CHEMICAL ENGINEERING TRANSACTIONS

VOL. 109, 2024

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Leonardo Tognotti, Rubens Maciel Filho, Viatcheslav Kafarov

ISBN 979-12-81206-09-0; **ISSN** 2283-9216

DOI: 10.3303/CET24109067

Biocrude Production by Hydrothermal Liquefaction from *Rugulopteryx Okamurae* Brown Macroalgae

M. Belén García-Jarana[a,*], Jezabel Sánchez-Oneto[a], M. Dolores Macías-Sánchez[a], Juan R. Portela[a], Ramón Terroba[a], José M. Abelleira-Pereira[a], Juan J. Mascarell[a], Carmen Garrido-Pérez[b]

[a]Department of Chemical Engineering and Food Technology, University of Cadiz, International Excellence Agrifood Campus (CeiA3), Campus Universitario de Puerto Real, 11510 Puerto Real (Cádiz), Spain.
[b]Department of Environmental Technologies, University Marine Research Institute (INMAR), University of Cadiz, Campus Universitario de Puerto Real, 11510 Puerto Real (Cádiz), Spain.
belen.garcia@uca.es

Nowadays, some populations of invasive marine macroalgae species cause environmental problems due to their excessive growth beyond their original niche. There are currently several investigations that are aimed at giving a possible valorization to the algal biomass waste that accumulates in coastal deposits. One of the technologies that are being applied to the treatment of algal biomass is Hydrothermal Liquefaction (HTL). This technology allows the transformation of organic matter into biocrude by means of a reaction in aqueous medium and at high temperature and pressure conditions. *Rugulopteryx okamurae*, an invasive macroalgae found on the coasts of many countries, has been used for the production of bio-oil by hydrothermal liquefaction. Although there are many variables that influence the process, the objective of this study is to carry out preliminary hydrothermal liquefaction tests of the mentioned algal biomass, without being subjected to previous pre-treatment. HTL experiments were carried out in water sub-critical conditions at a temperature range of 270–330 °C for reaction times between 5 and 60 min and with an initial biomass load between 5-15 % w/w. Maximum bio-crude yield (26.3 wt%) was obtained at 300 °C, 30 min, and 10 % w/w, while the highest HHV (8456.9 kcal/kg) was obtained at 330 ºC, 30 min, and 10 % w/w. The solid residue yields decreased continuously from 30.6 wt% to 12.1 wt% as the temperature increased from 270 to 330 °C.

1. Introduction

In the last years, large uncontrolled proliferations of algae are found on the coasts of many countries, causing a significant imbalance that affects both the native ecosystems and the tourism sector, which is of great economic importance in the affected areas (Thabard et al., 2011). *Rugulopteryx okamurae* is an invasive species of macroalgae known as Asian algae that accumulates on the coasts of Mediterranean Sea. Algae from the northwest Pacific have caused an environmental problem since the 1990s, as they threaten the native marine ecosystem. In autumn of 2015, *Rugulopteryx okamurae* was first found in the Strait of Gibraltar (Tarifa and Ceuta, Spain), and by 2016 it had colonised most of the rocky bottoms of the Strait's shoreline. According to the Spanish Ministry, the expansion of the brown seaweed *Rugulopteryx okamurae* in 2019 affected the coasts of the Bay of Cadiz, Malaga, Granada and Almeria. Therefore, it is already on the EU list of alien species of concern. Thus, given the exponential growth of Asian algae, the aim is to provide a possible valorization of this type of biomass that devastates the coasts of the Mediterranean, transforming it into a raw material of special interest.
There are currently several investigations that are aimed at giving a possible valorization to the algal biomass waste that accumulates in coastal deposits. One of the technologies that are being applied to the treatment of algal biomass is Hydrothermal Liquefaction (HTL). However, this process has not been studied so far for this specific type of macroalgae.

