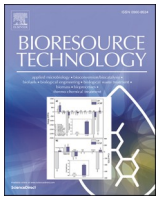
Bioresource Technology 391 (2024) 129928

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech



Solvothermal liquefaction of orange peels into biocrude: An experimental investigation of biocrude yield and energy compositional dependency on process variables

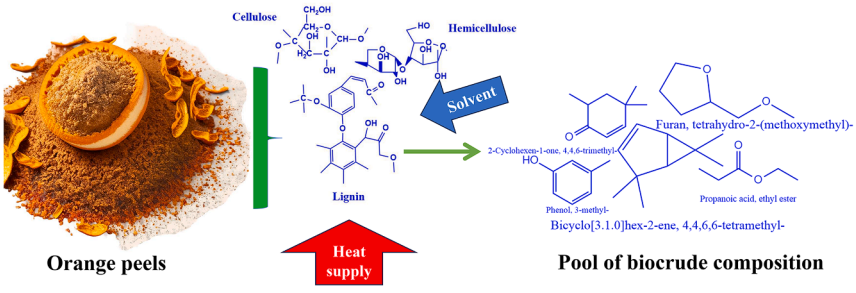
Ishaq Kariim [a,b,c,*], Ji-Yeon Park [c], Wajahat Waheed Kazmi [c,d], Hulda Swai [e], In-Gu Lee [c,d], Thomas Kivevele [a,*]

[a] School of Materials, Energy, Water and Environmental Sciences (MEWES), Nelson Mandela African Institution of Science and Technology, P.O Box 447, Arusha, Tanzania
[b] Chemical Engineering Department, Federal University of Technology, Minna P. M. B 65, Nigeria
[c] Bioresource Circulation Laboratory, Korea Institute of Energy Research (KIER), Yuseong-gu, Daejeon 34129, South Korea
[d] University of Science and Technology (UST), Yuseong-gu, Daejeon 34113, South Korea
[e] School of Life Sciences and Bioengineering (LiSBE), Nelson Mandela African Institution of Science and Technology, P.O Box 447, Arusha, Tanzania

HIGHLIGHTS

- Orange peels was liquefied in sub/supercritical environments without N_2 supply.
- The synergetic effects of process parameters promote biocrude's quality and yield.
- Biocrude HHV of 38.1 MJ/kg was obtained at 50% ethanol, 430 °C and 35 min.
- Biocrude' volatility and molecular weight depends on process variables.
- Orange peels is an excellent bioresource material for biocrude production.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Lignocellulose biomass
Solvothermal liquefaction
Sub/supercritical conditions
Sustainable biofuel
Waste management

ABSTRACT

The efficient valorization of biomass for energy-derived biocrudes is essential for effective waste management. However, the production of biocrudes with high energy and reduced oxygen contents during the liquefaction process requires further insight. Therefore, the impact of reaction temperature, residence time, and ethanol: acetone on the energy compositions and bioproduct's yield enhancement were investigated. The biocrudes obtained were characterized using elemental analysis, GC–MS, FTIR, GPC and TGA to understand the effects of process parameters on the biocrudes' compositions. An improved HHV (38.18 MJ/kg) and lower O/C ratio (0.11) were obtained at 430 °C, 35 min and 50% ethanol with a significant improvement in the enhancement factor, deoxygenation, and percentage hydrogenation of 2.63, 36.88%, and 77.87%, respectively. The presence of ketones, hydrocarbons, phenolics and aromatics of 23.74, 4.28, 37.20 and 17.81% respectively indicate the potential of the obtained biocrude as renewable energy sources upon further upgrading.

* Corresponding authors at: School of Materials, Energy, Water and Environmental Sciences (MEWES), Nelson Mandela African Institution of Science and Technology, P.O Box 447, Arusha, Tanzania (I. Kariim).
E-mail addresses: kariimi@nm-aist.ac.tz (I. Kariim), thomas.kivevele@nm-aist.ac.tz (T. Kivevele).

https://doi.org/10.1016/j.biortech.2023.129928
Received 26 August 2023; Received in revised form 11 October 2023; Accepted 26 October 2023
Available online 31 October 2023
0960-8524/© 2023 Elsevier Ltd. All rights reserved.

1. Introduction

The demand for fossil fuel energy resources for transportation and other purposes is continuously increasing due to human population and industrialization. Fossil fuels are prominent sources of energy worldwide, but their dependency has resulted in greenhouse gases emission which causes global warming. Coupled with these challenges, the non-renewable nature of fossil fuels is another setback whose sources for instance, the petroleum crude deposits, has been continuously depleting due to overdependency (Martins et al., 2019). The production of an alternative energy such as biofuel, is through the conversion of biomass materials via novel approaches having a tendency to meet the transportation's requirements. Biomass has been identified as one of the most efficient, effective, sustainable, and renewable energy sources which has the potential of reducing the dependency on fossil fuels and hence, protecting the environment.

Continuous agricultural activities in quest of providing staple food for the growing population and the intense growth in industrial activities have resulted to an increase in solid wastes generation whose disposal are causing environmental pollution (Chen et al., 2019; Okunola et al., 2019). Handling of such solid wastes are not effective as most often, they are burned or/and disposed to degrade in open landfills which result into products with hazardous consequences (Nanda and Berruti, 2021). Orange, a family of citrus species is one of the predominant crops cultivated in Muheza district, Tanga region of Tanzania which contributes to about 75% of household and 70% of council's generated revenue and this resulted to Tanzania being ranked 6th in Africa as citrus fruits' producer. The presence of cellulose, lignin and hemicellulose in orange peels have positioned it as an excellent feedstock for biofuel production (Divyabharathi and Subramanian, 2021). Oranges are always being processed into fruit juice through extraction process and huge quantity of peels are discharged into the surroundings as solid wastes. The need to convert orange peels into economic products such as biofuel is of importance to mitigate against indiscriminate burning and therefore, presenting orange peels as raw material for biofuel and useful chemicals producing industries, hence, creating a secondary income stream. Several conversion processes have been employed to convert solid wastes into useful products such as sustainable biofuels having potential as an alternative to conventional transportation fuels (Castello et al., 2019; Fernandes et al., 2021).

The valorization of orange peels into biocrude has been investigated by limited researchers using pyrolysis and liquefaction processes (Aboagye et al., 2017; Divyabharathi and Subramanian, 2021). Although, the application of liquefaction approach has received numerous attentions due to its high energy efficiency, production of biocrudes with higher heating value (HHV) among others when compared to pyrolysis process (Ong et al., 2019; Sun et al., 2020). Recently, the optimization of orange peels conversion into biocrude via solvothermal liquefaction process has been reported where the effects of process parameters such as temperature, residence time and total solid loading were optimized to enhance the biocrude HHV (Divyabharathi and Subramanian, 2021). Highest HHV of 32 MJ/kg was obtained which implies the presence of high composition of oxygenated compounds in the biocrude that hampered the overall quality of the biocrude. Hence, there is need to explore optimal reaction conditions that can enhance the HHV effectively and efficiently.

Determining optimal reaction conditions to tailor biocrude properties is critical for achieving economic feasibility, enhancing reactor design, and guaranteeing the production of high-quality biocrude. In this context, it is imperative to consider how process parameters can influence the enhancement of biocrude quality throughout the liquefaction process. The effects of residence time and reaction temperature have been widely studied on several biomass materials while the insight into the synergetic effects of organic solvents (ethanol and acetone) on the HHV, molecular weight and combustion properties of biocrude are still missing in literature (Fernandes et al., 2021; Wang et al., 2019). The intriguing characteristics of ethanol and acetone at supercritical conditions have made the search into the best compositional mix an interesting adventure during the liquefaction process (Malins, 2017; Park et al., 2019; Tekin and Karagöz, 2013). The available literature on orange peels conversion were domicile in the regime of pyrolysis and hydrothermal liquefaction processes with low reported HHV, making it necessary to investigate the synergetic effects of sub/supercritical conditions of ethanol and acetone on the biocrude characteristics.

The effects of ethanol and acetone ratio on the biomass conversion, yield and the composition of biocrudes on the liquefaction of waste hazelnut shell using sub- and supercritical solvents as a reaction medium have been reported by Demirkaya et al. (2019). Through pyrolytic cleavage, the efficiency of ethanol at supercritical conditions enhances the direct liquefaction of biomass through hydrogen donation and thereby, improved biomass conversion (Brand and Kim, 2015; Demirkaya et al., 2019). In the itemized literature, the application of initial nitrogen supply in the reactions are predominant and resulted to an increase in the operating cost. Hence, the investigation of dipolar aprotic (acetone) and polar protic (ethanol) solvents at supercritical conditions would enhance the solubilities of biomass, its intermediates and products, and improved percentage hydrogenation for biocrudes with high HHV (Brand and Kim, 2015).

Therefore, combining the excellent liquefaction properties of ethanol and acetone during the liquefaction process of orange peels would be a novel approach to obtaining high HHV biocrude and effective hydrodeoxygenation pathway. Though, the optimization of reaction temperature, residence time and catalyst loading have been reported to enhance the quality and yield of biocrudes at constant ratio of ethanol to acetone (Kariim et al., 2023). Literature on the dependency of process variables (temperature, time, and the concentration of ethanol in acetone) at sub/supercritical conditions on the properties of biocrudes derived from orange peels in the absence of initial nitrogen supply is lacking.

