



Optimization of Process Parameters on Hydrothermal Liquefaction of *Sambucus Ebulus* for Bio-oil Production

Amir Hosein Mohseni, Hadi Baseri*

School of Chemistry, Damghan University, Damghan, Iran

(Received 14 Feb. 2022; Final revised received 20 May 2022)

Abstract

Nowadays, the production of bio-oil and chemical intermediates from renewable energy sources is very important because of growing concerns about climate and environmental changes. In this work, the thermal liquefaction of *Sambucus ebulus* (Danewort plant) is studied with a focus on the yield and composition of the produced bio-oil. The produced bio-oil was characterized by FTIR, GC, and GC-MS analyses, and more than 35 different chemical components were identified in it. About 60 w% of the produced bio-oil is composed of five chemical components of acetic acid (21.29%), pentanoic acid (19%), acetone (10.64%), neophytadiene (5%), and α -pinene (4.4%). The effects of various process parameters of reaction temperature, time, and concentration of solution media on the yield and composition of products were studied. The maximum yield of the produced bio-oil is about 42% in a temperature of 160°C, a reaction time of 2 h, and 0.75 V% of ethyl acetate in the solution media.

Keywords: Thermal liquefaction, Danewort, Bio-oil, Yield of product.

*Corresponding author: Hadi Baseri, School of Chemistry, Damghan University, Damghan, Iran. E-mail: Baseri@du.ac.ir.

Introduction

Recently to the growing concerns of climate and environmental changes and regarding the depletion of fossil fuel reserves, the renewable energy source of biomass has great potential as a precursor for the production of biofuel and chemical intermediates [1,2]. Biomass is mainly composed of forestry and agricultural wastes with abundant reserves [3] and it can help to reduce greenhouse gas emissions [4,5].

Pyrolysis, gasification, and thermal liquefaction have been well recognized as effective processes for converting biomass into valuable products of biochar, bio-oil, and biogas. During these processes, some organic contents of solid biomass decomposed to smaller compounds such as bio-oil [6], which are extremely composed of oxygenated organic compounds with total oxygen contents of about 10% to 60 % [7]. Among the different thermal processing techniques, thermal liquefaction (TL) can convert wet biomass to liquid bio-oil. Due to their high water content, fresh plants and wet biomass are not suitable for other thermochemical processes like pyrolysis and gasification. However, in the TL process, the existing water in the biomass may act as a reactant in breaking down reactions and it can increase the reforming rate of biomass macromolecules into the biofuel [8].

The hydrothermal liquefaction process commonly occurs in a wet environment [9] in temperatures between 200 and 380°C and in pressures below 28 MPa [10]. Bio-oil, solid residues, and gas components are the main products of this process. Selection of the used solvent is important for the hydrothermal liquefaction process in which water and alcohols are the most common solvents because of their environmentally friendly natures and low costs [11, 12]. However, high-saturated vapor pressure and high critical temperature are the main drawbacks of using water, which leads to a relatively high-energy consumption [13].

Alcohols are very good choices as the solvent in this process because of their lower critical temperatures and saturated vapor pressures in comparison with water. Moreover, alcohols show good dissolving abilities for organic components, and they can effectively promote the progress of TL reactions because of their good abilities of hydrogen supply [14, 15]. Effects of different solvents on the liquefaction process are explored in the literature. For example, Zhu and his coworkers [16] studied the effects of single and mixed solvents on the liquefaction processes, and they show that the mixed solvent is better than the single solvent with a higher yield of produced bio-oil [17]. Cheng and his coworkers studied the effects of zinc-loaded HZSM-5 catalyst and liquefied biomass as the solvent on the yield of produced bio-oil. In addition, they show that these parameters have efficient effects on the liquefaction process [18]. Moreover, the effects of particle

size of biomass, type of catalyst, and different solvents on the yield of the produced bio-oil were studied by Li and his coworkers [19].

In this work, the waste of the Danewort plant is used as the biomass, and the effects of single and mixture solvents, reaction time, and temperature of the system were studied on the yield and composition of the produced bio-oil by TL process. Danewort or *Sambucus ebulus* is an unbranched perennial plant and spreads by underground rhizomes. It is native to Northwest Africa, Southern, and Central Europe, Southwest Asia (especially Northern Iran), and parts of North America. The Danewort plant has considerable nutritional value due to its accumulation of fibers, sugars, vitamins, and minerals, and it is used as a medical plant in different countries from Western Europe to the Middle East [20]. Danewort is very easy to grow in consistently moist, fertile soils, and there are many sources of this plant in the northern parts of Iran. Therefore, there are plentiful amounts of original and waste Danewort plants without any specific usage, and they can be considered as a source of wet biomass.

Experimental

Chemicals

Danewort plants were collected from the paddy fields and their neighbors in Somaesara in Gillan in northern parts of Iran. The plants were collected in autumn and they were air-dried at room temperature for three days. Then, they were ground by a knife grinder to sizes smaller than 1 mm and they were kept in closed flasks for other experiments. Nitrogen gas with purities higher than 99.5% was supplied from Sabalan gas Co. Iran. Ethanol and ethyl acetate with purities higher than 99% were purchased from Merck (Germany). Other required chemicals were supplied from Merck (Germany).