Paper Received: 15 January 2024; Revised: 15 February 2024; Accepted: 5 April 2024
Please cite this article as: García-Jarana M.B., Sánchez-Oneto J., Macías-Sánchez M.D., Portela J.R., Terroba R., Abelleira-Pereira J.M., Mascarell J.J., Garrido-Pérez C., 2024, Biocrude Production by Hydrothermal Liquefaction from Rugulopterix Okamurae Brown Macroalgae, Chemical Engineering Transactions, 109, 397-402 DOI:10.3303/CET24109067

Hydrothermal liquefaction (HTL) is an efficient technology that enables the transformation of different types of biomass into a dense liquid fuel, generally named bio-crude oil, with several energy applications (Kumar et al., 2018). HTL is carried out at moderate temperatures and pressures (250–350°C and 100–200 bar, respectively), using water as the main reaction medium (Tekin *et al.* 2014), and it can be performed with or without a catalyst (Liu et al., 2021). Under these conditions and short reaction times (15–60min), most organic molecules are depolymerized (Basar et al., 2021) and the generated fragments subsequently follow re-polymerization and condensation reactions which form water-insoluble biofuel. In fact, HTL can produce a crude-oil with a high calorific value that has the potential to be used as a sustainable fuel (Gollakota et al., 2018).
Some species of algae have been studied for bio-crude production from HTL process. Li et al. (2012) obtained a bio-crude yield of 32.1% at 340°C, 15 minutes and with a loading of 10% using *Sargassum patens* as feedstock. In another study, He et al. (2020) obtained their best bio-crude yield of 9.49% also at 340ºC, using algae of the genus *Sargassum sp*. At intermediate conditions, Niaz et al. (2020) studied HTL of *Saccharina japonica* obtaining a yield of 20.3% at 300ºC, 60 minutes and 9% of biomass loading, and Crespo et al. (2021) obtained the highest yield (10.25%) at temperatures of 300°C, reaction times of 60 min and *Sargassum polyceratium* biomass loading of 10%.
In the present study is performed preliminary HTL tests of *Rugulopteryx okamurae*. In the experimental design, tests were carried out at different temperatures, residence times and initial loading of algal biomass (biomass-to water ratio) in order to find the higher yield and heating value of biofuel produced from this raw material. A high pressure reactor of 300 mL volume was used for the HTL experiments. Around 140 mL of water were used as reaction medium and an inert nitrogen atmosphere was applied. Biofuel extractions were performed over the solids obtained in the reaction using dichloromethane as solvent.

2. Material and methods

2.1 *Rugulopteryx okamurae* algae

Samples of the brown macroalga *Rugulopteryx okamurae* were collected at the coastal waters of Caños de Meca (Barbate, Tarifa, Spain) during low tides in the spring.

2.2 Equipment and experimental procedure

Hydrothermal liquefaction tests were carried out in a 300 mL volume batch reactor made from 316 stainless steel by Autoclave Engineers. The vessel was fitted with a variable-speed stirrer (MagneDrive) and an electric furnace. A constant temperature was maintained at ± 2 ºC from the set point by means of an electronic controller (PID). The experimental system incorporates a rupture disk with a burst pressure of 20 Mpa as a safety device in case of pressure build-up in the reactor during an experiment.
The experiments carried out to determine the effect of operating conditions studied (temperature, reaction time and initial biomass loading) on biocrude yield (see Ec (1)) and its HHV from *Rugulopteryx okamurae* are listed in Table 1. Specifically, the effect of temperature was analysed within the range of 270 to 330ºC at a fixed time of 30 min and 9.1% biomass loading. In the other hand, the effect of reaction time was examined within the range of 5 to 60 min at a fixed temperature of 300 ºC and 9.1% loading. Finally, the effect of loading percentage was studied at 5%, 10%, and 15% at 3000ºC for 30 min. As this is a first study, to minimize the total cost of the treatment, this study has not considered applying any specific pretreatment to this algal biomass, only a simple rinse.
The weight of algae was introduced into the high pressure reactor for the biomass loading needed which was adjusted using a total volume of 140 mL with water as the reaction medium. Once the reactor is closed, the air inside is displaced by purging with N_2 for 3 minutes from a high-pressure N_2 bottle. The system was pressurized with nitrogen (to reach desired initial pressure) and it was then heated to the desired temperature for each experiment, with low stirring of 60 r.p.m. When the desired temperature was reached, this time was taken as the zero time for the reaction and these operating conditions were maintained for the reaction time studied. Once the reaction time has elapsed, the reactor is cooled in order to quench the reaction. When the mixture reached room temperature, gas phase sample is taken and analysed. The vessel was then opened and the contents of the reactor were collected.
To obtained the biocrude, the solid and liquid phases were first filtered to separate them, using vacuum filtration. Some of the biocrude produced is present in both phases. The solid phase is then subjected to solid-liquid extraction using an organic solvent (dichloromethane, DCM) to remove the biocrude. The remaining solid (biochar) is then dried in an oven to remove any remaining solution and to determine its yield (see Ec (2)) and HHV. The aqueous phase containing the biocrude is extracted also using DCM in a separating funnel for liquid-liquid extraction. After approximately 24 hours, phase separation is performed, and the exhausted aqueous phase is subjected to a second liquid-liquid extraction with DCM. The resulting extracts, containing the extracted