In this present study, the effects of temperature, residence time and solvent ratio (ethanol to acetone) were investigated to establish the dependency of several biocrudes' properties on the process variables during the solvothermal liquefaction (STL) of orange peels feedstock in sub/supercritical conditions. The relationships between several physiochemical parameters and the energy related quantities were established to understand the effect of severity of process conditions on biocrude's properties and to enable the best selection of process parameters which promotes high biocrudes' quality. Also, a reaction pathway for the solvothermal conversion of the orange feedstocks into biocrude through detailed considerations of the biocrudes' compositions was proposed. For the first time, in the absence of initial gas supply during the STL of orange peels, the dependency of enhancement factor, percentage deoxygenation, carbon recovery efficiency, percentage hydrogenation, carbon element index and energy recovery efficiency on process variables were established.

2. Materials and methods

2.1. Materials

Orange peels whose proximate and compositional contents used in this study have been presented elsewhere (Kariim et al., 2023). Ethanol and acetone with purity of 99 % and 97% respectively, were supplied by Scharlau (Barcelona, Spain) and LOBA Chemie (Mumbai, India) respectively.

$$HHV\left(\frac{KJ}{kg}\right) = 0.3386Carbon + 1.423Hydrogen - 0.154Oxygen - 0.145Nitrogen \quad (1)$$

$$Oxygen = 100 - C - H - N \quad (2)$$

2.2. Solvothermal liquefaction of orange peel

In all the cases of the STL experiment, a stainless-steel autoclave reactor having 500 mL volume capacity, 600 °C and 35 MPa maximum temperature and pressure respectively by Parr 4650, Illinois, USA was employed. The reactor was connected appropriately; feedstock and solvents were loaded as required using a constant weight of 10 g feedstocks and 100 mL solvents. For the first experiment case, the effects of temperature (230, 280, 330, 380, 430 and 480 °C) at constant reaction time of 15 min, 50:50 ethanol/acetone, 5 ± 1 °C/min heating rate, were investigated. Following the conclusion of the reaction, the reactor was rapidly cooled by continuously introducing water, and the resulting gas volume was determined by venting the reactor through the exhaust control valve into an inverted measuring cylinder filled with water (Kariim et al., 2023). The solid–liquid products that had formed during the experiment were transferred into a beaker and subjected to acetone washing until a clear solution became visible. The effects of reaction time (at a constant temperature that yielded the highest biocrude) and the solvent ratio (ethanol: acetone) at a constant temperature and time (which also resulted in the highest biocrude yield). This analysis aimed to understand how different process conditions influence the production of a high biocrude yield and enhance the energy contents.

2.2.1. Biocrude separation

Solid residue containing solvent and biocrude was filtered through a pre-weighed Whatman No. 1 filter paper under vacuum. The solid residue was completely washed with acetone until droppings of colorless filtrates were observed. The retained solid residue on the pre-weighed filter paper was dried at 110 °C for a period 6 h in a convention oven and the yield of the solid residues were determined by comparing the solid residue yield with the weight of the feedstock. The solvents were recovered from the filtrate through the application of rotary evaporator operating at reduced pressure of 0.2 bar and temperature of 79 °C for a period of 2 h in a pre-weighed round-bottomed flask. The yields of the biocrudes were further estimated by comparing the retained weight to the weight of the biomass feedstock. In all the cases studied, the biocrude yield, solid residue yield, volume of gas yield (mL/g) and the biomass conversions were obtained using the expression in Eqs. (3–6) respectively. The deduced parameters which are shown in Table 1 were obtained using the relationships presented by (He et al., 2020; Zhang et al., 2020)

$$Biocrude\ yield\ \left(\frac{w}{w}\%\right) = \frac{Weight\ of\ biocrude\ after\ solvent\ removal}{Weight\ of\ biomass\ feedstock} \times 100 \tag{3}$$

$$Solid\ residue\ yield\ \left(\frac{w}{w}\%\right) = \frac{Weight\ of\ solid\ residue\ after\ drying}{Weight\ of\ biomass\ feedstock} \times 100 \tag{4}$$

$$Biomass\ conersion\ \left(\frac{w}{w}\%\right) = 100 - \%\ Solid\ residue \tag{5}$$

$$Volume\ of\ gas\ produced\ \left(\frac{mL}{g}\right) = \frac{Volume\ of\ gas\ produced\ (mL)}{Weight\ of\ reactants\ (g)} \tag{6}$$

2.3. Biocrude characterization

The compositional analysis of the biocrudes were determined using Agilent GC-7890A coupled with MSD-5977A, USA and an auto-injector by Agilent 7683B series having HP-5 column with dimension 30 m × 0.25 mm × 0.25 μm. The analysis was conducted in He (99.999% purity) environment at 1 mL/min flow rate at an injection volume of 1.0 μL of 1:100 split ratio while the oven was maintained at an initial temperature of 45 °C and was increased progressively to 280 °C at 8 °C/min heating rate. The functional groups present in the feedstock and the biocrudes were determined using FTIR by Shimadzu (IRSpirit, USA). The elemental compositions (CHN) were characterized using CHN628 Analyzer while the Sulfur, S contents were obtained via SC-832DR (LECO. Co. USA) sulfur Analyzer. The thermal stability was determined using TGA SDT Q600 TA instrument (USA) operated in N_2 environment at a heating rate of 10 °C/min between 30 and 900 °C. The average molecular weight of the biocrudes were determined using Waters e2695 Gel Permeation Chromatograph (GPC) with tetrahydrofuran as solvent. The elemental analysis of the orange peels was determined while the oxygen content and the HHV of the orange peels and biocrudes were obtained using the correlation presented in Eqs. (1) and (2) (Liu et al., 2018).

3. Results and discussion

3.1. Characterization of the orange peels feedstock

The elemental compositions were shown in Table 1 and the thermal stability of the orange peels (see Supplementary materials) was presented for the initial evaluation of the suitability for biocrude production. From Table 1, the presence of carbon content of 41.47 wt% implies the transfer of carbon into biocrude which ultimately improved the shared HHV. The volatility nature of the orange peels was observed in the TGA (see Supplementary materials). This observation is linked to the presence of organic species which are depolymerized constituents of lignin, cellulose, and hemicellulose. At the initial stage of the analysis, between 30 and 160 °C, the weight loss was attributed to moisture content with 5.89 wt%. Further increase in temperature shows two dominant peaks degradation temperature (T_p) at 220.4 °C and 321.3 °C which are attributed to hemicellulose and lignin devolatilization respectively. This is in agreement with the study conducted by Hornung and Stenzel (2019). The possible valorization of the orange peels into biocrude is deducible by the volatile constituents of 57.70 wt% observed between 30 and 430 °C. Two main important information could be established from this observation; that the feedstock is potent for bioenergy production and that through adequate conversion approach within the degradation temperature, biocrude of high yield and conversion could be obtained.

3.2. Effect of operating conditions on bio-products' yield and biocrude's composition

The effects of process parameters, such as reaction temperature, reaction time, and the solvents' ratio (ethanol: acetone), were investigated on the biocrude yield, solid residue, volume of gas and the biomass conversion, and the results are presented in Fig. 1(a-f).

3.2.1. Effect of reaction temperature on bio-products' yield

In order to understand the effects of process parameters that favor the STL of orange peels biomass, the application of one-factor at a time was adopted to establish the correlations which exist between process variables and products' yield. The effects of reaction temperature at constant feed to solvent ratio of 1:10, reaction time (15 min) and ethanol: acetone ratio (50:50) were investigated and the result is as shown in Fig. 1a. As regards the biocrude yield, the biocrude yield was observed to increase progressively as the reaction temperature increases at constant time (15 min) and solvent ratio (50:50 of EtOH: acetone). The observable increase in biocrude yield as temperature increases is in accordance with the findings of Kazmi et al. (2023). The increase in biocrude yield due to an increment in temperature is attributed to an improved internal energy in the STL process and consequently promotes biomass decomposition. The percentage biocrude yield increases from 33.87 wt% at 230 °C to 73.30 wt% at 430 °C. The low biocrude yield of 33.87 wt% at 230 °C could be associated with low biomass conversion due to incomplete depolymerization (degradation of higher percentage of hemicellulose and partial cellulose and lignin) at the subcritical region of the solvents (Demirkaya et al., 2019; Khampuang et al., 2015).

Table 1
Elemental analysis of biocrudes produced at different reaction conditions.