Thermal Liquefaction Experiments

For TL of Danewort and investigation of the effects of various effective parameters on the yield and characteristics of the produced bio-oil, a small laboratory-scale reactor was used. A schematic schema of the used reactor was sketched in Fig. 1. For the TL process, a cylindrical stainless steel reactor with 50 ml volume (18 mm ID and 200 mm length) is used. Electrical heaters (500 W) with maximum working temperatures of 300(±3) °C heat the reactor. The pressure of the reactor is increased by adding N₂ gas from the gas cylinder up to 4 MPa, and it is monitored by pressure indicators. For a typical experiment, 3 g of dried biomass (fresh feed) was charged in the reactor glass cell, and 15 g of solvent (or solvent mixture with desired concentration) was added to the reactor vessel. Then, the reactor is closed, and the air is discharged by purging of N₂ gas in the

reactor. The pressure of the reactor increased to the desired value by adding N₂ gas, and the pressure is controlled to the desired value by a pressure control valve. The temperature of the system is increased by electrical heaters and adjusted/controlled to the desired value ($\pm 1\%$). For preventing solvent evaporation, in all of the experiments, the pressure of the system was adjusted to values higher than the equilibrium vapor pressure of the selected solvent in the reaction temperature. At the end of the experiment, the reactor is cooled to room temperature, and the pressure is decreased by the constant rate of 15 bar/hour. Then, the reactor opened, and the solid and liquid phases were separated by centrifuging (RPM=4000 and t=5 min). For calculation of the total yield of produced bio-oil, the remaining solid phase was dried at the 100 °C oven for 1 hour, and it was weighted. The differences between the weights of fresh feed and dried residue are used for the calculation of the total yield of the produced bio-oil. For the separation of solvent from the bio-oil, the liquid phase was rotary evaporated for 1 hour at 80 °C, and the remained bio-oil was weighed and stored in the closed flask till the time of other experiments. The yield of produced bio-oil was calculated by the following relation:

$$\text{Yield of bio - oil (\%)} = \frac{\text{weight of biomass (fresh feed)} - \text{weight of remained solid (dried residue)}}{\text{weight of biomass (fresh feed)}} \times 100 \quad (1)$$

For estimation of the weight percentages of light-oil and heavy-oil in the liquid product, the produced bio-oil was fractionated to heptane soluble (light-oil) and chloroform soluble (heavy-oil) fractions.

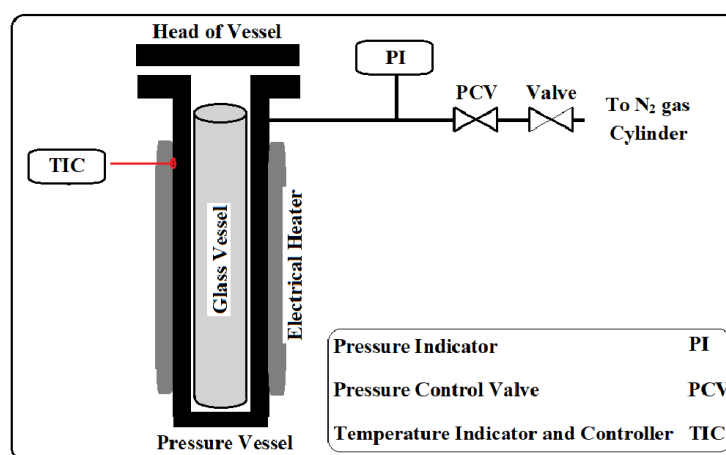


Figure 1. A schematic schema of the used reactor for the thermal liquefaction process.

FTIR analysis of bio-oil

Fourier transform infrared spectroscopic analysis was conducted on a Unicam 4600 FTIR spectrometer (Mattson, USA) for verification of the presence of functional groups and organic structure of the produced bio-oil. In the FTIR experiments, the KBr disc without a sample is used for the collection of background. Then, 1 drop of the produced bio-oil was placed on the KBr tablet, and the spectra were reported in the range of 400–4000 cm^{-1} .

GC and GC-MS analysis of bio-oil

GC and GC-MS analyses were used for the identification of the chemical compositions of the produced bio-oils. For GC-MS analyses, an Agilent 7890 system equipped with an HP5-MS capillary column (30 m length and 0.25 mm initial diameter) was used. The oven temperature was progressively increased as follows: (i) 40 °C for 10 min, (ii) from 40 °C to 200 °C at a heating rate of 5 °C/min, (iii) constant temperature of 200 °C for 30 min. The constant helium flow rate of 15 mL/min with a split ratio of 1:100 was used for carrier gas. The injector and detector temperatures were held constant at 270 °C. The GC analyses were carried out on a Varian Cp 3800 gas chromatography system equipped with a capillary column (30 m length and 0.25 mm ID) and a flame ionization detector. The oven temperature was maintained at 70 °C for 3 min, then, it increased to 120 °C at 5 °C/min and remained constant at 120 °C for 10 min, and then, it further increased to 200 °C at 5 °C/min and it kept constant at 200 °C for 10 min. The helium carrier gas was used with a 1 ml/min flow rate and 1:5 split ratio. 1 μl of the sample was injected in each of the experiments. The injector temperature was set to 180 °C, and the detector temperature was set to 200 °C.