biocrude and DCM, are then evaporated using a rotary evaporator to recover the biocrude and remove the solvent. The biocrude yield is determined through gravimetry.

$$Yield_{biocrude}(\%) = \frac{weight\ of\ biocrude\ obtained\ (g)}{dry\ weight\ of\ algae\ (g)} \cdot 100 \quad (1)$$

$$Yield_{biochar}(\%) = \frac{dry\ weight\ of\ solid\ obtained\ (g)}{dry\ weight\ of\ algae\ (g)} \cdot 100 \quad (2)$$

2.3 Analytical methods

The measurement of Higher Heating Value (HHV) was performed using an isoperibolic Parr 6400 Calorimeter oxygen pump. The energy released during the combustion of solid phase samples and initial biomass is absorbed inside the calorimeter, recording the temperature variation and its high heating value was quantified. Gas samples were analysed using an HP 6890 Series gas chromatograph with a Thermal Conductivity Detector (TCD). Two in-series columns were used to separate CO from CO_2. A temperature ramp from 55 to 160ºC was used. The system was calibrated with a standard gas mixture containing H_2, CO_2, O_2, N_2, CO and CH_4.

3. Results and discussion

The operating conditions used in HTL process have an important influence on the biocrude yields and quality in terms of HHV, apart from the type of biomass used. According to the optimal conditions found in Crespo et al. (2023), in which *Sargassum polyceratium* was used, initial conditions were selected as temperature of 300 ºC, 60 minutes and an initial load of 10%. From those initial conditions, several experiments were carried out to improve the yield obtained. Table 1 shows the operation conditions tested and the yield and its HHV obtained.

Table 1: Operating conditions tested with Rugulopteryx okamurae, yields of biocrude (solid and aqueous phases), HHV of biocrude and biochar

HTL test	Temperature (ºC)	Reaction time (min)	Biomass loading (%)	$Yield_{biocrude}$ (%)			$Yield_{biochar}$ (%)	HHV (Kcal/kg)	
				Solid phase	Aqueous phase	Both phases		Biocrude	Solid phase
1	300	30	10	18.3	8.0	26.3	22.6	7942.2	4937.6
2	270	30	10	5.0	4.7	9.7	30.6	7310.2	5145.1
3	330	30	10	16.3	5.6	21.9	12.2	8456.9	3638.9
4	300	5	10	12.8	2.2	15.0	28.1	8232.2	5297.1
5	300	60	10	12.4	2.6	15.0	14.4	8455.4	4577.7
6	300	30	5	11.7	9.0	20.8	21.4	8227.8	5943.5
7	300	30	15	17.7	4.1	21.8	18.9	8245.2	5119.5

3.1 Effect of temperature

Temperature is one of the main operating parameters that influences the HTL process, which directly affects the yield and quality of the biocrude obtained. The effect of temperature on the formation of biocrude was investigated in the range 270-330 ºC. The experiments on *Rugulopteryx okamurae* were carried out maintaining a biomass load of 10% and a reaction time of 30 minutes.