	Solvothermal liquefaction products				Elemental composition (%)					Deduced data from biocrude properties									
	Biocrude (wt.%)	Solid residue (wt.%)	Gas volume (mL/g)	Biomass conversion (wt.%)	N	C	H	S	O	O/C	H/C	HHV	EF	DO	CRE	HG	ER	CR	CEI
Orange feedstock	–	–	–	–	0.77	41.47	6.00	0.10	51.66	0.94	1.72	14.49	–	–	–	–			–
Effect of temperature																			
230,15 min,50:50	33.87	40.71	2.18	59.29	1.54	60.70	7.27	0.01	30.49	0.38	1.43	25.94	1.79	40.99	68.32	17.46	60.64	49.57	0.52
280,15 min,50:50	37.34	34.90	8.18	65.10	1.80	71.23	7.11	0.00	19.87	0.21	1.19	30.87	2.13	61.54	58.22	15.56	79.54	64.139	0.81
330,15 min,50:50	50.75	25.31	10.18	74.69	1.22	73.17	8.62	0.00	16.99	0.17	1.40	34.20	2.36	67.11	56.68	30.39	119.79	89.54	0.86
380,15 min,50:50	73.33	24.15	23.82	75.85	0.69	73.97	8.83	0.00	16.51	0.17	1.42	34.93	2.41	68.04	56.06	32.06	176.75	130.80	0.88
430,15 min,50:50	74.30	23.35	30.18	76.65	0.41	76.42	8.99	0.00	14.18	0.14	1.40	36.38	2.51	72.55	54.27	33.29	186.57	136.92	0.95
Effect of reaction time																			
430,5min,50:50	70.12	25.76	27.27	74.24	0.40	74.36	8.81	0.00	16.42	0.17	1.41	35.09	2.42	68.21	55.77	31.92	169.79	125.74	0.89
430,15 min,50:50	74.30	23.35	30.18	76.65	0.41	76.42	8.99	0.00	14.18	0.14	1.40	36.38	2.51	72.55	54.27	33.29	186.57	136.92	0.95
430,25 min,50:50	73.01	22.01	32.27	77.99	0.41	73.49	8.80	0.00	17.30	0.18	1.43	34.63	2.39	66.51	56.43	31.79	174.51	129.40	0.87
430,35 min,50:50	70.03	26.36	33.64	73.64	0.64	78.42	9.51	0.00	11.43	0.11	1.44	38.18	2.63	77.87	52.88	36.88	184.52	132.44	1.00
Effect of solvent ratio																			
430,15 min, 100EtOH	50.34	18.34	34.23	81.66	1.31	75.87	9.26	0.00	13.56	0.13	1.45	36.55	2.52	73.76	54.66	35.23	126.97	92.10	0.93
430,15 min, 75EtOH:25Acetone	68.53	23.60	32.12	76.40	0.40	75.37	8.78	0.00	15.45	0.15	1.39	35.53	2.45	70.09	55.02	31.63	168.02	124.56	0.92
430,15 min, 50EtOH:50Acetone	74.30	23.35	30.18	76.65	0.41	76.42	8.99	0.00	14.18	0.14	1.40	36.38	2.51	72.55	54.27	33.29	186.57	136.92	0.95
430,15 min, 25EtOH:75Acetone	77.88	21.08	25.35	78.92	0.59	76.83	9.25	0.00	13.33	0.13	1.44	37.00	2.55	74.19	53.98	35.16	198.85	144.29	0.96
430,15 min, 100Acetone	76.45	20.54	20.43	79.46	0.45	75.54	8.55	0.00	15.46	0.15	1.35	35.26	2.43	70.07	54.90	29.83	186.01	139.27	0.92

EF = Enhancement Factor; DO = Percentage Deoxygenation; CRE = Carbon Recovery Efficiency; HG = Percentage Hydrogenation; %ER = Energy recovery; CR = Carbon recovery; CEI = Carbon Element index; ERE = Energy Recovery Efficiency.

$$\mathrm{EF} = \frac{HHV\ of\ biocrude}{HHV\ of\ orange\ feedstock};\ DO = \left(1 - \frac{Carbon\ in\ biocrudes}{Carbon\ content\ in\ orange\ feedstock}\right);\ CRE = 100 - \%\ \mathrm{Decarbonization};$$

$$HG: \frac{H\ in\ biocrude - H\ in\ feedstock}{H\ in\ biocrude} \times 100;\ ER = \frac{HHV\ of\ biocrude}{HHV\ of\ feedstock};\ CR = \frac{C\ in\ biocrude}{C\ in\ feedstock} \times 100;\ CEI = \frac{Carbon\ element\ at\ time\ t - Carbon\ element\ of\ feedstock}{Carbon\ element\ at\ HHV\ condition - Carbon\ elemnt\ of\ feedstock} \times 100.$$

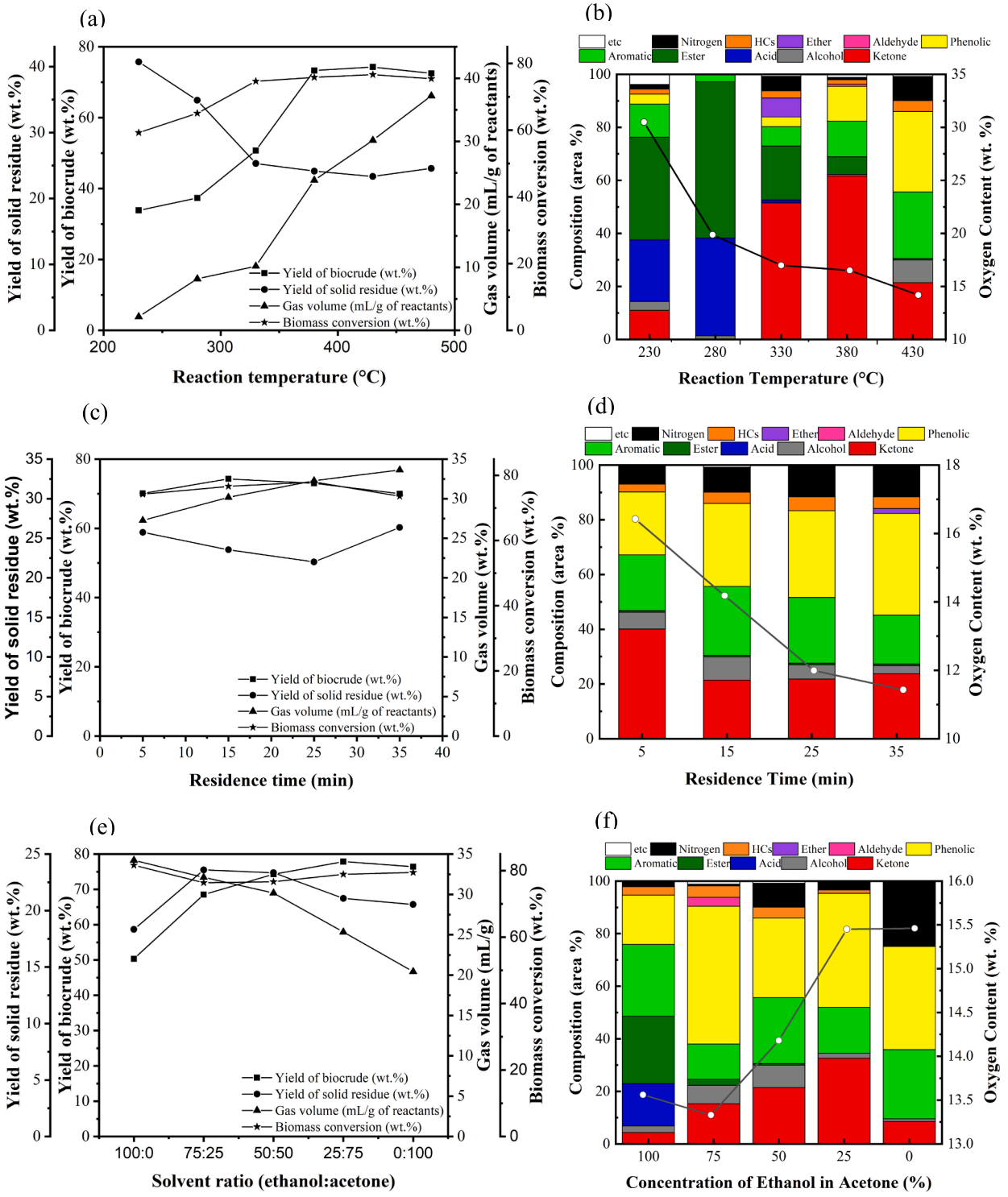


Fig. 1. Effects of reaction temperature on (a) bio-products' yield (b) biocrude compositions; residence time on: (c) bio-products' yield (d) biocrude compositions and solvent ratio on: (e) bio-products' yield (f) biocrude compositions.

Corroboratively, the TGA thermograph of the feedstock (see Supplementary materials) indicates the peak degradation temperature (T_p) of 220.4 and 321.3 °C. Reaction temperature of 230 °C are considered low for optimum STL of orange peels into biocrude which inferably would produce biocrudes with lower yield and biomass conversion. Lower biocrude formations were also observed at 280 and 330 °C. Thus, the temperature was not sufficiently high enough to weaken the crystallinity of the cellulose and the lignin, preventing the hydrolysis reaction into glucose and other monomers, which could have been further be converted into aromatics. At 480 °C, the biocrude yield reduces by 0.65 wt% compared to the biocrude yield obtained at 430 °C. The reduction in the biocrude yield could be a result of secondary cracking reactions, which led to biocrude acting as feedstock and, therefore, promote gasification process over liquefaction.

