarcane leaves

1. INTRODUCTION

New renewable energy sources have become more urgent due to increasing global energy demand coupled with rising atmospheric temperatures from fossil fuel combustion. As a result, several types of renewable fuels, such as biodiesel [1-3], bio-oil [4-6], synthesis gas [7-9], have been studied in recent years. Thermochemical Conversion (TCC) is a promising approach for converting solid biomass into liquid and gaseous products. The TCC has been widely researched for several years [10] and is widely utilized. The core technologies involved in TCC include direct combustion, pyrolysis, gasification [11], hydrothermal liquefaction (HTL), and hydrothermal gasification. Both pyrolysis and HTL processes generate bio-oil. However, pyrolysis is significantly limited by its requirement of dry feedstock before the process can be initiated [12]. Furthermore, the drying process is an energy- and time-intensive procedure, and the resulting bio-oil has a high oxygen content [13]. Furthermore, the typical pyrolysis temperature is enormously high, ranging from 500-700 °C [14]. Nevertheless, hydrothermal technologies are relatively new & they have not been widely employed on a commercial scale yet.

Sugarcane is among the most important agricultural plants in Thailand. However, each year, 22 million tons (14% of the sugar cane crop) of sugarcane leaves are disposed of in fields or burned before harvesting [15]. This pre-harvesting process causes environmental problems such as particle dust, smoke, unpleasant smells, as well as producing CO₂ of

* Corresponding author: K. Pianthong
E-mail address: k.pianthong@gmail.com



1,303 g/kg, CO of 65 g/kg, and NO_x of 1.5 g/kg [16]. Therefore, it would be highly desirable to utilize sugarcane leaves as an energy resource.

Some studies on sugarcane leaves (SCL) pyrolysis have been carried out. A maximum yield of 63.2% for sugarcane pyrolysis at a pyrolysis temperature of 900 °C with a heating rate of 15 °C/min has been reported [17]. Furthermore, the result shows the properties of bio-oil and biochar obtained from SCL by fast pyrolysis at 550 °C with a feed rate of 150 g/h. The results indicated that the bio-oil yield was 53.34%, with a higher heating value of 15.77±1 M.J./kg.

HTL is a thermal depolymerization process that can convert wet biomass into crude oil at medium to high-pressure conditions [17]. Additionally, HTL exhibits several advantages over other thermochemical processes and has thus been widely investigated for its potential applicability in crude bio-oil synthesis [18]. For instance, the HTL process does not require a drying process to remove water from the feedstock [19, 20]. Moreover, the HTL process uses pressurized water as a solvent, and hence, this process is environmentally friendly [21]. In recent years, an increasing number of researchers have focused on HTL with various types of feedstock [22]. Several high-water-content feedstocks can be converted to bio-oil via the HTL process [23-26].

Several homogenous and heterogeneous catalysts have been employed in the HTL process to improve bio-oil yields and properties [27, 28], with Na₂CO₃ being the most commonly used generic catalyst in ongoing studies on the HTL of lignocellulosic biomass [29, 30]. The composition and yield of the HTL process depend on the type of feedstock and process conditions. However, previous works have only focused on local raw materials [31-36] and some aquatic biomass [37-43]. For example, sorghum bagasse was also reported as a high yield feedstock of about 61% with a K₂CO₃ catalyst [44]. Furthermore, rice straw, wheat stalk, and corn straw are also used as hydrothermal liquefaction feedstocks [45-47]. In addition, there are reported on hydrothermal co-liquefaction of rice straw and waste cooking-oil mode and obtain oil yield about 88.7% [48]. Furthermore, the high pressure and temperature required to reach the critical point of water pose considerable challenges for successfully implementing the hydrothermal process. Therefore, a co-solvent has sometimes been used to reduce the reaction temperature and pressure of the HTL process, one consisting of a mixture of water with a liquid with a lower critical point (e.g., methanol or ethanol) being optimal [38, 49]. However, no report on sugar cane leaves, and co-solvent for the HTL process has been published.

Therefore, this work aims to investigate the effect of reaction temperature and co-solvent (ethanol + deionized (DI) water) ratio on bio-oil (BCO) yield and conversion from sugarcane leaves via HTL. A comprehensive investigation is critical to understand which parameters (or combinations) will significantly affect the HTL yield and conversion. Thus, the influences of reaction temperature, ethanol-to-water ratio (EPW), bio-oil composition, and water-soluble product (WSP) properties are discussed.

2. EXPERIMENTAL SETUP

2.1 Feedstock preparation process and analysis

Fresh sugarcane (*Saccharum officinarum* L.) cultivar, Khon Kaen 3, was obtained from a farm in the Ubon Ratchathani province, Thailand. In general, the moisture content of the fresh SCL is about 15%-25%. To maintain a consistent feedstock concentration in each experiment, the SCLs were dried at 105 °C for 48 h. Subsequently, the dry SCL was ground using a rotary mill and screened using a wire cloth laboratory sieve with a mesh size of 0.25 mm (60 meshes). The feedstock samples were analyzed following the ASTM D7582, ASTM D5373, ASTM D4239, and ASTM D5865 standards [50]. The Rigaku Thermo Plus, 2 TG-DTA TG8120 model, was employed for a thermogravimetric (TGA) study. SCL analyzes were performed at 10 °C / min heating level. The study was performed over a temperature range of 28 °C to 800 °C in the presence of a nitrogen atmosphere. The flow rate of nitrogen was 20 mL/min. In addition, 3.70 mg SCL samples were used for analysis. The SCL preparation procedure is illustrated in Fig. 1, and the compositions and properties are listed in Table 1. The catalyst (Na₂CO₃), deionized (DI) water, ethanol (99.99%), and dichloromethane (DCM) were purchased from a local chemical supplier (Chemipan Crop., Bangkok, Thailand).