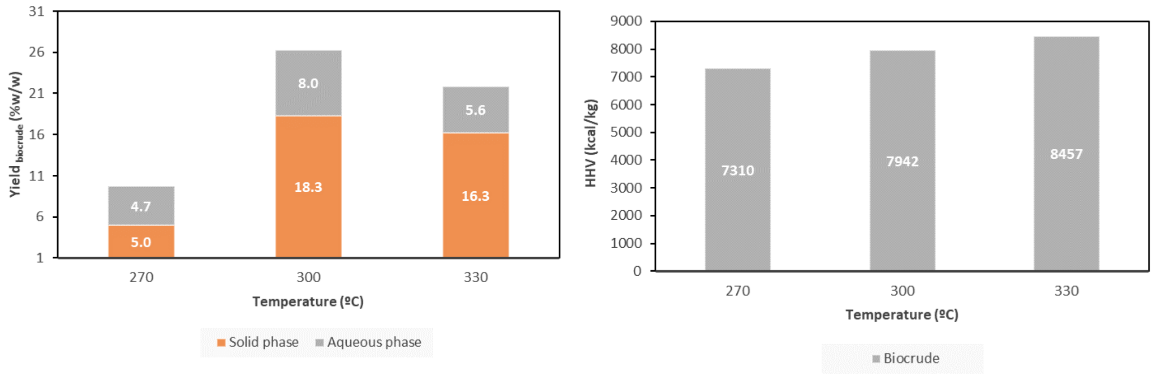

Figure 1: Effect of temperature on A) biocrude yield (solid and aqueous phases) and B) HHV of biocrude at 10% biomass load and 30 minutes.

As can be seen in Figure 1, an improvement in the biocrude was obtained when the temperature is increased until 300 °C. However, the yield decrease when the temperature continues to increase. These results are in accordance with the literature, the optimum temperature is around 300°C, since low temperatures lead to greater proportions of solid products and high temperatures produce greater amounts of gaseous products, while the biocrude oil yield is reduced (Brindhadevi et al., 2021). At 300°C, the biocrude obtained had a HHV of 7942 kcal/kg (see Figure 1B). However, this result is not the maximum, which is obtained at 330°C. In a previous study, Ramirez et al. (2015) established that the calorific value is directly proportional to the carbon and hydrogen fraction of the biocrude, while the oxygen and nitrogen content has a negative effect on the HHV. The results suggest that the carbon and hydrogen content in the biocrude is higher at the maximum reaction temperature studied.

3.2 Effect of reaction time

Usually, short residence times are required to effectively break down the compounds present in biomass because hydrolysis and decomposition reactions are quite fast in HTL process. However, longer reaction times can lead to reduce the yield of biocrude with higher amounts of gas and solids as new decomposition reactions occur (Yin and Tan, 2012). The effect of reaction time on the formation of biocrude in the HTL of *Rugulopteryx okamurae* was studied in the range 5-60 minutes. In all experiments a temperature of 300 ºC and 10% biomass load were kept constant.

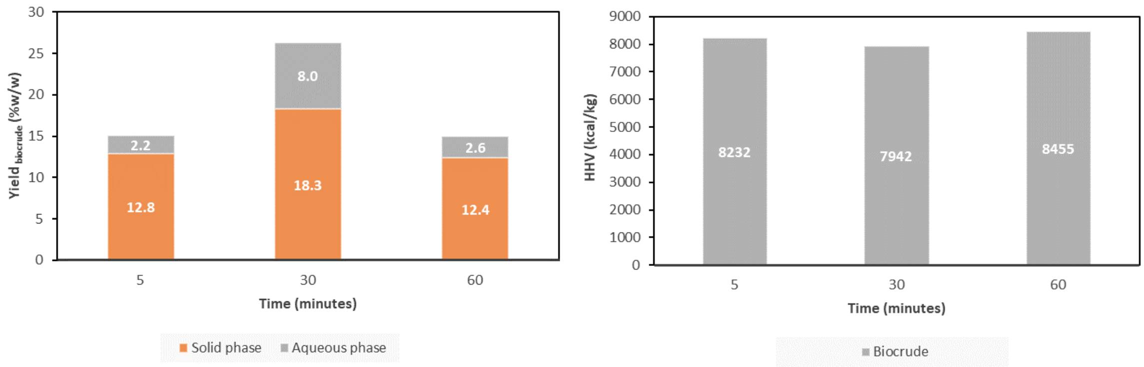

Figure 2: Effect of reaction time on A) biocrude yield (solid and aqueous phases) and B) HHV of biocrude at 300 ºC and 30 minutes.