Furthermore, the yield of biochar and the percentage conversion of orange peels exhibited an inverse relationship throughout the findings. This observation is in accordance with the findings of Demirkaya et al. (2019) who reported the effects of process parameters on the sub/

supercritical valorization of hazelnuts. For instance, 40.71, 34.90 and 25.31 wt% of solid residue were obtained at the reaction temperature of 230, 280 and 330 °C respectively. The temperature of 230 °C is below the peak degradation profile of lignin and the supercritical temperature of the two solvents hence, lower solvothermal cracking occurs and produces higher solid residue over biocrude formation with high acid contents. At a temperature closer to the T_p of the orange peels and at the supercritical regions on the solvents, 330 °C, the conversion was highly enhanced and resulted in a noticeable decrease in solid residue yield with 27.47 % when compared to the reaction temperature of 280 °C. The conversion follows an inverse relationship with solid residue yield inline with the established relationship as described in Eq.(5); the higher the yield of solid residue, the lower the biomass conversion.

The gas volume formation (mL/g of reactants) is an important factor which indicate the quantity of gaseous product obtained as a result of possible chemical reactions and cracking of large molecular weight compounds including the solvent during the solvothermal process (Brand and Kim, 2015). As previously described in various literature, that, the liquefaction process of biomass follows a complex reaction schemes involving decarbonylation, dehydroxylation, decarboxylation, deoxygenation and dehydration reactions which lead to CO_2, CO and H_2O formation (Li et al., 2021). The biomass conversion increases as temperature increases from 59.29 to 76.65 wt% at 230 to 430 °C as shown in Table 1. This finding is in accordance with the report of Li et al. (2021) who reported the effect of process variables on the thermochemical conversion of *Gracilaria corticata* microalgae into biocrude, and Biswas et al. (2020) who investigated the effects of temperature and solvent on bioproducts' formation.

3.2.2. Effect of reaction time on bio-products' yield

The effects of reaction temperature at constant feed to solvent ratio of 1:10, reaction temperature (430 °C), and using an ethanol: acetone ratio (50:50) were investigated, and the results are shown in Fig. 1c. Residence time has been reported as an important parameters during the STL of biomass (Malins, 2017). Fig. 1c shows that the yield of biocrude increased from 70.12 wt% at 5 min to 74.30 wt% at 15 min of the reaction time, followed by a subsequent decrease to 70.03 wt% at 35 min. The first progression (5–15 min) indicates that there was enough residence time for high depolymerization of orange peels' constituents, resulting into an enhanced biomass conversion and promoting the aggregation of the produced gases into hydrocarbon monomers. According to the findings of Caprariis et al. (2017), the possible competition between the decompositions of the orange peels and the repolymerization reaction within biocrude's fragments during the degradation of holocellulose could lead to a reduction in the biocrude yield at longer reaction times, as observed between 25 and 35 min. The conversion of biocrude into volatiles, a secondary product, may account for the decrease in biocrude yield. This observation has also been reported in the findings of Bakari et al. (2021) who studied the effects of reaction parameters on the valorization of rice husks. At the optimal reaction time of 15 min, a preference for higher aggregation of gases and solid decomposition over repolymerization, condensation, and cyclization reactions was observed, which could contribute to the formation of gaseous products and solid residues. This observation is also supported by the report of Rachel-Tang et al. (2017), who presented the catalytic solvolysis of biomass into biocrude.

3.2.3. Effect of solvent ratio on bio-products yield

The effects of solvent ratio, while maintaining a constant feed to solvent ratio of 1:10, reaction temperature (430 °C), and residence time of 15 min were investigated and the results are presented in Fig. 1e. Ethanol and acetone have been highlighted as promising solvents in the STL of biomass feedstock (Demirkaya et al., 2019; Fernandes et al., 2021). From Fig. 1e, the effects of solvents' ratio were studied by increasing the ratio of acetone in ethanol; 100:0, 75:25, 50:70, 27:75 and 0:100 (EtOH: acetone) during the STL of the orange peels. The products yield, while using pure ethanol under constant reaction conditions, were observed to be 50.34 wt%, 18.34 wt%, 34.23 mL/g of reactant and 81.66 wt% of biocrude yield, solid residue, gas product and biomass conversion, respectively. Meanwhile, the biocrude yield, solid residue yield and the gas yield obtained in pure acetone medium were 76.45 wt%, 20.54 wt% and 20.43 mL/g, respectively. The significant increase in the yield of biocrude derived from acetone could be linked to the improved solubility potentials of extractives and lignin, coupled with the cracking of organic soluble and intermediates at elevated temperature and the synergetic contribution of the dipolar aprotic characteristics of acetone at the supercritical conditions (Demirkaya et al., 2019). The addition of acetone to the ethanol medium enhances the biocrude yield compared to using pure ethanol as a solvent to 68.53, 74.30, and 77.88 wt% for 75:25, 50:50 and 25:75 (ethanol: acetone), respectively. The significant rise in biocrude yield upon the addition of acetone implies that acetone has contributory impact, promoting the enrichment of both polar and nonpolar soluble components in the orange peels' feedstock. At the solvent ratio of 75: 25 (acetone: ethanol), the percentage biocrude yield increases as compared to pure acetone by 1.84 wt%. This indicates the synergistic effects of acetone and ethanol as an excellent solvent mixture during the orange peels' valorization process, leading to an improvement in the biocrude yield.

3.3. Effect of reaction conditions on biocrudes' compositions

3.3.1. Effects of reaction temperature on biocrude's compositions

To determine the effect of reaction temperature quantitatively and qualitatively on the compositional make-up of the produced biocrude, GC–MS analysis was utilized, and the results are presented in Fig. 1b. The detailed composition of the biocrudes as obtained from the GC–MS spectral are shown (see Supplementary materials). The presence of several oxygenated and non-oxygenated compounds was identified and presented based on their respective percentage area. The compositions were classified based on acid, alcohol, aldehydes, aromatics, phenols, ketones, ethers, esters, hydrocarbons, nitrogen containing compounds, and others (include heteroatoms, like chlorine, and sulfur containing aromatic compounds). The identified compounds were produced through the depolymerization and decomposition of lignin, hemicellulose and cellulosic components of the orange peels, forming a complex mixture (Divyabharathi and Subramanian, 2021).

Although, the variation in the itemized compositions differs across various reaction conditions, providing insights into the optimum process parameters to be adopted for tailoring the biocrude properties of interest. For instance, at lower temperatures of 230 °C and 280 °C, as shown in Fig. 1b, the biocrudes exhibit the highest compositions of acids and esters. This indicates that esterification and hydrolysis reactions are favored at lower reaction temperature (Kariim et al., 2023). This observation further reveals that the production of high ester contents and acids were favored at low temperatures. The formation of ketones with percentages of 10.94%, 51.50%, 61.72%, and 21.45% at temperatures of 230 °C, 330 °C, 380 °C, and 430 °C, respectively, suggests a possible hydrogen transfer from the produced alcohol. Additionally, aldehyde formation, accounting for 0.80%, was also observed at 380 °C. The possible conversion of alcohol to ketones and aldehydes through hydrogen transfer mechanism has been reported by Jun et al., (1998). The noteworthy observation here is the increasing trend in ketone selectivity at elevated temperatures of 330 °C, 380 °C, and 430 °C. This indicates a substantial conversion of aromatic ethers into ketones and their derivatives, likely driven by hydrogenation and hydrolysis processes. This possible reactions phenomena is supported by the study of Meng et al. (2017), who investigated the synthesis of ketones from biomass-derived feedstock using solid catalysts.

As the temperature increases from 330 °C to 430 °C, the selectivity to acids formation was inhibited. This shows that, high temperature above the peak degradation temperature of orange feedstocks in the co-solvent environment retards hydrolysis reaction for acids formation. The most

favorable conditions for the synthesis of aromatic ethers were observed at 330 °C, accounting for 7.15 % of the biocrude through etherification reactions. A similar observation was reported by Rorrer et al. (2019), where ethers were linked to the etherification reactions of acids, ketones, aldehydes and esters. Moreover, the biocrude obtained at different temperatures exhibits a lower hydrocarbon content and a higher selectivity towards oxygenated compounds, indicating the need for additional upgrading using the hydrodeoxygenation approach. The highest observable composition of hydrocarbon in all the reaction conditions shown in Fig. 1b indicates that 430 °C is the most favorable reaction condition for further study.