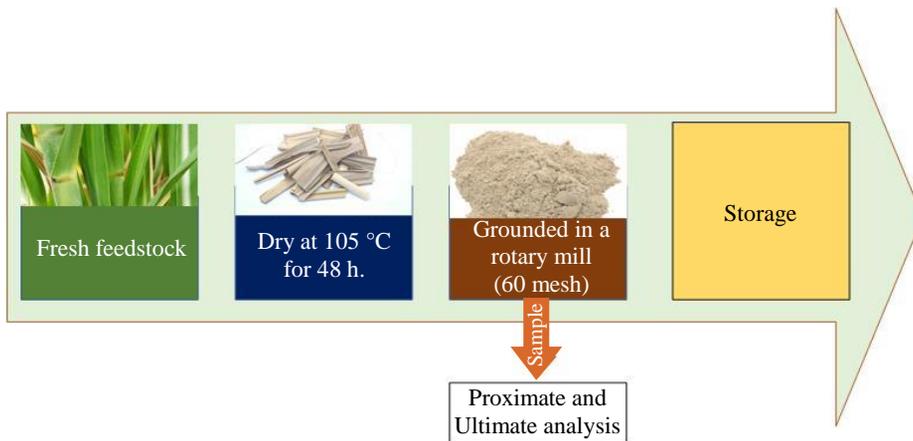


Fig. 1. SCL preparation for the HTL process

2.2 Hydrothermal liquefaction apparatus and procedure

The HTL experiments were performed in a high-pressure experimental unit, as illustrated in Fig. 2. The experimental unit included a 100 mL non-stirred batch Ni-alloy reactor with an internal diameter of 25 mm (Model: CY-100x, Zhengzhou CY Scientific Instrument Co., Ltd.). A 3.0 kW electric heater was equipped with an automatic temperature controller to heat the reactor, and the reaction temperature was detected using a K-type thermocouple attached to the bottom of the heating chamber. The operating pressure was detected using an in-built pressure transducer, which was also used to detect overpressure conditions.

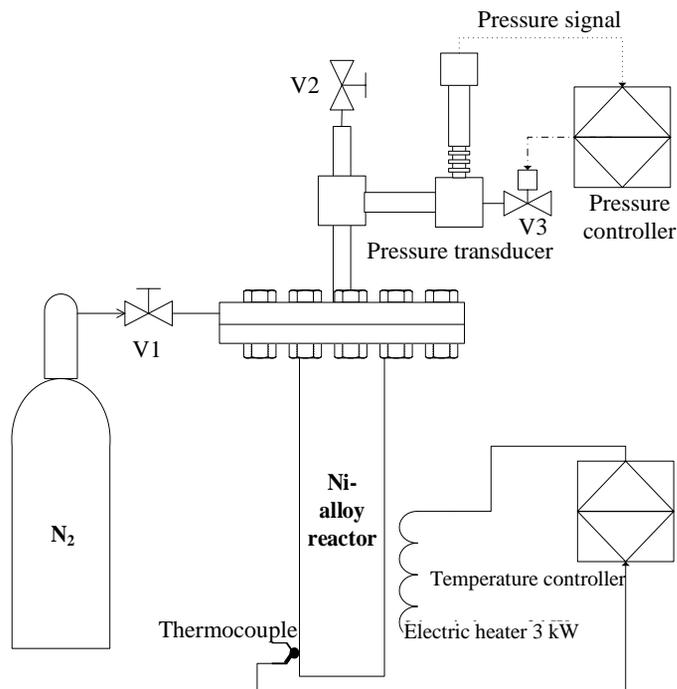


Fig. 2. Hydrothermal experimental unit with a capacity of 100 mL.

First, 5 g of SCL powder was mixed with 45 g of the solvent (ethanol and DI water) and 0.5 g of Na_2CO_3 . Next, nitrogen gas was used to purge the reactor for 5 min, and an initial pressure of 1.0 MPa was established. Afterward, the reactor was heated using an electrical heater, the heating rate for all the experiments being constant at 10 °C/min. The pressure throughout the reaction was autogenously increased from 6.0-15.0 MPa.

2.3 Separation procedure

The procedure for the separation of the liquefaction product is shown in Fig. 3. Once the preferred reaction time was reached, the reactor was cooled down rapidly to ambient temperature by being quenched in water; the gaseous products (GAS) inside were then vented without further analysis. Furthermore, DCM was used to extract the bio-oil from the solid residue and the reactor wall. Liquid and solid residues (SR) were removed from the reactor and separated by filtration. Subsequently, the reactor was washed with 100 mL DCM to rinse out any reaction products that may have been attached to it. This washing procedure was repeated three times for each testing condition. The resultant WSP was separated from the DCM solution with a separatory funnel. The water- WSP was seen to dissolve in this portion.

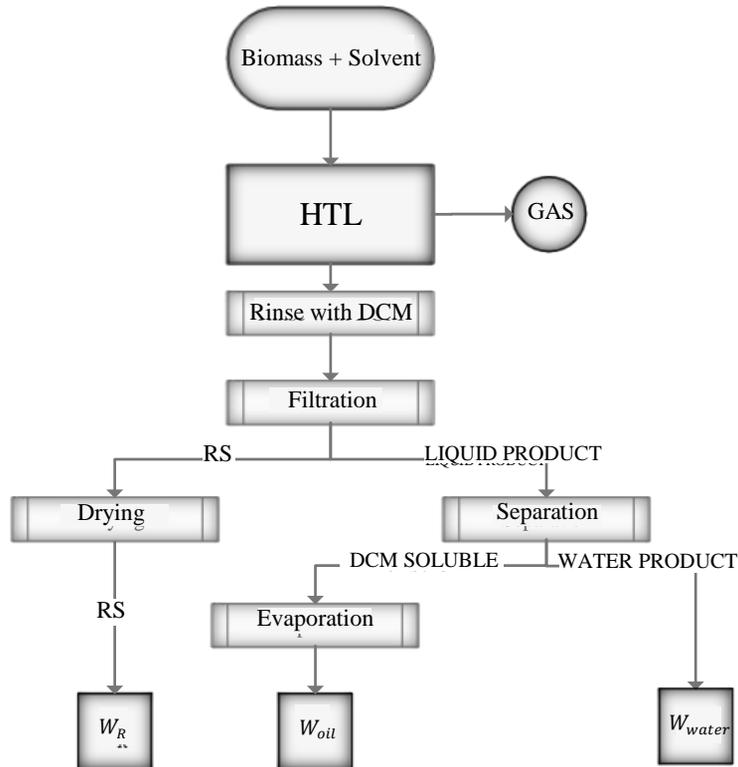


Fig. 3. Product separation procedure for the HTL process

Finally, the SR from the filtration was dehydrated at 105 °C for 48 h. The DCM was removed from the BCO by a rotary evaporator. Subsequently, all the products were weighed to calculate the yield. The conversion and BCO and GAS yields were calculated according to Eq. (1)-(3), respectively, as described below:

$$Conversion(\%) = \left[1 - \frac{W_{SR}}{W_B} \right] \times 100\% \quad (1)$$

$$BCO_{Yield} = \left(\frac{W_{oil}}{W_B} \right) \times 100\% \quad (2)$$

$$Yield_{WSP+GAS} = \left(1 - \frac{(W_{oil}+W_{SR})}{W_B} \right) \times 100\% \quad (3)$$