Elemental analysis

The CHNS analysis was carried out on a Vario MACRO cube analyzer, Elementar (Hanau, Germany) with combustion and reduction tubes in constant temperatures of 1150 and 850°C.

Results and discussion

In this section, the bio-oil produced by thermal liquefaction of the Danewort plant was characterized and the effects of two solvents of ethanol and ethyl acetate and the mixture of them on the yield and composition of the produced bio-oil were investigated. Moreover, the effects of reaction time and temperature on the yields of the products were investigated. One of the experiments was replicated three times, and the relative standard deviations of the experiments were calculated to be about 92%.

For a typical experiment ($T=160^{\circ}\text{C}$, 2-hour reaction time, and reaction pressure of 20 bar), the weight percentages of dried residue and produced bio-oil are about 60 w% and 40 w%. Moreover, 42 w% of the produced bio-oil is light-oil and 58 w% of the produced bio-oil is heavy-oil.

FTIR analysis of produced bio-oil

FTIR analysis was used for the detection of the functional groups of the produced bio-oil, and the results were depicted in Figure 2. Based on the reported results by Gao and his coworkers [21], the most abundantly chemical bonds in the bio-oil produced from biomass are O-H, C-O, C-H, and C=O. In the present study, a wide peak at about 3400 cm^{-1} is attributed to O-H functional groups, which shows the presence of phenols, water, or alcohols in the produced bio-oil. The sharp peaks located in about 2924 cm^{-1} refer to C-H functional groups in cyclic or aliphatic alkyls [22]. Moreover, the C=O groups in the carboxylic acids or esters appeared in about 1717 cm^{-1} [23]. The peaks located at 1052 to 1246 cm^{-1} were related to the vibrations of C-O bonds of carboxylic acids or alcohols in the produced bio-oil [24]. The peaks located at 2369 cm^{-1} may be attributed to C-C bonds in unsaturated compounds [22]. The bending vibration of the C-H functional group is corresponded to the peak at about 800 cm^{-1} , and it was associated with aromatic structures [25,26,27].

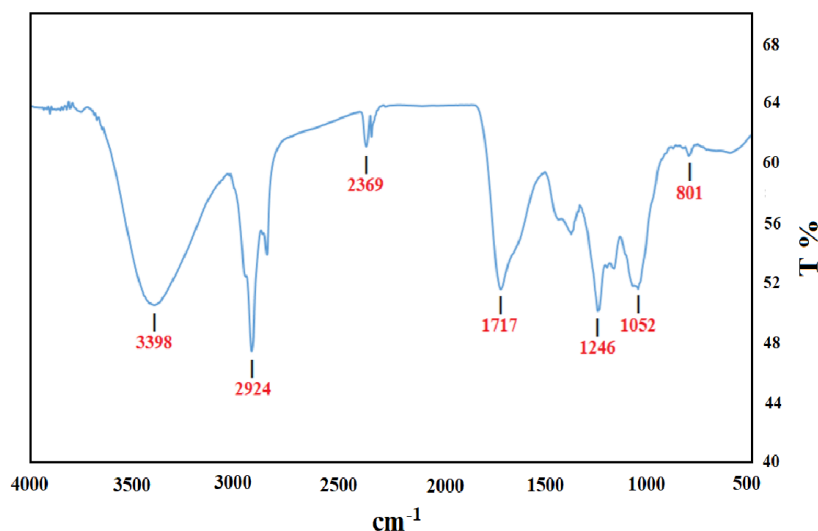


Figure 2. The FTIR spectra of the produced bio-oil by thermal liquefaction of Danewort plant.

CHNS analysis

For a better understanding of the characteristics of fresh Danewort plant and the produced bio-oil, the CHNS analysis was carried out and the results were depicted in Table 1. By comparison between the Danewort plant and the produced bio-oil ($T=160^{\circ}\text{C}$, $t=2$ hour, and 50% concentration of ethyl acetate), it is observed that the produced bio-oil has higher carbon and nitrogen contents

and lower hydrogen contentment than Danewort plant. The reported results are in agreement with the results of Wang and his coworkers [28].

Table 1. CHNS analysis results (w%) of dried Danewort plant and the produced bio-oil by TL of Danewort plant.

Samples	C	H	N
Danewort plant	70.3	4.21	0.94
Bio-oil	77.32	4.11	1.20

Based on the results of table 1, about 70 w% of the used solid biomass is composed of carbon atoms and the carbon recovery to the oil phase is about 31%.