3.3.2. Effects of reaction time on biocrude's compositions

At the constant reaction temperature of 430 °C, with a feed to solvent ratio of 1:10, and residence time ranging from 5 to 35 min, and solvent ratio of 50:50 EtOH: acetone. Like the temperature effect, various compounds were identified and classified, as illustrated in Fig. 1d. Notably, acids and aldehydes were not favored throughout the studied residence time at 430 °C. Primarily from Fig. 1d, three main compounds; ketones, aromatics and phenolics were highly selectively produced during the studied conditions. About 40.07 % of ketones were selectively produced at the residence time of 5 mins, while the concentration reduced to 21.44 % at 15 mins. The formation of phenols and their derivates were associated to the decomposition of lignin and carbohydrates through a series of reactions involving hydrolysis and subsequent methoxy groups hydrolysis. This is in accordance with the findings reported by Carpio et al. (2021) who reported the effects of reaction time and temperature on the hydrothermal liquefaction of demineralized wastewater algal biomass. From the result presented in Fig. 1d, the percentage composition of phenolics increases with increasing residence time. The stability of the produced ester-containing compounds and their derivatives becomes noticeable as the residence time increases, with a clear indication of a complete esterification reaction throughout the observations, resulting in no formation of acids. Hence, high temperature solvothermal of orange peels favors the complete esterification reaction over reversed esterification. The formation of nitrogen-containing aromatics increases with prolonged residence time. This phenomenon can be attributed to the inherent instability of the aromatic intermediates produced, which exhibit a high tendency to react with nitrogen and other heteroatoms as the residence time is extended.

3.3.3. Effects of solvent ratio on biocrude's compositions

The effects of EtOH to acetone ratio on the compositional make-up of the produced biocrudes at constant reaction temperature and residence time were evaluated and the results are shown in Fig. 1f. Based on the result presented in Fig. 1f, there is an increase in the percentage composition of ketones as the acetone loading on ethanol increases. For instance, at 100 % ethanol (0 % acetone), the observable presence of ketones is 4.36 % and this increases to 15.30, 21.44 and 32.58 % at 75, 50 and 25 %ethanol in acetone, respectively. This implies that the introduction of acetones in ethanol solvent enhances the ketonization reaction by improving hydrogen transfer mechanisms through solvent cracking and carboxylic acids conversion. This process is capable of carbon dioxide and water formation which is in accordance with the report of Pacchioni, 2014 who reported the ketonization of carboxylic acids during the biomass conversion over ZrO_2 and TiO_2. The biocrude produced in 100 % ethanol as solvent favors hydrolysis and reverse esterification which could be associated with the production of acids (Kazmi et al., 2023).

3.4. Energy composition and Van-Krevelen plot

Table 2 shows the elemental compositions and deduced energy related parameters of the biocrudes obtained at several reaction conditions. The production of high quality biocrude via STL process has been observed to depend on various process parameters and adequate attention has been channeled to evaluate the inter-relationship that exists through several correlation factors. The HHV is one of the most important parameters which could be identified to be primarily depends on the degree of HDO process. From Fig. 2a, the HHV (MJ/kg) increases with an increasing reaction temperature; from 26.96 to 36.38 MJ/kg at 230 to 430 °C reaction temperature. HHV was observed to possess a direct relationship between the deoxygenation (%) and hydrogenation (%) except at the reaction temperature of 280 °C where a little decrease in the hydrogenation process was observed. The decrease in HHV is supported with the compositional results shown in Fig. 1b where reversed esterification which led to high acid formation was observed over esterification reaction. Similar observation of increasing temperature on the HHV of biocrude has been reported in various literature during the catalytic HDO of waste coffee oil in supercritical ethanol medium (Kazmi et al., 2023).

The progressive increase in HHV as temperature increases promotes the enhancement factor (EF) which compares the HHV of biocrude at a certain condition to the HHV of the initial feedstock as shown in Fig. 2a. The HHV observed at the effect of reaction time was noticed to follow a sinusoidal effect where the HHV increases from 5 to 5 min with a decrease at 25 min reaction time. This sudden decrease in the HHV could be associated with the cracking of side alkyl chains, which mostly contain H and C. As a result, an increase in the oxygen content is observed at the residence time of 25 min, as shown in Fig. 2b and Table 1. Highest HHV was obtained to be 38.18 MJ/kg at the reaction temperature of 430 °C, 35 min residence time and 50:50 EtOH to acetone ratio with the highest enhancement factor of 2.63. The HHV of 38.18 MJ/kg observed is higher than the reported HHV of 37.76 MJ/kg obtained during the catalytic depolymerization of orange peels over Fe supported carbon nanospheres and 25% ethanol in acetone as reported by Kariim et al. (2023) and Divyabharathi and Subramanian (2021) who reported 32 MJ/kg. Furthermore, the introduction of 75 % acetone was found to improve the HHV from 36.66 MJ/kg at 100 % EtOH to 37.00 MJ/kg due to an improved deoxygenation process during the depolymerization process as depicted in Fig. 2c.

The Van-Krevelen plot which is shown in Fig. 2d shows the degree of hydrodeoxygenation (HDO) process where O/C and H/C are important parameters that depict biocrude properties. The lowest O/C ratio was observed to be 0.11 as compared to the starting orange peels with 0.94 as shown in Fig. 2d. Biocrude with the lowest O/C and H/C ratio was

Table 2
TGA result of some selected biocrude based on HHV.

Sample	Onset temp. (T_{onset}) (°C)	Peak degrad Temp, T_p (°C)	< 180 °C (Light volatiles) (wt.%)	180–360 °C Medium volatiles (wt.%)	360–550 °C Heavy oils (wt.%)	>550 °C Inorganics and coke (wt.%)	Total volatiles (30–900 °C) (wt.%)
430 °C,15 min,50 % EtOH50%acetone	205.20	250.40	8.54	77.11	9.62	0.57	95.84
430 °C,35 min,50 % EtOH50%acetone	131.80	222.60	26.99	63.52	5.86	1.160	97.65
430 °C,15 min,100 % EtOH	129.50	258.10	18.36	59.10	12.58	1.150	91.19
430 °C,15 min,75 % EtOH50%acetone	215.20	251.60	8.59	75.70	10.84	0.45	95.58

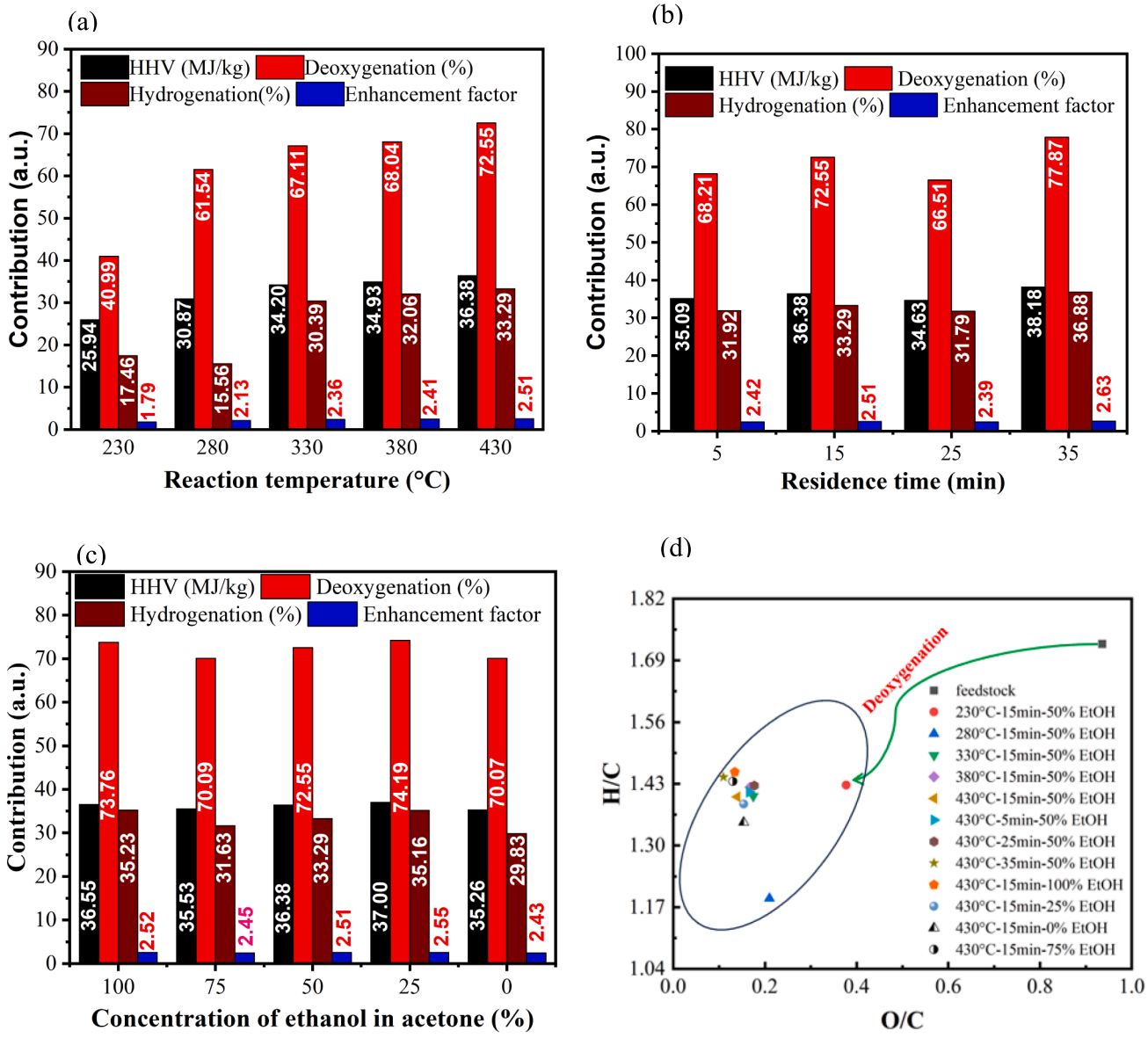


Fig. 2. Inherent biocrude properties relative to (a) reaction temperature (b) residence time (c) solvent ratio and (d) Van-Krevelen plot.

obtained at the reaction temperature of 430 °C, 35 min reaction time and 50:50 solvent ratio of EtOH to acetone. In order to enhance the H/C ratio of the biocrude with an O/C ratio of 0.11, it is necessary to conduct a hydrodeoxygenation (HDO) process by selectively developing a catalyst for improved conversion. Also, the decrease in oxygen and nitrogen contents in the biocrude obtained throughout the process conditions as compared to the starting orange peels feedstock are associated to the possible reactions such as dehydration and de-methanation during the solvothermal process (Liu et al., 2022).