In these equations, conversion (%) is the percentage of the solid fuel to the liquid and gaseous products, BCO_{Yield} is the BCO yield (wt.%), $Yield_{WSP+GAS}$ is the yield of the WSP and gaseous product (wt.%), W_B is the mass of the SCL (g), W_{oil} is the BCO weight (g), and W_{SR} is the weight of the solid residue (g).

2.4 BCO properties analysis

The composition of the BCO obtained from the HTL was analyzed using gas chromatography-mass spectrometry (GC-MS). The GC (Perkin Elmer Clarus 680) was directly linked to the MS (Perkin Elmer Clarus SQ8C). The injection port and detector operated at 250 °C for 10 min with the GC oven heated to 45 °C and then heated to 250 °C at a rate of 3 °C/min. The operating conditions were reaction temperature 350 °C, reaction time 60 min, and DI water quantity 5 g.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of feedstock

The Ultimate analysis, proximate analysis, and calorific value are commonly used to characterize the properties of solid biomass fuel. The proximate analysis offers a primary means of determining the behavior of a solid biomass fuel when it is heated. The proximate analysis also lists the feedstock's moisture content, volatile matter, ash, and fixed carbon content. It is noted that a high content of volatile organic material results in high volatility and reactivity and therefore encourages the processing of large amounts of liquid and gas products. In contrast, the presence of fixed carbon contributes to the formation of charcoal [51]. The existence of low hydrocarbons, high HHV, volatile matter, and low sulfur levels also clearly indicates that SCL is a reliable and suitable alternative source for the production of liquid fuels. Also, the primary purpose of the ultimate analysis is to determine the elementary composition of the solid fuel material. The calorific value of the fuel is a direct measure of the chemical energy content of the fuel. Table 1 indicates that the hydrogen, carbon, and oxygen contents in SCL were valued to be 5.97%, 47.1%, and 42.28%, respectively.

Furthermore, Table 1 also indicates that SCL is a sulfur-free and low-nitrogen-containing feedstock. High levels of carbon and hydrogen have a beneficial impact on higher heating values (HHV), while high levels of oxygen minimize HHV [52]. Table 2 indicates that the amount of volatile matter in SCL is 79.09%, while the fixed carbon and ash content in SCL is 17.16% and 3.75%, respectively.

Table 1: SCL composition is determined by proximate and ultimate analysis

Group	Component	Amount (%)
Proximate analysis	Volatile matter	79.09
	Fixed carbon	17.16
	Ash	3.75
Ultimate analysis	Hydrogen	5.97
	Carbon	47.10
	Nitrogen	0.73
	Oxygen	42.28
	Sulfur	0.17

3.2 Thermogravimetric analysis (TGA) of SCL

The TGA analysis provided the relationship between the temperature and the biomass's mass loss (wt.%). It is usually employed to determine the temperature range, which gives the high rate of decomposition of the biomass. From Fig. 4, the thermal decomposition of SCL started at approximately 200 °C, and sharp decomposition occurred between 250-350 °C. Furthermore, over 95% of the SCL was decomposed when the temperature reached approximately 600 °C. Therefore, the high percentage of mass loss observed from the TGA analysis suggests that 250-350 °C was an appropriate temperature for optimizing SCL conversion to a bio-oil.

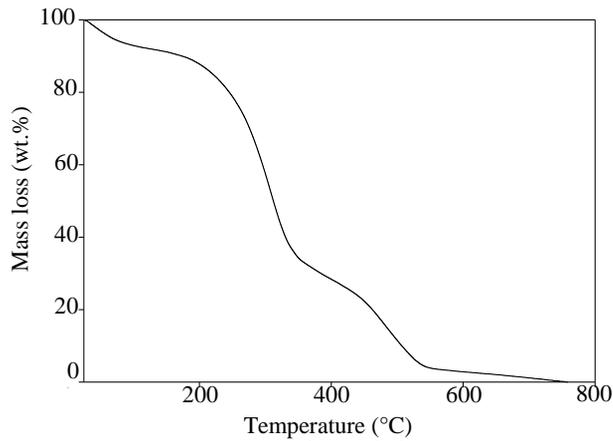


Fig. 4. TGA curve of SCL.

3.3 Effect of reaction temperature on liquefaction product yield

The effect of the reaction temperature on liquefaction product yields can be observed in Fig. 5. This line chart illustrates the results corresponding to three reaction temperatures 250 °C, 300 °C, and 350 °C. The EPW values were 0:1, 1:10, 1:5, 1:2.5, and 1:1, the reaction time in each run being fixed at 60 min. According to the ultimate analysis of SCL, SCL is an oxygen-rich feedstock (42.28%), while the amount of C and hydrogen is 47.1% and 5.97%, respectively. In the HTL process, the C and H will typically convert to BCO with some bio-char and gaseous products. Theoretically, if all C and H become BCO, the maximum yield should be 53.07%. In this study, the maximum BCO yield is 34.8 wt.%, which is 65.57% of the theoretical yield. The data indicate the bio-oil yields at EPWs of 0:1, 1:10, and 1:1 significantly increased when the temperature was increased from 250 °C to 300 °C. Following that, they then decreased when the temperature was increased to 350 °C. This bio-oil yield trend was similar to that reported in previous studies [53-55]. In particular, high temperatures are not suitable for the production of liquid oils in terms of operating costs and liquid oil yields. Ultimately, there are two hypotheses for this behavior. First, secondary decompositions and Bourdard gas reactions are activated at high temperatures leading to gas production [56]. Second, the recombination of free radical reactions leads to char formation due to their high concentrations. At higher temperatures, these two processes dominate, thereby reducing the production of biomass oil.