GC-Mass analysis

The chemical composition of the bio-oil produced by TL of the Danewort plant was probed by GC-MS analysis. The chemical components of the produced bio-oil and their concentrations were listed in Table 2. The GC-MS analysis shows more than thirty different chemical components in the produced bio-oil. The major components of the produced bio-oil are acetic acid (21.29%), pentanoic acid (19%), acetone (10.64%), neophytadiene (5%), and α -pinene (4.4%). However, oxygenated compounds such as acids and ketones show higher weight percentages of the product, but other hydrocarbons like alkenes and amines scarcely existed in it. Other researchers reported the relatively same results. For example, as mentioned by Divyabharathia and Subramanian [29], the bio-oil obtained from the pyrolysis is similar to bio-oil obtained from the TL process. They show that the aliphatic and aromatic hydrocarbons, alcohols, and organic acids are the main components of the bio-oil produced by hydrothermal liquefaction of agricultural wastes. However, as mentioned by Xiujuan and his coworkers [7], the weight percentages of oxygenated compounds are about 10% to 60%. The presence of alcohols and carboxylic acids in the produced bio-oil was reported in some other papers [30].

Table 2. GC-MS analysis of the produced bio-oil by TL of Danewort plant.

No.	Name	R.T. (min)	Conc. (w%)	Formula
1	Acetone	1.868	10.64	(CH ₃) ₂ CO
2	Formic Acid	1.929	1.84	H ₂ CO ₂
3	Butanal	2.586	1.23	C ₄ H ₈ O
4	Butanal, 3-Methyl	2.64	1.15	C ₅ H ₁₀ O
5	Propanoic Acid	3.175	1.53	C ₃ H ₆ O ₂
6	Acetic Acid	3.45	21.29	C ₂ H ₄ O ₂
7	α -Pinene	4.199	4.37	C ₁₀ H ₁₆
8	Butanoic Acid	5.819	0.54	C ₄ H ₈ O ₂
9	3- δ carene	9.044	2.22	C ₁₀ H ₁₆

10	2-Propanone	17.014	1.61	C ₄ H ₁₀ N ₂
11	Ethyl 2-hydroxypropanoate	18.79	0.31	C ₅ H ₁₀ O ₃
12	Furfural	22.46	0.61	C ₅ H ₄ O ₂
13	2- Furancarboxaldehyde	25.275	3.52	C ₅ H ₄ O ₂
14	Butyrolactone	26.50	0.38	C ₄ H ₆ O ₂
15	2-Furanmethanol	27.545	0.38	C ₅ H ₆ O
16	Pentanoic Acid	27.73	18.99	C ₅ H ₁₀ O ₂
17	2,2,4,5-tetramethyl-4-hexan-3-one	28.233	2.00	C ₁₀ H ₁₈ O
18	1,3- Disilacyclobutane, 1,1,3,3-tetramethyl	28.49	0.31	C ₆ H ₁₆ Si ₂
19	Dimethylsilan	29.83	0.31	C ₂ H ₈ Si
20	Neophytadiene	33.215	4.75	C ₂₀ H ₃₈
21	1H-Pyrrole-2-carboxaldehyde	35.18	0.46	C ₅ H ₅ NO
22	Hydroxy Dimethyl Furanone	35.37	0.84	C ₆ H ₈ O ₃
23	Butanedioic acid, hydroxyl, diethyl ester	35.58	0.38	C ₈ H ₁₄ O ₅
24	N,N- Dimethyl Propionamid	37.96	0.54	C ₅ H ₁₁ NO
25	2-Ethoxythiazole	38.259	0.84	C ₅ H ₇ NOS
26	Hexadecanoic acid	39.41	0.61	C ₁₆ H ₃₂ O
27	2,3- Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	39.69	2.00	C ₆ H ₈ O ₄
28	Gunidine, N,N,N',N'-tetramethyl	40.46	0.31	C ₅ H ₁₃ N ₃
29	Butane dioic acid	41.73	1.53	C ₄ H ₆ O ₄
30	Benzofuran	41.90	1.00	C ₈ H ₆ O
31	3-Pyridinol	42.24	3.83	C ₅ H ₅ NO
32	O-Diethyl benzene	42.58	0.92	C ₁₀ H ₁₄
33	Phytol	46.49	1.76	C ₂₀ H ₄₀ O
34	Other chemicals		7	

Effects of the process parameters on the yield of produced bio-oil

Reaction temperature, reaction time, type, and concentration of solvent are some of the main important process parameters in the TL process. In this section, the effects of these three parameters on the yield of the produced bio-oil were studied. Figure 3 (A) shows the effect of reaction temperature on the yield of the produced bio-oil in 1 hour reaction time and 75 V% concentration of ethyl acetate in the used solvent. By increasing the temperature from 120 to 160 °C the yield of produced bio-oil increased from 28% to 41%. The same results were reported in the literature [31] for hydrolyses of rice straw by subcritical water. By increasing temperature, the ionization constant of solvent increases and it leads to facilitating the hydrolysis of cellulose and hemicelluloses into monosaccharides [32]. In this study, for decreasing reaction temperature and pressure, the mixture of ethyl acetate and ethanol is used as the solvent, because of their lower values of vapor pressure, critical pressure, and boiling temperature in comparison with water.