3.5. Biocrude's properties correlation

The percentage deoxygenation (DO), percentage hydrogenation (HG), carbon recovery (CR), carbon recovery efficiency (CRE), enhancement factor (EF) and energy recovery (ER) were correlated and fitted with carbon element index (CEI) as depicted (see Supplementary materials). The results presented in (see Supplementary materials) contained the fitting model, the regression line, correlation coefficient, R^2 and the fitting equation in all cases. The physiochemical properties presented were suitable to a polynomial expression $y = cx^2 + bx + a$ as adopted from the findings of He et al. (2020) where the effect of residence time possesses the highest correlation coefficient, R^2 of above 0.9 for the percentage DO, HG and CRE.

From the results presented (see Supplementary materials), the information from the polynomial is highly relevant to providing the severity of the liquefaction process during the investigation of the effects of residence time followed by temperature and solvent ratio as the CEI increases. From the correlation coefficients, the b and c parameters signify the elements' sensitivity as a function of CEI and then, depends on the severity of the liquefaction conditions. The energy properties analysis of the liquified orange peels which shows the relationship between enhancement factor and energy recovery on the carbon element index at various reaction conditions are presented (see Supplementary materials). As the severity of the process conditions increases, most especially, when the effects of temperature and time were considered, the EF and ER increases with a gradual corresponding increase in the CEI. Hence, the relationships established through the polynomial fittings help in correlating between the energy parameters (EF and ER) and the liquefaction conditions. A more direct relationships were observed in the effects of temperature and residence time on the enhancement factor

where the regression coefficient, R^2 were greater than 0.9.

3.5.1. Combustion and molecular weight distribution analysis of biocrudes

The thermogravimetric analysis is an important tool which reveals the thermal stability of biocrude, boiling point range to enable the quantification of the presence of several fractions and the inherent coke formation due to the possible presence of polyaromatics hydrocarbons in the biocrude. Fig. 3a and b show the TGA and the DTG plots of biocrudes having the highest heating values in the present reaction conditions considered. The deduced data presented in Table 2 shows the variations in the thermal properties due to the different fractions contained in the biocrude.

From Fig. 3a and b, the different compositions which are present in the biocrude are observable in the thermal responses and indicate the present of different fractions of obtainable fuel-grades as a function of fractionation. The main fractions in the biocrudes were categorized into light volatiles, medium volatiles, heavy oil and inorganic and cokes with temperature ranges from < 180 °C, 180–360 °C, 360–550 °C and greater than 550 °C respectively as presented in Table 2. From the deduced data shown in Table 2, the onset temperature, T_{onset} is the temperature at which the biocrude begins to be volatilized. Considering the effect of residence time at constant solvent ratio of 50:50 EtOH: Acetone and reaction time of 430 °C, the volatility increases from 205.20 °C and 131.80 °C as the residence time increases from 15 min to 35 min respectively. This implies that, the longer reaction time produces higher fractions of volatiles from the depolymerization of the orange peels' constituents over a shorter residence time though there is a corresponding decrease in the medium volatile components i.e., gasoline and diesel range fuel. The overall percentage volatile content of 97.65 wt% as compared to 95.84 wt% were obtained at 35 and 15 min of residence time respectively. Also, the effect of acetone addition in ethanol to the thermal decomposition of biocrude at constant reaction temperature

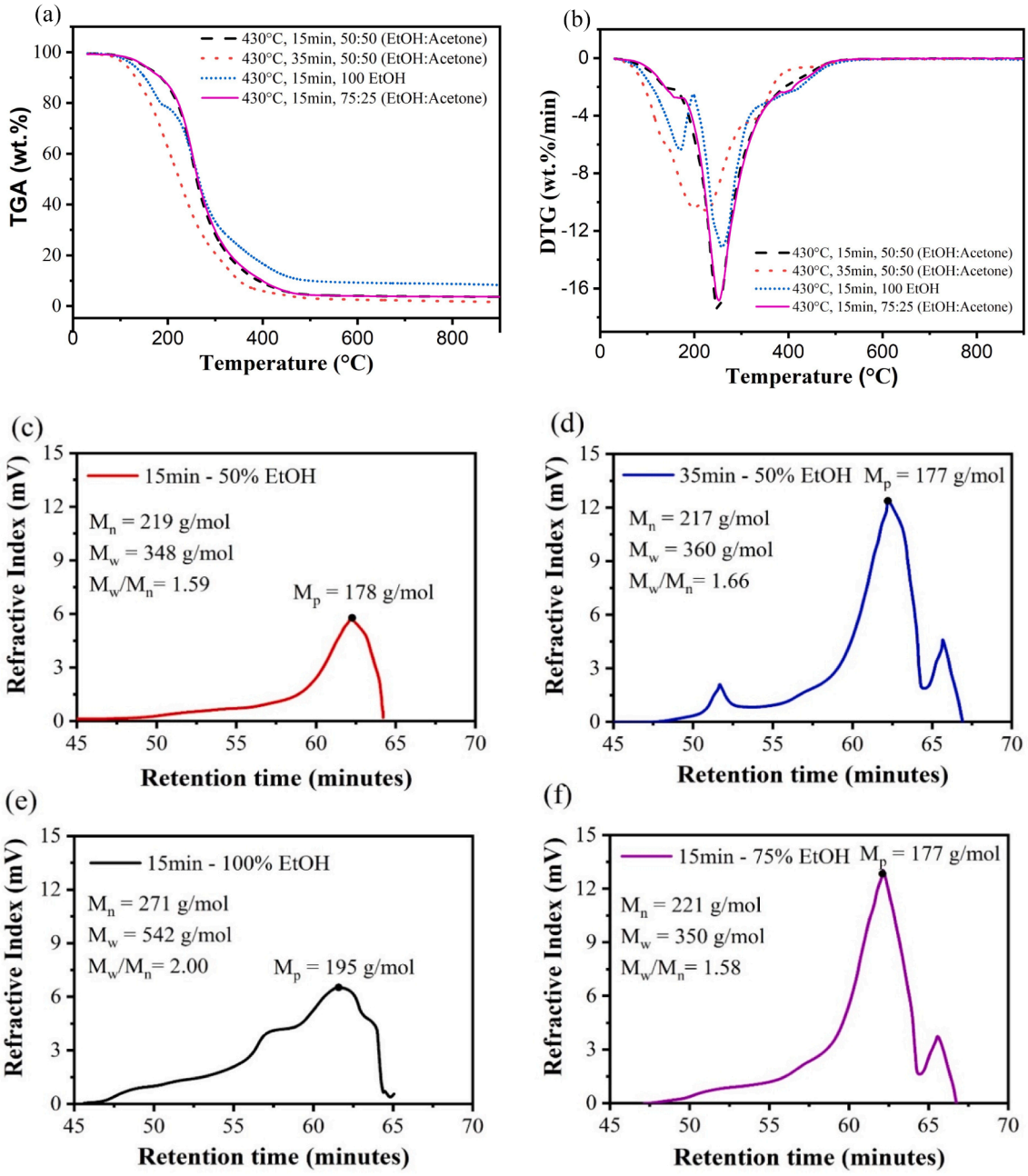


Fig. 3. (a) TGA and (b) DTG (c-f) GPC plots of biocrudes obtained with the highest HHV.

and residence time of 430 °C and 15 min, respectively were observed. Therefore, to produce biocrude with high fractions of jet and diesels range fuels, the application of reaction condition with 430 °C, 50:50 ratio of EtOH: acetone and 15mins residence time proves superior though, a further increase in acetone content to 75% shows a slight increment in the formation of gasoline, and heavy oils production with a slight decrease in the formation of inorganics and cokes as shown in Table 2. Additionally, it was noted that the use of 100% ethanol resulted in an increased production of heavy oils in the biocrude, 12.58 wt%, accompanied by the lowest onset temperature of 129.50 °C.