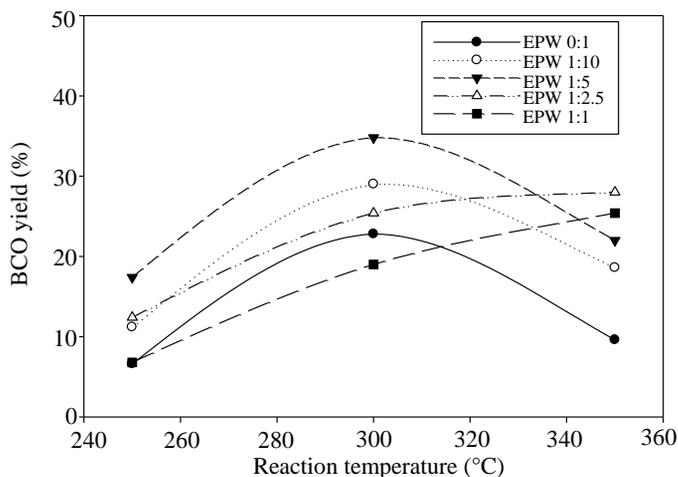


Fig. 5. The yield of crude bio-oil (BCO) with different EPW ratios at various reaction temperatures

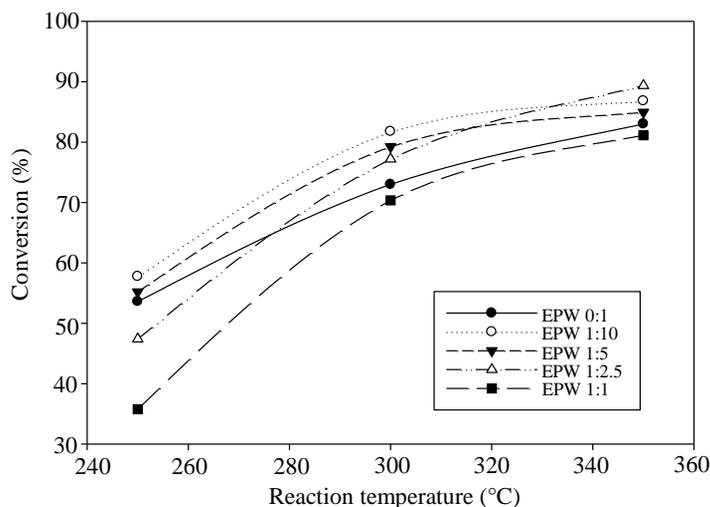


Fig. 6. Conversion of sugarcane leaves with different EPW ratios at various reaction temperatures.

Furthermore, previous studies suggest that the incomplete decomposition of the biomass at temperatures < 280 °C will limit bio-oil production [57] in the HTL process. In contrast, for EPWs of 1:5 and 1:2.5, the yield increased steadily. In general, a high reaction temperature led to the fragmentation of polymers into the oil phase. Further increases in reaction temperature led to an enhanced decomposition of the oil portion into gas. However, the bio-oil yields corresponding to the EPWs of 1:5 and 1:2.5 exhibited a different trend as the EPW exceeds 1:2.5, wherein the critical temperature of the co-solvent is approximately 285.85 °C [58], the actual liquefaction temperature at 300 °C being higher than that of the critical value. As the ethanol content increased, the critical pressure and temperature of the co-solvent decreased. Therefore, the liquefaction process in this study was performed under sub/supercritical conditions. As a result, the maximum bio-oil yield of 34.8% was obtained with an EPW of 1:1 at 300 °C. These results match those observed in previous studies that considered the hydrothermal aspects of rice straw and algae [58, 59]. Earlier studies have shown that decomposition and degradation have been strong reactions to low-temperature biomass liquefaction [60, 61]. However, the formation of gas products and char becomes significant at high temperatures due to the breakdown and repolymerization of the generated liquid products [31, 62].

Figure 6 demonstrates that the conversion increases with the increase in the reaction temperature for all the EPW ratios. The maximum conversion is 89.36% when using an EPW of 1:2.5 at 350 °C. The minimum conversion of 35.80% was obtained when an EPW of 1:1 was employed at a temperature of 250 °C. The reason for this finding is that a reaction temperature greater than 250 °C allows BCO to convert to synthesis gas due to condensation, re-polymerization, or cracking reactions; this being concluded from the TGA curve, which shows that SCL decomposition starts at a low temperature and occurs sharply when the temperature is above 250 °C.

3.4 Effect of ethanol-to-water ratio (EPW) on HTL product contents

The products obtained from the HTL process can be divided into three main groups: BCO, RS, and WSP+GAS. The proportion of each HTL product group at various reaction temperatures is presented in the bar charts of Fig.7-Fig.9. Fig. 7 shows that the bio-oil yield rises from 6.6% to 17.4%, related to the EPW increasing to 1:5 then decreasing after that. In contrast, the RS decreases slightly when the EPW increases from 0:1 to 1:5 and increases steadily. The WSP and GAS yields reacted inversely to the EPW for a reaction temperature of 250 °C.