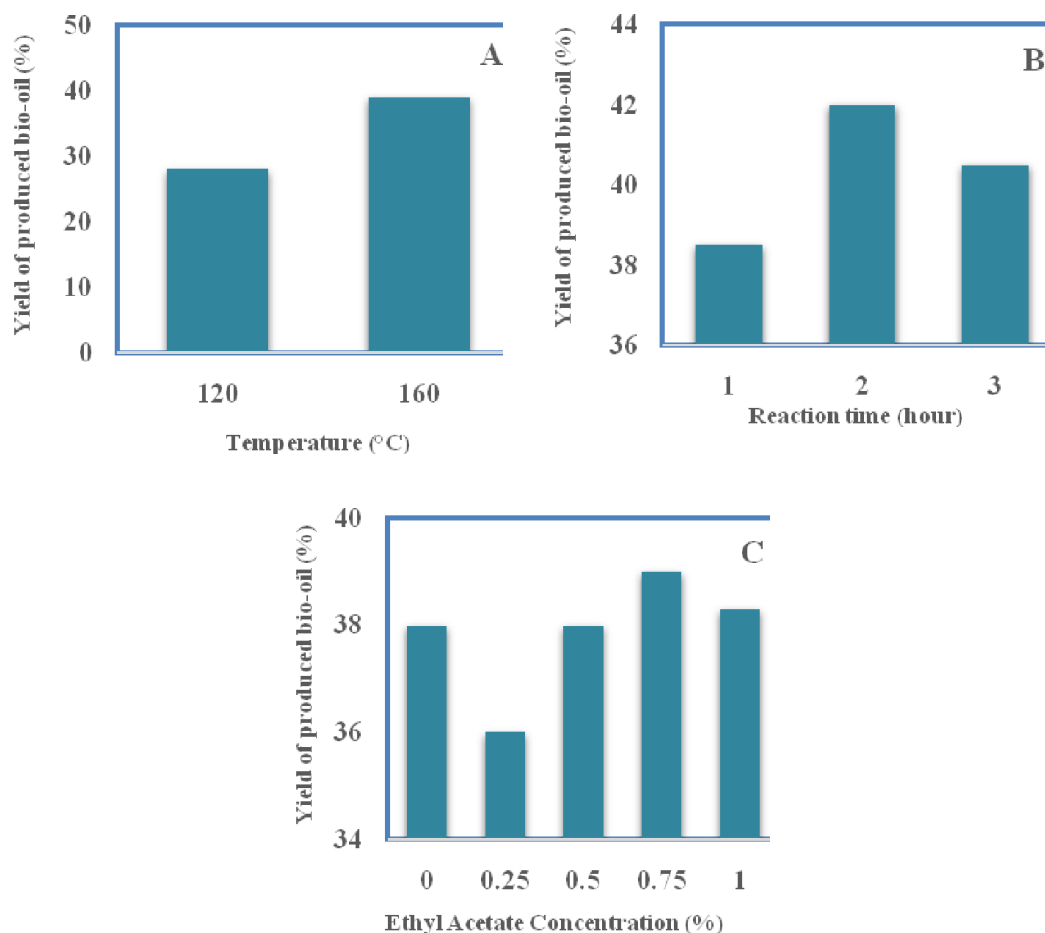


Figure 3. Effects of the process parameters on the yield of produced bio-oil.

The effects of reaction time on the yield of produced bio-oil are depicted in Fig. 3 (B). As can be seen, the yield of reaction increased from 38% to 42% by an increase of the reaction time from 1 to 2 hours. But, it decreased slowly to about 41% by more increase of the reaction time to 3 hours. As expected, by an increase in reaction time, the liquefaction reaction continued and it leads to an increase in the yield of the produced bio-oil. But, as mentioned by Pinto and his coworkers [33] the decrease in the yield of produced bio-oil by increasing the reaction time to 3 hours may be attributed to enhanced TL of different existing compounds, which leads to the formation of volatile and non-recovered components.

Water is the most widely used solvent in the TL process because of its inexpensive cost, ready availability, and favorable environmental factors. However, the use of different organic solvents, such as alcohols, acetone, phenol, and toluene in TL process may lead to enhance bio-oil yields for varying feedstocks like lignin and microalgae [34,35]. Generally, higher conversions may achieve by using higher solvent polarities and the use of organic co-solvents [36]. Because they lead to the higher solubility of organic compounds. Moreover, higher hydrogen donation abilities of solvents

are achieved [37]. Moreover, depending on the critical temperatures and pressures of the added organic solvent, the conducting of the TL process can occur under milder reaction conditions [38]. In this work, the mixture of ethanol and ethyl acetate is used as TL reaction medium. Ethanol is selected because of its ready availability, lower dielectric constant, and good solving ability, as well as its environmentally friendly nature [39] and ethyl acetate, is selected because of its lower critical temperature and pressure in comparison with other common organic solvents. Effects of the concentration of the solution on the yield of produced bio-oil were depicted in Fig. 3 (C). As can be seen, the maximum and minimum yields of the reaction occurred in 25% and 75% volume concentrations of ethanol in ethyl acetate.