The molecular weight distribution of the biocrudes obtained with the lowest oxygen content and highest HHV were presented in Fig. 3(c-f) where the effects of residence time and percentage ethanol loading could be understood. Based on the results presented, it can be observed that the average and peak molecular weights of the biocrudes displayed variations depending on the reaction conditions, including temperature, solvent ratio, and residence time. At 50% ethanol ratio, 430 °C and different residence time of the solvothermal reaction from 15 to 35 min (Fig. 3c and 3d), the molecular weight increases from 348 g/mol to 360 g/mol respectively. The increase in weight could be associated with an observable increase in esters and ketones contents in the biocrude which were identified as large molecular weight compounds as contained in the GC–MS results in Fig. 1d though the higher content of phenol; a lower molecular weight present in Fig. 3d could meant to have limited effect in the overall properties. The increase in average molecular weight in biocrude has been reported previously to depend on higher content of esters and acids (Liu et al., 2022). The use of 100% ethanol as solvent in the solvothermal process resulted in esterification reaction as the most pronounced phenomenon leading to 25.60% of ester and reverse-esterification with 16.15% of acid. This higher selectivity of esters formation resulted in the highest average molecular weight compounds with 542 g/mol in the biocrude as shown in Fig. 3e. Corroboratively, this GPC result further correlates with the TGA/DTG of the biocrude obtained which shows the highest heavy biocrude composition of 12.58 wt% as shown in Table 2. The introduction of acetone at 25% concentration into the ethanol drastically reduced the average molecular weight from 542 to 350 g/mol due to an improved selectivity to phenolics compounds (light molecular weight compounds) and absence of acids formation.

3.5.2. *Functional groups in the produced biocrudes*

The FTIR spectra of the obtained biocrudes are shown (see Supplementary materials) where the effects of operating parameters were depicted. The FT-IR spectra of the biocrude as depicted shows a distinctive absorption peak that indicated the presence of different functional groups which corresponding to specific compounds. From the FTIR spectra, the peak at 3405 cm^{-1} on the effect of temperature is associated with O-H stretching vibration due to the presence of phenols, alcohols and accompanied moisture from hydrolyzed cellulose. Broader peaks were observed on the biocrudes produced at 230 °C and 280 °C. The broader peaks formation could be associated to the presence of large amount of alcohols and water content as against those observed at 330,380 and 430 °C. The peaks observed at 2954, 2923 and 2871 cm^{-1} are associated to the formation of = CH groups due to asymmetric stretching vibration indicating the presence of alkyl groups acetone (Ali et al., 2014; Matin and Aydin, 2022). The peaks at 2954 cm^{-1} become prominent from 330 to 430 °C with similar patterns of the spectral were observed throughout the biocrudes obtained on the effect of residence time and the solvent ratio except the presence of peak at 1574 cm^{-1} at 100%. From the FTIR spectral (see Supplementary materials), the details of peaks assignment for all the biocrudes are presented with the observable variation due to changes in the reaction conditions.

3.6. *Reaction mechanisms and pathways*

The proposed reaction pathways for the biocrude production during the STL process of orange peels have been presented (see Supplementary materials). Through the products' compositions at varied reaction conditions as shown in Fig. 1 b, d and f, several reactions were observed to be taking place. Such reactions include esterification, hydrolysis, reversed-esterification, etherification, ketonization, deoxygenation and hydrogenation reactions. Within an ethanol medium, it is conceivable that cellulose depolymerization in the feedstock could transform into alcohols and esters, while there have been reports of the production of ketones and aromatic ketones (Galebach et al., 2018; Tao et al., 2013). Furthermore, the depolymerization of cellulose in the presence of acetone produces high content of ketones at supercritical conditions (Wang et al., 2019). The ketones produced could act as an intermediate product which is capable of further conversion through metal acid catalyst via dehydration and hydrogenation into hydrocarbons pools (Serrano-Ruiz et al., 2010). The existence of furan within the biocrude might result from cellulose dehydration, while the potential for alkane formation through hydrogenolysis and hydrodeoxygenation reactions is plausible (Xin et al., 2020). Regarding the conversion of lignin content in biomass feedstock, it is possible to polymerize lignin into aliphatic/aromatic esters, phenolics, and ketones. (Limarta et al., 2018). Also, the formation of aromatic compounds (lignin monomers) has been reported to be produced through depolymerization, alkylation and hydrogenolysis reactions while repolymerization reactions could lead to the formation of char (Huang et al., 2014). The formation of a high content of hetero-atom aromatics, esters, and phenols has been reported during the initial reaction period (0–30 min) (Riaz et al., 2016). With detailed considerations of the possible reactions in the system, due to the complex nature of the orange peels' compositions, then, the mechanisms were proposed (see Supplementary materials).

4. Conclusion

Variation of reaction temperature and residence time in Sub/supercritical environment exhibited an immense contribution into STL of orange peels. The synergetic effects of 50%-ethanol resulted in an excellent liquefaction for biocrude with high HHV, deoxygenation, hydrogenation with lower oxygen content. An increase in temperatures during the STL process lowers the hydrolysis reaction. The highest composition of light volatiles and overall volatility-biocrude was favored at an increased residence time of 35 min. The findings confirm that supercritical conditions at 50:50 (ethanol: acetone) enhance the overall performance of STL of orange peels into high quality biocrude in absence of initial nitrogen supply.

CRediT authorship contribution statement

Ishaq Kariim: Conceptualization, Methodology, Software, Data curation, Formal analysis, Funding acquisition, Investigation, Writing – original draft, Writing – review & editing. **Ji-Yeon Park:** Formal analysis, Writing – review & editing, Supervision. **Wajahat Waheed Kazmi:** Formal analysis, Writing – review & editing. **Hulda Swai:** Supervision. **In-Gu Lee:** Supervision, Funding acquisition, Writing – review & editing. **Thomas Kivevele:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

Acknowledgements

The supports received from the Partnership for Skills in Applied Sciences, Engineering and Technology-Regional Scholarship and Innovation Fund (PASET-RSIF) with project number P165581, Junior Faculty Development programme under the UM6P/EPFL Excellence in Africa Initiative with grant number 9150 and the Research and Development Program of the Korea Institute of Energy Research (KIER-C3-2474) were highly appreciated.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2023.129928.

References

Aboagye, D., Banadda, N., Kiggundu, N., Kabenge, I., 2017. Assessment of orange peel waste availability in ghana and potential bio-oil yield using fast pyrolysis. Renew. Sustain. Energy Rev. 70, 814–821. https://doi.org/10.1016/j.rser.2016.11.262.

Ali, N., Saleem, M., Shahzad, K., Saleem, R.M., Chughtai, A., 2014. Effect of temperature on the bio oil yield from pyrolysis of maize stalks in fluidized bed reactor. J. Pakistan Inst. Chem. Eng. 42, 79–86.

Bakari, R., Kivevele, T., Huang, X., Jande, Y.A.C., 2021. Sub- and supercritical water gasification of rice husk: Parametric optimization using the I - Optimality criterion. https://doi.org/10.1021/acsomega.0c06318.

Biswas, B., Bisht, Y., Kumar, J., Yenumala, S.R., Bhaskar, T., 2020. Effects of temperature and solvent on hydrothermal liquefaction of the corncob for production of phenolic monomers.

Brand, S., Kim, J., 2015. Liquefaction of major lignocellulosic biomass constituents in supercritical ethanol. Energy 80, 64–74. https://doi.org/10.1016/j.energy.2014.11.043.

Caprariis, B.D., Filippis, P.D., Petrullo, A., Scarsella, M., 2017. Hydrothermal liquefaction of biomass : Influence of temperature and biomass composition on the bio-oil production. Fuel 208, 618–625. https://doi.org/10.1016/j.fuel.2017.07.054.

Carpio, R.B., Zhang, Y., Kuo, C.T., Chen, W.T., Schideman, L.C., de Leon, R., 2021. Effects of reaction temperature and reaction time on the hydrothermal liquefaction of demineralized wastewater algal biomass. Bioresour. Technol. Reports 14, 100679. https://doi.org/10.1016/j.biteb.2021.100679.

Castello, D., Haider, M.S., Rosendahl, L.A., 2019. Catalytic upgrading of hydrothermal liquefaction biocrudes: Different challenges for different feedstocks. Renew. Energy 141, 420–430. https://doi.org/10.1016/j.renene.2019.04.003.

Chen, X., Che, Q., Li, S., Liu, Z., Yang, H., Chen, Y., Wang, X., Shao, J., Chen, H., 2019. Recent developments in lignocellulosic biomass catalytic fast pyrolysis: Strategies for the optimization of bio-oil quality and yield. Fuel Process. Technol. 196, 106180 https://doi.org/10.1016/j.fuproc.2019.106180.

Demirkaya, E., Dal, O., Yüksel, A., 2019. Liquefaction of waste hazelnut shell by using sub- and supercritical solvents as a reaction medium. J. Supercrit. Fluids 150, 11–20. https://doi.org/10.1016/j.supflu.2019.03.019.

Divyabharathi, R., Subramanian, P., 2021. Biocrude production from orange (Citrus reticulata) peel by hydrothermal liquefaction and process optimization. Biomass Convers. Biorefinery 12, 183–194. https://doi.org/10.1007/s13399-021-01383-3.