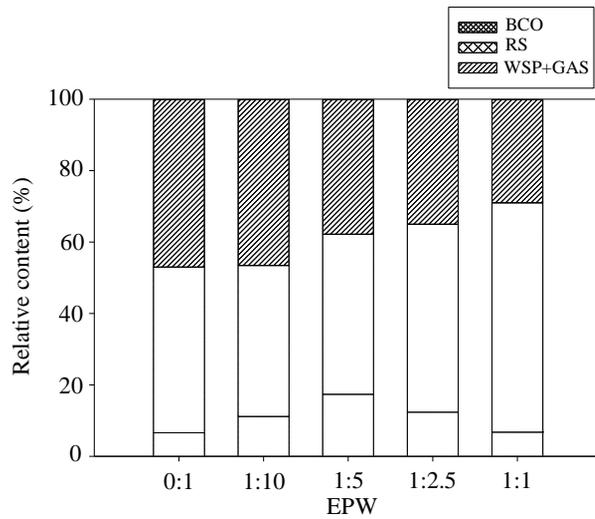


Fig. 7. HTL product content versus EPW at a reaction temperature of 250 °C

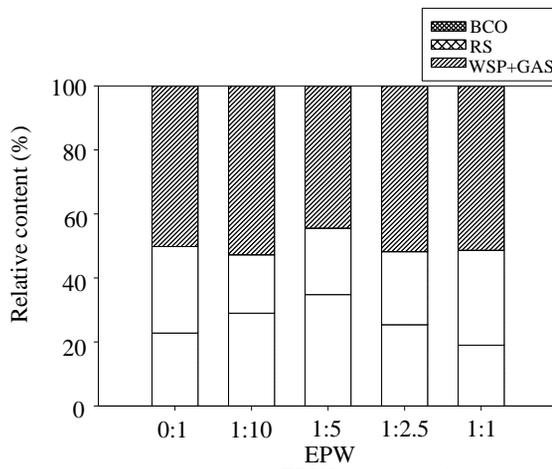


Fig. 8. HTL product content versus EPW at a reaction temperature of 300 °C

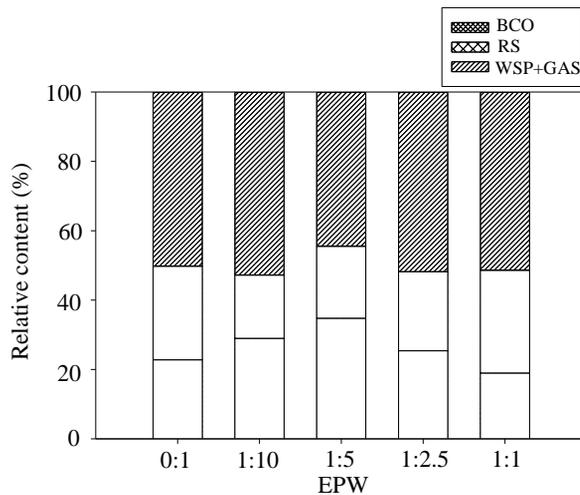


Fig. 9. HTL product content versus EPW at a reaction temperature of 350 °C

Interestingly, this trend could also be observed in Fig. 8, which shows that the maximum BCO yield (34.8 wt.%) and minimum WSP and GAS yields (44.44 wt.%) were obtained with an EPW of 1:5 at 300 °C. The results presented in Fig. 9 indicate that the BCO yield increases steadily over the EPWs of 0:1 to 1:5. Consequently, BCO yield decreases slightly to 25.4 wt.% at an EPW of 1:1 at 350 °C. In summary, the conversion rate generally tends to increase with an increase in the EPW, which reaches its maximum value and then decreases when the EPW ratio becomes excessively high. The maximum conversion rate of 89.36% was obtained with an EPW of 1:1.25. Overall, these results indicate that the EPW considerably affects the conversion rate at temperatures below 300 °C.

It has been reported [63] that reaction times exceeding 30 min led to the formation of larger-molecular weights due to re-condensation or reaction crosslinking between ethanol groups and monomeric phenol. These results match those observed in earlier studies by Yuan et al. [58], who studied the HTL product content of rice straw using a co-solvent of ethanol and water. Their experimental results indicated that increasing the proportion of ethanol in the mixture from 10% to 50% encouraged rice straw conversion and reduced the oxygen content of the bio-oil.

3.5 Chemical composition of BCO and WSP analysis

The composition of the BCO obtained from the HTL using Na₂CO₃ as a catalyst was analyzed using gas chromatography-mass spectrometry (GC-MS). The GC (Perkin Elmer Clarus 680) was directly linked to the MS (Perkin Elmer Clarus SQ8C). The injection port and detector operated at 250 °C for 10 min with the GC oven heated to 45 °C and then heated to 250 °C at a rate of 3 °C/min. The operating conditions were reaction temperature at 350 °C, reaction time at 60 min, and DI water quantity at 5 g.

Table 2 presents the chemical composition of the BCO compound. The primary compound composition is stated as a percentage (%) of the maximum area. Twenty conditions were considered for the SCL HTL. Oleic acid methyl ester, hexadecenoic acid methyl ester, and o-guaiacol were the major compounds. These findings suggest that BCO primarily consists of fatty acids accounting for more than 95% of its composition. Furthermore, the presence of fatty acid methyl ester suggests formal condensation of the oleic acid carboxy group with methanol [39]. Therefore, it can be assumed that the transesterification reaction occurred during the HTL process. Loubna also observed and reported a similar trend [33].

Table 2: GC/MS analysis result for the BCO obtained from the HTL of SCL at a reaction temperature of 350 °C and EPW = 0:1

No.	RT	Compound	Area %
1	3.138	Cyclopentanone	4.52
2	4.109	2-Cyclopenten-1-one	2.87
3	4.309	2-Methylcyclopentan-1-one	0.77
4	6.745	2-Methyl-2-cyclopenten-1-one	9.15
5	10.922	3-Methyl-2-cyclopenten-1-one	0.41
6	12.597	Phenol	7.49
7	12.737	Phenol	1.27
8	12.792	Phenol	1.00
9	12.922	Pyrrole-2-carboxaldehyde	2.68
10	13.117	2,3-Dimethyl-2-cyclopenten-1	3.02
11	15.788	2,3-Dimethyl-2-cyclopenten-1	3.85
12	17.459	m-Cresol	0.98
13	18.875	o-Guaiacol	9.99
14	19.06	2-Cyclopenten-1-one, 3,4,5-trimethyl-	3.75
15	23.982	Phenol, 4-methyl	5.76
16	28.999	4-Ethylguaiacol	3.15
17	54.614	Hexadecanoic acid, methyl ester	17.15
18	59.736	Cyclohexene, 1,2-dimethyl-	1.52
19	59.991	Oleic acid, methyl ester	19.57
20	60.876	Methyl tridecanoate	1.10

Furthermore, the WSP produced from the HTL process was analyzed at the Environmental Protection Center (Ubon Ratchathani University). Notably, the WSP from the process had a pH of 5.07, indicating the weak carboxylic acid [64]. A biochemical oxygen demand (BOD) of 12,600 mg/L, a chemical oxygen demand (COD) of 51,000 mg/L, and a conductivity of 20.5 mS/cm. Thus, the WSP was weakly acidic and highly conductive (i.e., approximately 100-fold) compared to DI water. Therefore, the water treatment process is also required before releasing the WSP to public water resources.