In Figure 2, the results show that increasing the reaction time to 30 min an increment is obtained with a 18.3% in biocrude yield (see Figure 2A). However, continuing to increase time harms the bio-crude production yield. Moreover, higher reaction times do not lead to an increase in HHV (see Figure 2B). This trend is highly dependent on the type of biomass used. Furthermore, the optimum reaction time depends on the reaction temperature and leads to products of different yields and quality (Eboibi et al., 2014).

3.3 Effect of biomass loading

Generally, lower biomass loads improve the production of biocrude and gases, because greater quantities of solvent increases stability and solubility of the molecules generated by depolymerization reactions, reducing the amount of waste leftovers (Portela et al. 2021).

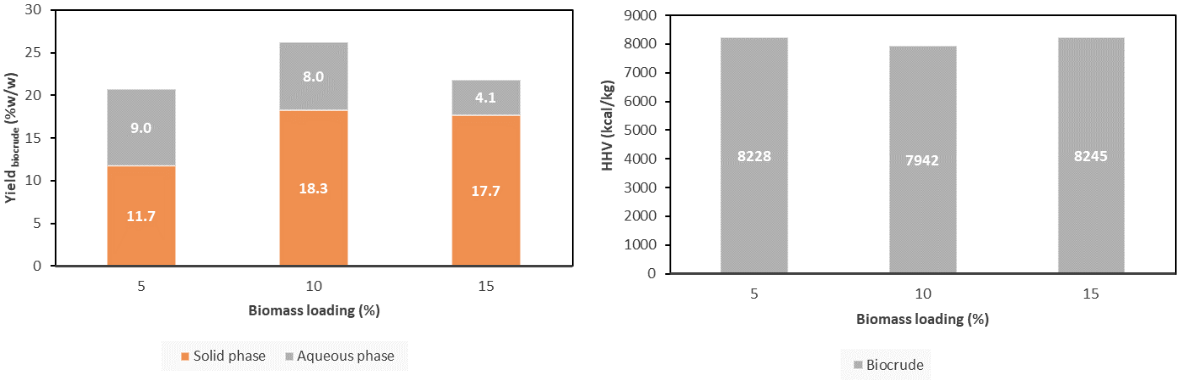

Figure 3: Effect of biomass loading on A) biocrude yield (solid and aqueous phases) and B) HHV of biocrude at 300 ºC and 10% load.

As can be seen in Figure 3, biomass loading had significant increase in biocrude yield when the biomass loading was increased from 5% to 10% respectively. However, the biocrude yield obtained decreased with a biomass loading of 15% w/w is present due to degradation of biomass by polymerization, condensation and cyclization reactions. Similar results are obtained by Yan et al. (2014) when undried macroalgae *Enteromorpha prolifera* was studied. Biocrude yield increased from 12.21 wt% to 15.21 wt% when biomass-to-water ratio was reduced from 1:1 to 1:3, but the yield obtained was decreased when biomass-to-water ratio decreased to 1:4. The result indicated further increase in water was not profitable to the yields.
Based on the results obtained, the optimized conditions have been 30 minutes of reaction time, a biomass load of 10% and 300ºC to obtain the maximum biocrude yield (26.3 wt%), although it is necessary to increase said temperature to 330ºC to achieve the highest HHV (8456.9 kcal/kg).
Regarding the gas phase, only CO, CO_2, N_2, and O_2 were identified, with no presence of H_2 or CH_4. The majority of the identified gases were N_2, ranging from 65.2% to 88.9%, and CO_2, ranging from 4.3% to 29.5%. The presence of N_2 is due to its use in establishing an initial pressure inside the reactor.

4. Conclusions

HTL is a feasible technology for obtaining biocrude from the brown macroalgae *Rugulopteryx okamurae*. Therefore, it would be a good option to remove the environmental problem that is causing the accumulation of invasive algae on the coasts while promoting the transition from the consumption of fossil fuels to another type of energy source, which is crucial for transitioning to a sustainable production system that better manages available resources. The maximum biocrude yield obtained was 26.3 wt% for the HTL experiment with an initial load of 10% w/v, 300°C and 30 minutes. While the highest HHV (8456.9 kcal/kg) was obtained at 330 ºC, 30 min, and 10 % w/w. Therefore, similar HHV values can be obtained with *Rugulopteryx okamurae* as with lignocellulosic biomass or other types of microalgae. However, to continue advancing in the scaling of the process, the next stage would be to study the continuous process on a laboratory scale.