Relatively same results were reported by Chen and his coworkers [40] and Feng and his coworkers [41] for TL of *Dunaliellatertiolecta* and the mixture of algal and lignocellulosic biomass with water-ethanol as the reaction medium. They found that the yield of produced bio-oil decreased by the increase of the ethanol concentration from 40 V% for *Dunaliellatertiolecta*, and 50 V% for algal and lignocellulosic mixture biomass. Moreover, based on the reported results by Han and his coworkers [42], excessive amounts of ethanol in the co-solvent mixtures do not contribute to a higher yield of the produced bio-oil.

Effects of process parameters on the yield of the main components in the produced bio-oil

As mentioned later, acetone, acetic acid, pentanoic acid, α -pinene, and neophytadiene, are the five major components of the produced bio-oil, which contain about 60 w% of the bio-oil. In this section, the effects of temperature, time of reaction, and solution concentration on the yield of these major components in the produced bio-oil were studied.

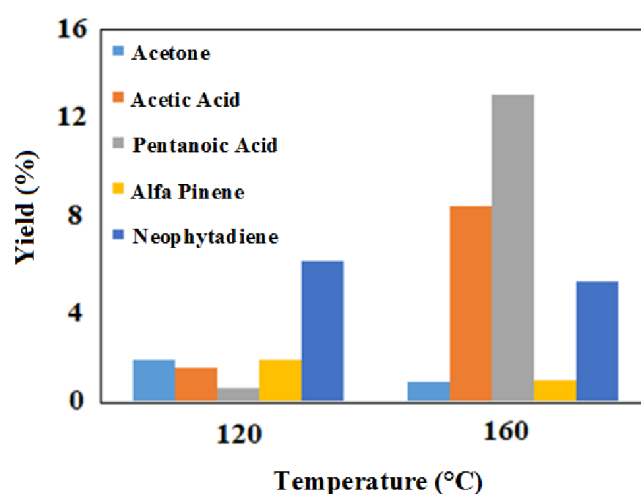


Figure 4. Effects of reaction temperature on the yield of five main components of the produced bio-oil.

Figure 4 shows the effect of reaction temperature on the yield of five major components of the produced bio-oil. As can be seen, by an increase in the temperature from 120 °C to 160 °C, the yields of acetic acid and pentanoic acid increased sharply, but the yields of acetone, α -pinene, and neophytadiene decreased.

By increase of reaction temperature, volatile components with higher vapor pressures like acetone, and molecules with low thermal stabilities like α -pinene, and neophytadiene may be produced with lower yields in comparison with acetic acid and pentanoic acid molecules with relatively lower vapor pressures and higher thermal stabilities. The same results were obtained by Abaide and his coworkers [31]. They show that the organic acids most likely result from cellulose or hemicellulose degradation. For rice straw, by an increase of temperature from 180 to 220 °C, the yields of organic acids increased because of increasing the degradation rate of sugars components.

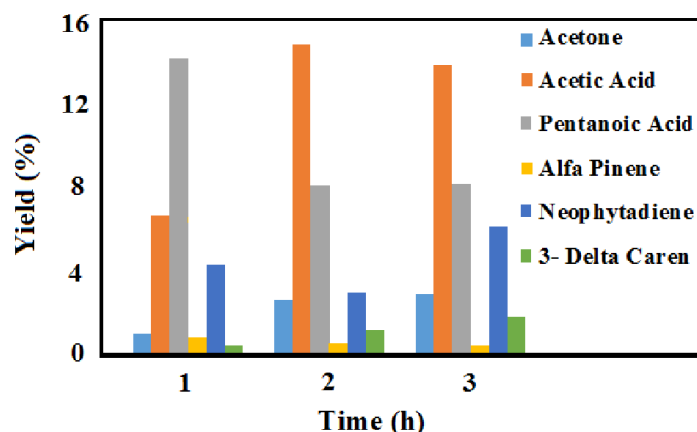


Figure 5. The effect of reaction time on the yields of major components in the produced bio-oil.

The effects of reaction time on the yields of major components of the produced bio-oil are depicted in Figure 5. As can be seen, by the increase in reaction time, the yields of acetone, acetic acid, and 3- δ caren increased simultaneously with decreasing the yield of pentanoic acid. As mentioned later, by the increase of reaction time from 1 to 2 hours, the total yield of the produced bio-oil increased significantly, and clearly, the yield of each component increased too. However, the decrease in the yield of pentanoic acid may be attributed to increasing the secondary degradation reaction of pentanoic acid molecules in the reactor vessel.