4. CONCLUSION

The present study was performed to determine the influence of reaction temperature and ethanol concentration on the conversion and bio-oil yield from the HTL process of the SCL using Na_2CO_3 as a catalyst. The experiment was conducted in an autoclave batch reactor in a nitrogen atmosphere. The proximate analysis showed that SCL has 79.09% volatile matter and 17.16% fixed carbon. The estimated analysis showed that SCL has a high content of carbon and oxygen of 47.1% and 42.28%, respectively. Because of its high volatile matter, the TGA analysis showed that the SCL starts decomposition at temperatures in the range low to high of 250-350 °C. The results indicate that the co-solvent (ethanol + DI water) enhanced bio-oil yield at these operating conditions. A similar result was reported by Cheng et al. [63]. The yield from lignin degradation by co-solvent (ethanol + water) was also higher than that of water. However, a low conversion occurred with an increase in the EPW, especially at 250 °C. The maximum BCO yield of 34.8 wt.% was obtained from an EPW ratio of 1:5 and a reaction temperature of 300 °C.

Furthermore, a high conversion could be achieved at all EPW ratios at a reaction temperature of 350 °C. The current analysis shows that the main components of the BCO obtained from the HTL of SCL were fatty acids. This is consistent with other reported findings. Finally, the WSP from the HTL process exhibited a high BOD, COD, and conductivity. As a result, the water treatment process is also required before releasing the WSP into public water resources.

ACKNOWLEDGMENTS

This research was supported by a grant from the Energy Policy and Planning Office (EPPO) of Thailand's Ministry of Energy. In addition, the Ph.D. scholarship for the first author (PHD/0218/2558) was supported by the Royal Golden Jubilee (RGJ) Ph. D. program, the Thailand Research Fund (TRF), and the Graduate School of Engineering (Mechanical Engineering) Ubon Ratchathani University.

NOMENCLATURE

BCO	bio-crude oil
BCO_{yield}	bio-crude oil yield (wt.%)
W_B	biomass weight (g)
W_{SR}	solid residue weight (g)
W_{oil}	bio-oil weight (g)

REFERENCES

- [1] Tripatara, A., Karin, P., Phairote, W., Charoenphonphanich, C., Masomtob, M., Chollacoop, N., et al. Effect of biodiesel on compression ignition engine's combustion behavior and particle emission, *Journal of Research and Applications in Mechanical Engineering*, Vol. 8, 2020, pp. 92-100.
- [2] Pianthong, K. and Thaiyasuit, P. Production of biodiesel from rubber seed oil and its effects to engine performances, *GMSARN International Journal*, Vol. 5, 2011, pp. 1-10.
- [3] Thaiyasuit, P., Pianthong, K. and Worapun, I. Acid esterification-alkaline transesterification process for methyl ester production from crude rubber seed oil, *Journal of Oleo Science*, Vol. 61, 2012, pp. 81-88.
- [4] Amutio, M., Lopez, G., Alvarez, J., Olazar, M. and Bilbao J. Fast pyrolysis of eucalyptus waste in a conical spouted bed reactor, *Bioresource Technology*, Vol. 194, 2015, pp. 225-232.
- [5] Barbanera, M., Pelosi, C., Taddei, A.R. and Cotana, F. Optimization of bio-oil production from solid digestate by microwave-assisted liquefaction, *Energy Conversion and Management*, Vol. 171, 2018, pp. 1263-1272.