Fernandes, A.C., Biswas, B., Kumar, J., Bhaskar, T., Muraleedharan, U.D., 2021. Valorization of the red macroalga Gracilaria corticata by hydrothermal liquefaction: Product yield improvement by optimization of process parameters. Bioresour. Technol. Rep. 15, 100796 https://doi.org/10.1016/j.biteb.2021.100796.

Galebach, P.H., McClelland, D.J., Eagan, N.M., Wittrig, A.M., Buchanan, J.S., Dumesic, J. A., Huber, G.W., 2018. Production of alcohols from cellulose by supercritical methanol depolymerization and hydrodeoxygenation. ACS Sustain. Chem. Eng. 6, 4330–4344. https://doi.org/10.1021/acssuschemeng.7b04820.

He, Z., Zhang, F., Tu, R., Jia, Z., Cheng, S., Sun, Y., Wu, Y., Shen, X., Jiang, E., Xu, X., 2020. The influence of torrefaction on pyrolysed biomass: The relationship of bio-oil composition with the torrefaction severity. Bioresour. Technol. 314 https://doi.org/10.1016/j.biortech.2020.123780.

Hornung, A., Stenzel, F., 2019. Biochar - Just a black matter is not enough! Biochar II. Prod. Charact. Appl. https://doi.org/10.1007/s13399-021-01284-5.

Huang, X., Korányi, T.I., Boot, M.D., Hensen, E.J.M., 2014. Catalytic depolymerization of lignin in supercritical ethanol. ChemSusChem 7, 2276–2288. https://doi.org/10.1002/cssc.201402094.

Jun, C.H., Huh, C.W., Na, S.J., 1998. Direct synthesis of ketones from primary alcohols and 1-alkenes. Angew. Chem., Int. Ed. 37, 145–147. https://doi.org/10.1002/(SICI)1521-3773(19980202)37:1/2<145::AID-ANIE145>3.0.CO;2-0.

Kariim, I., Yusufu, O.W., Hulda, S., Thomas, K., 2023. Catalytic hydrothermal liquefaction of orange peels into biocrude: An optimization approach by Central Composite Design. J. Anal. Appl. Pyrolysis 173, 106032. https://doi.org/10.1016/j.jaap.2023.106032.

Kazmi, W.W., Park, J.Y., Amini, G., Lee, I.G., 2023. Upgrading of esterified bio-oil from waste coffee grounds over MgNiMo/activated charcoal in supercritical ethanol. Fuel Process. Technol. 250, 107915 https://doi.org/10.1016/j.fuproc.2023.107915.

Khampuang, K., Boreriboon, N., Prasassarakich, P., 2015. Alkali catalyzed liquefaction of corncob in supercritical ethanol-water. Biomass Bioenergy 83, 460–466. https://doi.org/10.1016/j.biombioe.2015.10.022.

Li, Y., Zhu, C., Jiang, J., Yang, Z., Feng, W., Li, L., Guo, Y., 2021. Catalytic hydrothermal liquefaction of Gracilaria corticata macroalgae: Effects of process parameter on bio-oil up-gradation. Bioresour. Technol. 319, 124163 https://doi.org/10.1016/j.biortech.2020.124163.

Limarta, S.O., Ha, J.M., Park, Y.K., Lee, H., Suh, D.J., Jae, J., 2018. Efficient depolymerization of lignin in supercritical ethanol by a combination of metal and base catalysts. J. Ind. Eng. Chem. 57, 45–54. https://doi.org/10.1016/j.jiec.2017.08.006.

Liu, C., Kong, L., Wang, Y., Dai, L., 2018. Catalytic hydrothermal liquefaction of spirulina to bio-oil in the presence of formic acid over palladium-based catalysts. Algal Res. 33, 156–164. https://doi.org/10.1016/j.algal.2018.05.012.

Liu, T., Yang, L., Jiao, H., Jin, Z., Chen, P., Leng, S., Zhou, W., 2022. Fractional distillation of biocrude from hydrothermal liquefaction of microalgae: Upgrading of fuel properties. Algal Res. 68, 102888 https://doi.org/10.1016/j.algal.2022.102888.

Malins, K., 2017. Production of bio-oil via hydrothermal liquefaction of birch sawdust. Energy Convers. Manag. 144, 243–251. https://doi.org/10.1016/j.enconman.2017.04.053.

Martins, F., Felgueiras, C., Smitkova, M., Caetano, N., 2019. Analysis of fossil fuel energy consumption and environmental impacts in European countries. Energies 12, 1–11. https://doi.org/10.3390/en12060964.

Matin, N.H., Aydin, E., 2022. Reviewing the effect of pyrolysis temperature on the Fourier-transform infrared spectra of biochars 2022, 160–173. doi.org/10.2478/ahr-2022-0020.

Meng, Q., Hou, M., Liu, H., Song, J., Han, B., 2017. Synthesis of ketones from biomass-derived feedstock. Nat. Commun. 8 https://doi.org/10.1038/ncomms14190.

Nanda, S., Berruti, F., 2021. Municipal solid waste management and landfilling technologies: a review. Environ. Chem. Lett. 19, 1433–1456. https://doi.org/10.1007/s10311-020-01100-y.

Okunola, A.A., Kehinde, I.O., Oluwaseun, A., Olufiropo, E.A., 2019. Public and environmental health effects of plastic wastes disposal. A Review. J. Toxicol. Risk Assess. 5 https://doi.org/10.23937/2572-4061.1510021.

Ong, H.C., Chen, W.H., Farooq, A., Gan, Y.Y., Lee, K.T., Ashokkumar, V., 2019. Catalytic thermochemical conversion of biomass for biofuel production: A comprehensive review. Renew. Sustain. Energy Rev. 113, 109266 https://doi.org/10.1016/j.rser.2019.109266.

Park, J.Y., Jeon, W., Lee, J.H., Nam, B., Lee, I.G., 2019. Effects of supercritical fluids in catalytic upgrading of biomass pyrolysis oil. Chem. Eng. J. 377, 120312 https://doi.org/10.1016/j.cej.2018.11.010.

Rachel-Tang, D.Y., Islam, A., Taufiq-Yap, Y.H., 2017. Bio-oil production via catalytic solvolysis of biomass. RSC Adv. 7, 7820–7830. https://doi.org/10.1039/c6ra27824h.

Riaz, A., Kim, C.S., Kim, Y., Kim, J., 2016. High-yield and high-calorific bio-oil production from concentrated sulfuric acid hydrolysis lignin in supercritical ethanol. Fuel 172, 238–247. https://doi.org/10.1016/j.fuel.2015.12.051.

Rorrer, J.E., Bell, A.T., Toste, F.D., 2019. Synthesis of biomass-derived ethers for use as fuels and lubricants. ChemSusChem 12, 2835–2858. https://doi.org/10.1002/cssc.201900535.

Serrano-Ruiz, J.C., Braden, D.J., West, R.M., Dumesic, J.A., 2010. Conversion of cellulose to hydrocarbon fuels by progressive removal of oxygen. Appl. Catal. B Environ. 100, 184–189. https://doi.org/10.1016/j.apcatb.2010.07.029.

Sun, L., Wang, Z., Chen, L., Yang, S., Xie, X., Gao, M., Zhao, B., Si, H., Li, J., Hua, D., 2020. Catalytic fast pyrolysis of biomass into aromatic hydrocarbons over Mo-modified ZSM-5 catalysts. Catalysts 1–10. https://doi.org/10.3390/catal10091051.

Tao, H.X., Xie, X.A., Tang, C.Z., Tian, W.G., 2013. Mechanism of ketones formation from cellulose liquefaction in sub- and supercritical ethanol. Ranliao Huaxue Xuebao/J. Fuel Chem. Technol. 41, 60–66. https://doi.org/10.1016/s1872-5813(13)60010-9.

Tekin, K., Karagöz, S., 2013. Non-catalytic and catalytic hydrothermal liquefaction of biomass. Res. Chem. Intermed. 39, 485–498. https://doi.org/10.1007/s11164-012-0572-3.

Wang, X., Xie, X., Sun, J., Liao, W., 2019. Effects of liquefaction parameters of cellulose in supercritical solvents of methanol, ethanol and acetone on products yield and compositions. Bioresour. Technol. 275, 123–129. https://doi.org/10.1016/j.biortech.2018.12.047.

Xin, H., Hu, X., Cai, C., Wang, H., Zhu, C., Li, S., Xiu, Z., Zhang, X., Liu, Q., Ma, L., 2020. Catalytic production of oxygenated and hydrocarbon chemicals from cellulose hydrogenolysis in aqueous phase. Front. Chem. 8, 1–20. https://doi.org/10.3389/fchem.2020.00333.

Zhang, Y., Chen, F., Chen, D., Cen, K., Zhang, J., Cao, X., 2020. Upgrading of biomass pellets by torrefaction and its influence on the hydrophobicity, mechanical property, and fuel quality. Biomass Convers. Biorefinery 12, 2061–2070. https://doi.org/10.1007/s13399-020-00666-5.