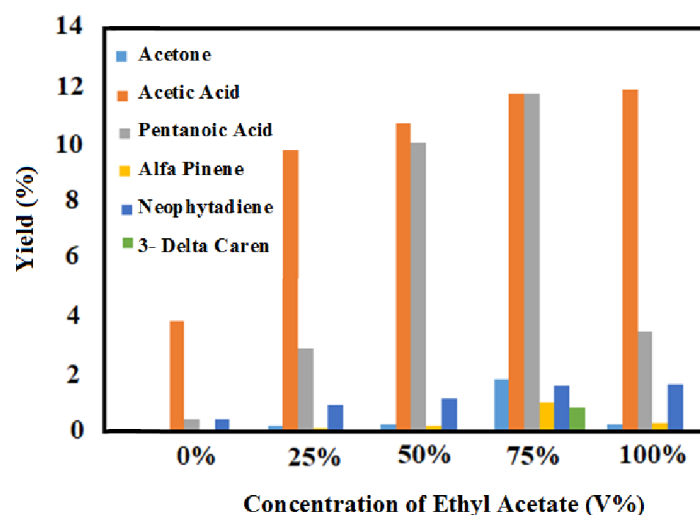


Figure 6. Effect of the concentration of ethyl acetate in the reaction medium on the yields of major components of the produced bio-oil.

The effects of the concentration of the reaction medium on the yields of different components in the produced bio-oil are illustrated in figure 6. By increase of ethyl acetate concentration in the reaction solution (medium) from 0 to 100 V%, the yields of acetic acid and neophytadiene increased continuously. However, for the yields of other major components, the maximum values are observed in 75 V% of ethyl acetate in the reaction solution. These maximum yields of components may be attributed to the maximum of the total yield of the produced bio-oil at this point.

Conclusion

TL process of the Danewort plant was conducted by using a batch liquefaction method with a mixture of ethanol and ethyl acetate as the reaction medium, and it leads to the production of bio-oil by a maximum yield of about 45%. Effects of various process parameters on the yield and composition of the produced bio-oil were studied, and based on the reported results, the maximum yield of the produced bio-oil is obtained at 160 °C reaction temperature, the reaction time of 2 hours, and 0.75 V% of ethyl acetate concentration in the reaction medium. The increase in temperature leads to an increase in the yields of acetic acid and pentanoic acid. By increasing of reaction time, the yield of pentanoic acid decreased, but the yields of acetic acid and acetone increased. Moreover, with an increase in the concentration of ethyl acetate in the reaction medium, the yield of acetic acid increased. However, the maximum yields of pentanoic acid and acetone were obtained in 0.75 V% of ethyl acetate in the reaction solution.

Acknowledgment

The authors gratefully acknowledge the partial support of this work by Damghan University.

References

- [1] G. Kabir, B.H. Hameed, *Renew. Sust. Energ. Rev.*, 70, 945 (2017).
- [2] H.A. Baloch, M.T.H. Siddiqui, S. Nizamuddin, N.M. Mubarak, M. Khalid, M.P. Srinivasan, G.J. Griffin, *J. Anal. Appl. Pyrolysis*, 153, 104944 (2021).
- [3] S. Aflaki, P. Hajikarimi, E.H. Fini, B. Zada, *J. Mater. Civ. Eng.*, 26(3), 429 (2014).
- [4] M. Chen, B. Leng, S. Wu, Y. Sang, *Constr. Build. Mater.*, 66, 286 (2014).
- [5] B. Khoshnevisan, N. Duan, P. Tsapekos, M.K. Awasthi, Z. Liu, A. Mohammadi, I. Angelidaki, D.C.W. Tsang, Z. Zhang, J. Pan, L. Ma, M. Aghbashlo, M. Tabatabaei, H. Liu, *Renew. Sust. Energ. Rev.*, 135, 110033 (2021).
- [6] S. Biswas, D.K. Sharma, *Int. J. Green Energy*, 793, 811 (2021).
- [7] G. Xiujuan, W. Shurong, W. Qi, G. Zuogang, L. Zhongyang, *Chin. J. Chem. Eng.*, 19(1), 116 (2011).
- [8] B.E.-O. Eboibi, D.M. Lewis, P.J. Ashman, S. Chinnasamy, *Bioresour. Technol.*, 174, 212 (2014).
- [9] U. Jena, K.C. Das, *Energy Fuels*, 25, 5472 (2011).
- [10] A. Aierzhati, J. Watson, B. Si, M. Stablein, T. Wang, Y. Zhang, *Energy Convers. Manag.*, 10, 100076 (2021).
- [11] H.J. Huang, X.Z. Yuan, *Prog. Energy Combust. Sci.*, 49, 59 (2015).
- [12] P.S. Rajan, K.P. Gopinath, J. Arun, K.G. Pavithra, A.A. Joseph, S. Manasa, *Renew. Sust. Energ. Rev.*, 144, 111019 (2021).
- [13] D. C. Elliott, P. Biller, A.B. Ross, A.J. Schmidt, S.B. Jones, *Bioresour. Technol.*, 178, 147 (2015).
- [14] Z. Bi, J. Zhang, E. Peterson, Z. Zhu, C. Xia, Y. Liang, T.J.F. Wiltowski, *Fuel*, 188 (429), 112 (2017).
- [15] R. Posmanik, D. Cantero, A. Malkani, D. Sills, J.J.T.J.o.S.F. Tester, *J. Supercrit. Fluids*, 119, 26 (2017).
- [16] Z. Zhu, L. Rosendahl, S.S. Toor, D. Yu, G.J.A.E. Chen, *Appl. Energy*, 137, 183 (2015).
- [17] S. Cheng, I.D'. cruz, M. Wang, M. Leitch, C. Xu, *Energy Fuels*, 24, 4659 (2010).
- [18] S. Cheng, *Electronic Theses and Dissertations.*, 1223 (2017).
- [19] Q. Li, D. Liu, L. Song, P. Wu, Z.J.E. Yan, *Fuels*, 28(11), 6928 (2014).
- [20] M. Jabbari, B. Daneshfard, M. Emtiazy, A. Khiveh, M.H. Hashempur, *J. Evid.-Based Integr. Med.*, 22(4), 996 (2017).
- [21] Z. Gao, N. Li, S.Yin, W. Yi, *Energy*, 175, 1067 (2019).
- [22] B. Zhang, H. Feng, Z. He, S. Wang, H. Chen, *Energy Convers. Manag.*, 159, 204 (2018).