- [6] Nonchana, T. and Pianthong, K. Bio-oil synthesis from cassava pulp via hydrothermal liquefaction: effects of catalysts and operating conditions, *International Journal of Renewable Energy Development*, Vol. 9, 2020, pp. 329-337.
- [7] Pu, G., Zhou, H.P. and Hao G.T. Study on pine biomass air and oxygen/steam gasification in the fixed bed gasifier, *International Journal of Hydrogen Energy*, Vol. 38, 2013, pp. 15757-15763.
- [8] Li, W., Li, Q., Chen, R., Wu, Y. and Zhang, Y. Investigation of hydrogen production using wood pellets gasification with steam at high temperature over 800 °C to 1435 °C, *International Journal of Hydrogen Energy*, Vol. 39, 2014, pp. 5580-5588.
- [9] Manatura, K. and Jau-Huai, L. Equilibrium modeling of raw and torrefied leucaena in a downdraft fixedbed gasifier, *Journal of Research and Applications in Mechanical Engineering*, Vol. 5, 2017, pp. 74-81.
- [10] Suzuki, A., Nakamura, T., Yokoyama, S.Y., Ogi, T. and Koguchi, K. Conversion of sewage sludge to heavy oil by direct thermochemical liquefaction, *Journal of Chemical Engineering of Japan*, Vol. 21, 1988, pp. 288-293.
- [11] Basu, P. *Biomass gasification and pyrolysis: practical design and theory*, 2010, Elsevier, Massachusetts.
- [12] Brown, R.C. *Thermochemical processing of biomass: conversion into fuels, chemicals and power*, 2011, Wiley-Blackwell, Oxford.
- [13] Mohan, D., Pittman, C.U. and Steele P.H. Pyrolysis of wood/biomass for bio-oil: a critical review, *Energy & Fuels*, Vol. 20, 2006, pp. 848-889.
- [14] Babu, B.V. Biomass pyrolysis: a state-of-the-art review, *Biofuels, Bioproducts and Biorefining*, Vol. 2, 2008, pp. 393-414.
- [15] StrathKirn Inc. Sugarcane as a feedstock for biofuels : an analytical white paper, 2009, National Corn Growers Association, USA.
- [16] França, D.D.A., Longo, K.M., Neto, T.G.S., Santos, J.C., Freitas, S.R., Rudorff, B.F.T., et al. Pre-Harvest sugarcane burning: determination of emission factors through laboratory measurements, *Atmosphere*, Vol. 3, 2012, pp. 164-180.
- [17] Akhtar, J. and Amin, N.A.S. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass, *Renewable and Sustainable Energy Reviews*, Vol. 15, 2011, pp. 1615-1624.
- [18] Tungal, R. and Shende, R. Hydrothermal liquefaction of pinewood (*Pinus ponderosa*) for H₂, biocrude and bio-oil generation, *Applied Energy*, Vol. 134, 2014, pp. 401-412.
- [19] Yang, W., Li, X., Liu, S. and Feng, L. Direct hydrothermal liquefaction of undried macroalgae *Enteromorpha prolifera* using acid catalysts, *Energy Conversion and Management*, Vol. 87, 2014, pp. 938-945.
- [20] Gan, J., Yuan, W., Johnson, L., Wang, D., Nelson, R., and Zhang, K., Hydrothermal conversion of big bluestem for bio-oil production: The effect of ecotype and planting location, *Bioresource Technology*, Vol. 116, 2012, pp. 413-420.
- [21] Christensen, P.R., Mørup, A.J., Mamakhel, A., Glasius, M., Becker, J. and Iversen, B.B. Effects of heterogeneous catalyst in hydrothermal liquefaction of dried distillers grains with solubles, *Fuel*, Vol. 123, 2014, pp. 158-166.
- [22] Dimitriadis, A. and Bezergianni, S. Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: a state of the art review, *Renewable and Sustainable Energy Reviews*, Vol. 68, 2017, pp. 113-125.
- [23] Jiang, J. and Savage, P.E. Influence of process conditions and interventions on metals content in biocrude from hydrothermal liquefaction of microalgae, *Algal Research*, Vol. 26, 2017, pp. 131-134.
- [24] Saber, M., Golzary, A., Hosseinpour, M., Takahashi, F. and Yoshikawa K. Catalytic hydrothermal liquefaction of microalgae using nanocatalyst, *Applied Energy*, Vol. 183, 2016, pp. 566-576.
- [25] Cantero-Tubilla, B., Cantero, D.A., Martinez, C.M., Tester, J.W., Walker, L.P. and Posmanik, R. Characterization of the solid products from hydrothermal liquefaction of waste feedstocks from food and agricultural industries, *The Journal of Supercritical Fluids*, Vol. 43(2), 2017, pp.665-673.
- [26] Posmanik, R., Cantero, D.A., Malkani, A., Sills, D.L. and Tester J.W. Biomass conversion to bio-oil using sub-critical water: study of model compounds for food processing waste, *The Journal of Supercritical Fluids*, Vol. 119, 2017, pp. 26-35.
- [27] Anastasakis, K. and Ross, A.B. Hydrothermal liquefaction of the brown macro-alga *Laminaria Saccharina*: effect of reaction conditions on product distribution and composition, *Bioresource Technology*, Vol. 102, 2011, pp. 4876-4883.
- [28] Duan, P. and Savage, P.E. Hydrothermal liquefaction of a microalga with heterogeneous catalysts, *Industrial & Engineering Chemistry Research*, Vol. 50, 2011, pp. 52-61.
- [29] Shakya, R., Whelen, J., Adhikari, S., Mahadevan, R. and Neupane, S. Effect of temperature and Na₂CO₃ catalyst on hydrothermal liquefaction of algae, *Algal Research*, Vol. 12, 2015, pp. 80-90.