Acknowledgments

We gratefully acknowledge the company CEPSA – CEPSA Foundation Chair, for the financial support for this work and the collaboration of the researchers of RECOVER Project (PY 18-TR-3406, Regional Government Junta de Andalucía, Spain).

References

Basar I.A., Liu H., Carrere H., Trably E., Eskicioglu C., 2021, A review on key design and operational parameters to optimize and develop hydrothermal liquefaction of biomass for biorefinery applications. Green Chemistry, 23, 1404 – 1446.

Brindhadevi K., Anto S., Rene E.R., Sekar M., Mathimani T., Chi N.T.L., Pugazhendhi A., 2021, Effect of reaction temperature on the conversion of algal biomass to bio-oil and biochar through pyrolysis and hydrothermal liquefaction, Fuel, 285, 119106.

Crespo, A., Abelleira-Pereira, J.M., Mascarell, J.J., Garcia-Jarana, B., Sanchez-Oneto, J., Portela, J.R., Martinez de la Ossa, E., Duran, E., 2023, Bio-crude Production by Hydrothermal Liquefaction of an Invasive Marine Algae (*Sargassum polyceratium*). Chemical Engineering Transactions, 98, 249 – 254.

Eboibi B.E., Lewis D.M., Ashman P.J., Chinnasamy S., 2014, Effect of operating conditions on yield and quality of biocrude during hydrothermal liquefaction of halophytic microalga *Tetraselmis* sp., Bioresource Technology, 170, 20 – 29.

Gollakota, A. R. K., Kishore, N. and Gu, S., 2018, A review on hydrothermal liquefaction of biomass. Renewable and Sustainable Energy Reviews, 81, 1378 – 1392.

He, S., Zhao, M., Wang, J., Cheng, Z., Yan, B. and Chen, G., 2020, Hydrothermal liquefaction of low-lipid algae Nannochloropsis sp. and Sargassum sp.: Effect of feedstock composition and temperature. Science of the Total Environment, 712, 135677.

Kumar, M., Olajire Oyedun, A., Kumar, A., 2018, A review on the current status of various hydrothermal technologies on biomass feedstock, Renew. Sust. Energ. Rev. 81, 1742 – 1770.

Li, D., Chen, L., Xu, D., Zhang, X., Ye, N., Chen, F. and Chen, S., 2012. Preparation and characteristics of bio-oil from the marine brown alga Sargassum patens C. Agardh. Bioresource Technology, 104, 737 – 742.

Liu B., Wang Z., Feng L., 2021, Effects of reaction parameter on catalytic hydrothermal liquefaction of microalgae into hydrocarbon rich bio-oil, Journal of the Energy Institute, 94, 22 – 28.

Portela, J.R., García-Jarana, B., Sánchez-Oneto, J., Benmakhlouf, N., Outili, N., Meniai, A., 2021, Application of hydrothermal processes to biomass and organic wastewaters to produce sustainable energy, Recent Adv. Renew. Energy Technol. 1, 149 – 175.

Ramirez J., Brown R., Rainey T., 2015, A review of hydrothermal liquefaction bio-crude properties and prospects for upgrading to transportation fuels, Energies, 8, 6765–6794.

Tekin, K., Karagöz, S. and Bektaş, S., 2014, A review of hydrothermal biomass processing, Renew. Sust. Energ. Rev. 40, 673 – 687.

Thabard, M., Gros, O., Hellio, C. and Maréchal, J.P., 2011. Sargassum polyceratium (Phaeophyceae, Fucaceae) surface molecule activity towards fouling organisms and embryonic development of benthic species. Botanica Marina, 54(2), 147 – 157.

Yang, W., Li, X., Liu, S., Feng, L., 2014, Direct hydrothermal liquefaction of undried macroalgae *Enteromorpha prolifera* using acid catalysts. Energy Conversion and Management 87, 938 – 945.

Yin, S. and Tan, Z., 2012, Hydrothermal liquefaction of cellulose to bio-oil under acidic, neutral and alkaline conditions. Applied Energy, 92, 234 – 239.