- [23] R. Singh, T. Bhaskar, B. Balagurumurthy, *Process Saf. Environ. Prot.*, 93, 154 (2015).
- [24] Z. Shuping, W. Yulong, Y. Mingde, I. Kaleem, L. Chun, J. Tong, *Energy*, 35(12), 5406 (2010).
- [25] M.H. Eikani, F. Golmohammad, H.S. Amoli, Z.B. Sadr, *Sep. Sci. Technol.*, 48(8), 1194 (2013).
- [26] S. Thiruvankadam, S. Izhar, H. Yoshida, M. K. Danquah, R. Harun, *Appl. Energy*, 154, 815 (2015).
- [27] D. Zhou, L. Zhang, S. Zhang, H. Fu, J. Chen, *Energy Fuels*, 24(7), 4054 (2010).
- [28] Z. Wang, L. Li, R. Hu, X. Wang, C. Pan, S. Kang, S. Ren, Z. Lei, H. Shui, *Fuel Process. Technol.*, 176, 167 (2018).
- [29] R. Divyabharathia, P. Subramanian, *Mater. Today: Proc.*, 45,603 (2020).
- [30] Y. Ding, B. Shan, X. Cao, Y. Liu, M. Huang, B. Tang, *J. Clean. Prod.*: (2020) 125586.
- [31] E. R. Abide, S. R. Mortari, G. Ugalde, A. Valerio, S.M. Amorim, M.D. Luccio, R de F.P.M. Moreira, R.C. Kuhn, W.L. Priamo, M.V. Tres, G.L. Zobot, M.A. Mazutti, *J. Clean. Prod.*, 209, 386 (2019).
- [32] N. Akiya, P.E. Savage, *Chem. Rev.*, 102 (8), 2725 (2002).
- [33] A.R.R. Pinto, F. Antas, R.C.D. Santos, S. Bowra, P. Simoes, S. Barreiros, A. Paiva, *J. Anal. Appl. Pyrol.*, 127, 68 (2017).
- [34] B. Jin, P. Duan, C. Zhang, Y. Xu, L. Zhang, F. Wang, *Chem. Eng. J.*, 254, 384 (2014).
- [35] T.H. Pedersen, L. Jasiūnas, L. Casamassima, S. Singh, T. Jensen, L.A. Rosendahl, *Energy Convers. Manag.*, 106, 886 (2015).
- [36] T. Aysu, H. Durak, *Biofuel, Bioprod. Biorefin.*, 9, 231 (2015).
- [37] T.H. Pedersen, I.F. Grigoras, J. Hoffmann, S.S. Toor, I.M. Daraban, C.U. Jensen, S.B. Iversen, R.B. Madsen, M. Glasius, K.R. Arturi, *Appl. Energy*, 162, 1034 (2016).
- [38] J.L. Wagner, J. Perin, R.S. Coelho, V.P. Ting, C.J. Chuck, T. Teixeira Franco, *Waste Biomass Valorization*, 9, 1867 (2018).
- [39] M. P. Caporgno, J. Pruvost, J. Legrand, O. Lepine, M. Tazerout, C. Bengoa, *Bioresour. Technol.*, 214, 404 (2016).
- [40] Y. Chen, Y. Wu, P. Zhang, D. Hua, M. Yang, C. Li, Z. Chen, J. Liu, *Bioresour. Technol.*, 124, 190 (2012).
- [41] H. Feng, B. Zhang, Z. He, S. Wang, O. Salih, Q. Wang, *Energy*, 155, 1093 (2018).
- [42] Y. Han, K. Hoekman, U. Jena, P. Das, *Energies*, 13, 124 (2020).