- [30] Jena, U., Das, K.C. and Kastner, J.R. Comparison of the effects of Na_2CO_3 , $\text{Ca}_3(\text{PO}_4)_2$, and NiO catalysts on the thermochemical liquefaction of microalga *Spirulina platensis*, *Applied Energy*, vol. 98, 2012, pp. 368-375.
- [31] Liu, Z. and Zhang, F.S. Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks, *Energy Conversion and Management*, Vol. 49, 2008, pp. 3498-3504.
- [32] Yip, J., Chen, M., Szeto, Y.S. and Yan, S. Comparative study of liquefaction process and liquefied products from bamboo using different organic solvents, *Bioresource Technology*, Vol. 100, 2009, pp. 6674-6678.
- [33] Jasiūnas, L., Pedersen, T.H., Toor, S.S. and Rosendahl, L.A. Biocrude production via supercritical hydrothermal co-liquefaction of spent mushroom compost and aspen wood sawdust, *Renewable Energy*, Vol. 111, 2017, pp. 392-398.
- [34] Pedersen, T.H., Jasiūnas, L., Casamassima, L., Singh, S., Jensen, T. and Rosendahl, L.A. Synergetic hydrothermal co-liquefaction of crude glycerol and aspen wood, *Energy Conversion and Management*, Vol. 106, 2015, pp. 886-891.
- [35] Malins, K. Production of bio-oil via hydrothermal liquefaction of birch sawdust, *Energy Conversion and Management*, Vol. 144, 2017, pp. 243-251.
- [36] Tekin, K., Karagöz, S. and Bektaş, S. Hydrothermal liquefaction of beech wood using a natural calcium borate mineral, *The Journal of Supercritical Fluids*, Vol. 72, 2012, pp. 134-139.
- [37] Lee, S. and Shah, Y.T. *Crop oils, biodiesel, and algae fuels*, 2012, CRC Press, USA.
- [38] Chen, Y., Wu, Y., Zhang, P., Hua, D., Yang, M., Li, C., et al. Direct liquefaction of *Dunaliella tertiolecta* for bio-oil in sub/supercritical ethanol-water, *Bioresource Technology*, Vol. 124, 2012, pp. 190-198.
- [39] Dote, Y., Sawayama, S., Inoue, S., Minowa, T. and Yokoyama, S.Y. Recovery of liquid fuel from hydrocarbon-rich microalgae by thermochemical liquefaction, *Fuel*, Vol. 73, 1994, pp. 1855-1857.
- [40] Jin, B., Duan, P., Xu, Y., Wang, F. and Fan, Y. Co-liquefaction of micro- and macroalgae in subcritical water, *Bioresource Technology*, Vol. 149, 2013, pp. 103-110.
- [41] Minowa, T., Yokoyama, S.Y., Kishimoto, M. and Okakura, T. Oil production from algal cells of *Dunaliella tertiolecta* by direct thermochemical liquefaction, *Fuel*, Vol. 74, 1995, pp. 1735-1738.
- [42] Ross, A.B., Biller, P., Kubacki, M.L., Li, H., Lea-Langton, A. and Jones, J.M. Hydrothermal processing of microalgae using alkali and organic acids, *Fuel*, Vol. 89, 2010, pp. 2234-2243.
- [43] Shuping, Z., Yulong, W., Mingde, Y., Kaleem, I., Chun, L. and Tong, J. Production and characterization of bio-oil from hydrothermal liquefaction of microalgae *Dunaliella tertiolecta* cake, *Energy*, Vol. 35, 2010, pp. 5406-5411.
- [44] Bi, Z., Zhang, J., Peterson, E., Zhu, Z., Xia, C., Liang, Y., et al. Biocrude from pretreated sorghum bagasse through catalytic hydrothermal liquefaction, *Fuel*, Vol. 188, 2017, pp. 112-120.
- [45] Ding, Y.J., Zhao, C.X. and Liu, Z.C. Catalytic hydrothermal liquefaction of rice straw for production of monomers phenol over metal supported mesoporous catalyst, *Bioresource Technology*, Vol. 294, 2019, Article number: 122097.
- [46] Chen, Y., Cao, X., Zhu, S., Tian, F., Xu, Y., Zhu, C., et al. Synergistic hydrothermal liquefaction of wheat stalk with homogeneous and heterogeneous catalyst at low temperature, *Bioresource Technology*, Vol. 278, 2019, pp. 92-98.
- [47] Chen, Y., Duan, P., Dong, L., Zhu, C., Jin, L. and Tian, F. The study of hydrothermal liquefaction of corn straw with Nano ferrite + inorganic base catalyst system at low temperature, *Bioresource Technology*, Vol. 333, 2021, Article number: 125185.
- [48] Zhang, C., Han, L., Yan, M., Xia, J., Rong, N., Baloch, H. A., et al. Hydrothermal co-liquefaction of rice straw and waste cooking-oil model compound for bio-crude production, *Journal of Analytical and Applied Pyrolysis*, Vol. 160, 2021, Article number: 105360.
- [49] Yamazaki, J., Minami, E. and Saka, S. Liquefaction of beech wood in various supercritical alcohols, *Journal of Wood Science*, Vol. 52, 2006, pp. 527-532.
- [50] Milne, T.A., Brennen, A.H. and Glenn, B.H. *Sourcebook of methods of analysis for biomass and biomass-conversion processes: solar technical information program*, 1990, US Department of Energy, USA.
- [51] Jahirul, M.I., Rasul, M.G., Chowdhury, A.A. and Ashwath, N. Biofuels production through biomass pyrolysis -a technological review, *Energies*, Vol. 5, 2012, pp. 4952-5001.
- [52] Abnisa, F. and Wan Daud, W.M.A. Optimization of fuel recovery through the stepwise co-pyrolysis of palm shell and scrap tire, *Energy Conversion and Management*, Vol. 99, 2015, pp. 334-345.
- [53] Loubna, H., Balistrout, M., Burnens, G., Loubar, K. and Tazerout, M. Hydrothermal liquefaction of oil mill wastewater for bio-oil production in subcritical conditions, *Bioresource Technology*, Vol. 218, 2016, pp. 9-17.
- [54] Zhou, D., Zhang, L., Zhang, S., Fu, H. and Chen, J. Hydrothermal liquefaction of macroalgae *Enteromorpha prolifera* to bio-oil, *Energy & Fuels*, Vol. 24, 2010, pp. 4054-4061.

- [55] Toor, S.S., Rosendahl, L. and Rudolf, A. Hydrothermal liquefaction of biomass: a review of subcritical water technologies, *Energy*, Vol. 36, 2011, pp. 2328-2342.
- [56] Abu El-Rub, Z., Bramer, E.A. and Brem, G. Review of catalysts for tar elimination in biomass gasification processes, *Industrial & Engineering Chemistry Research*, Vol. 43, 2004, pp. 6911-6919.
- [57] Yu, Y., Lou, X. and Wu, H. Some recent advances in hydrolysis of biomass in hot-compressed water and its comparisons with other hydrolysis methods, *Energy & Fuels*, Vol. 22, 2008, pp. 46-60.
- [58] Yuan, X.Z., Li, H., Zeng, G.M., Tong, J.Y. and Xie, W. Sub- and supercritical liquefaction of rice straw in the presence of ethanol-water and 2-propanol-water mixture, *Energy*, Vol. 32, 2007, pp. 2081-2088.
- [59] He, Y., Liang, X., Jazrawi, C., Montoya, A., Yuen, A., Cole, A.J., et al. Continuous hydrothermal liquefaction of macroalgae in the presence of organic co-solvents, *Algal Research*, Vol. 17, 2016, pp. 185-195.
- [60] Li, H., Yuan, X., Zeng, G., Huang, D., Huang, H., Tong, J., et al. The formation of bio-oil from sludge by deoxy-liquefaction in supercritical ethanol, *Bioresource Technology*, Vol. 101, 2010, pp. 2860-2866.
- [61] Xu, C. and Lancaster, J. Conversion of secondary pulp/paper sludge powder to liquid oil products for energy recovery by direct liquefaction in hot-compressed water, *Water Research*, Vol. 42, 2008, pp. 1571-1582.
- [62] Miller, J., Evans, L., Littlewolf, A. and Trudell, D. Batch Microreactor Studies of Lignin Depolymerization by Bases. 1. Alcohol Solvents, 2002, Sandia National Laboratories, USA.
- [63] Cheng, S., Wilks, C., Yuan, Z., Leitch, M. and Xu, C. Hydrothermal degradation of alkali lignin to bio-phenolic compounds in sub/supercritical ethanol and water-ethanol co-solvent, *Polymer Degradation and Stability*, Vol. 97, 2012, pp. 839-848.
- [64] Zhang, X., Scott, J., Sharma, B.K. and Rajagopalan, N. Advanced treatment of hydrothermal liquefaction wastewater with nanofiltration to recover carboxylic acids, *Environmental Science: Water Research & Technology*, Vol. 4, 2018, pp. 520-528.