Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary information

Disintegration of wet microalgae biomass with deep-eutectic-solvent-assisted hydrothermal treatment for sustainable lipid extraction

Rui Huang[a], Yu He[a], Xianrui Yao[a], Yujie Yu[a], Wenlu Song[c], Weijuan Yang[b], Jun Cheng[b]*

[a] *Electrical Engineering College, Guizhou University, Guiyang, 550025, China*

[b] *State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China*

[c] *Department of Life Science and Engineering, Jining University, Jining 273155, China*

* Corresponding author: Prof. Dr. Jun Cheng, State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China. Tel.: +86 571 87952889; fax: +86 571 87951616. E-mail: juncheng@zju.edu.cn

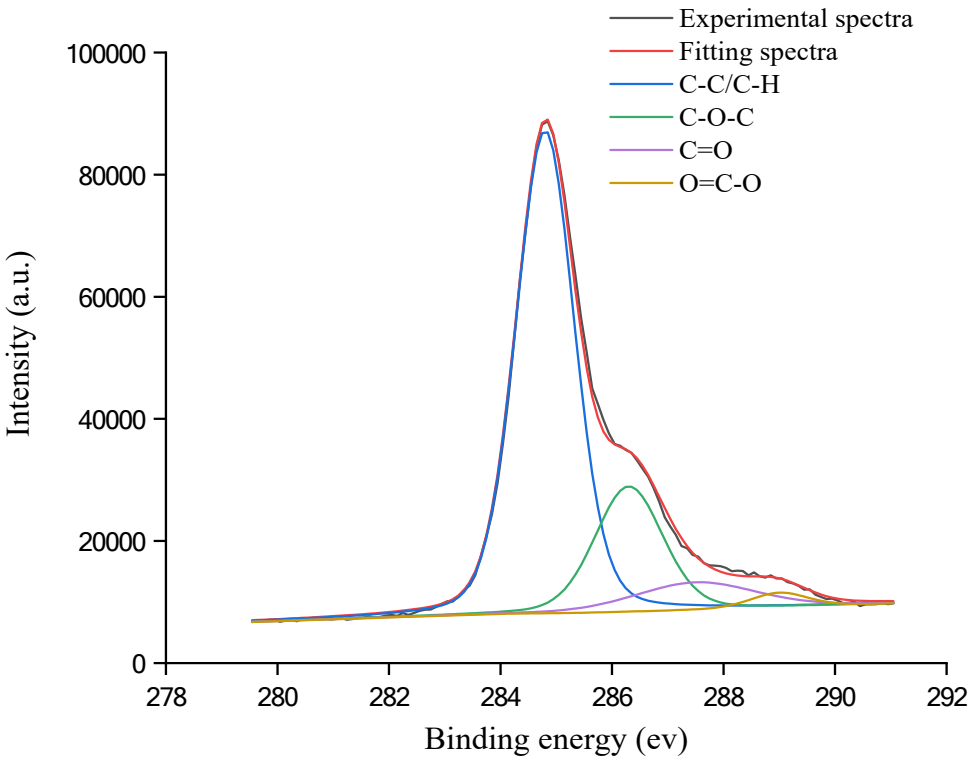


Figure S1 XPS C1s spectra of raw microalgae biomass

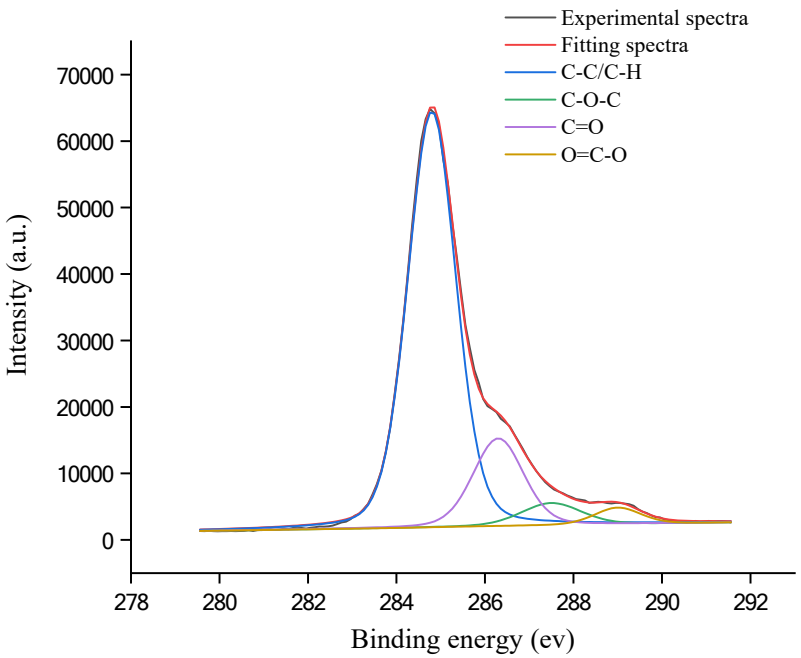


Figure S2 XPS C1s spectra of solid residue after traditional HTT

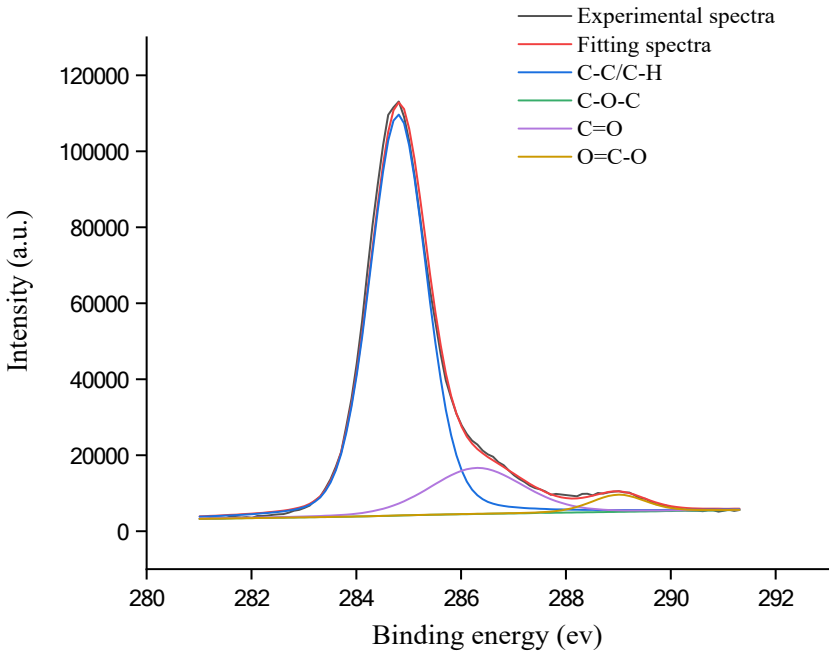


Figure S3 XPS C1s spectra of solid residue after acid-assisted HTT

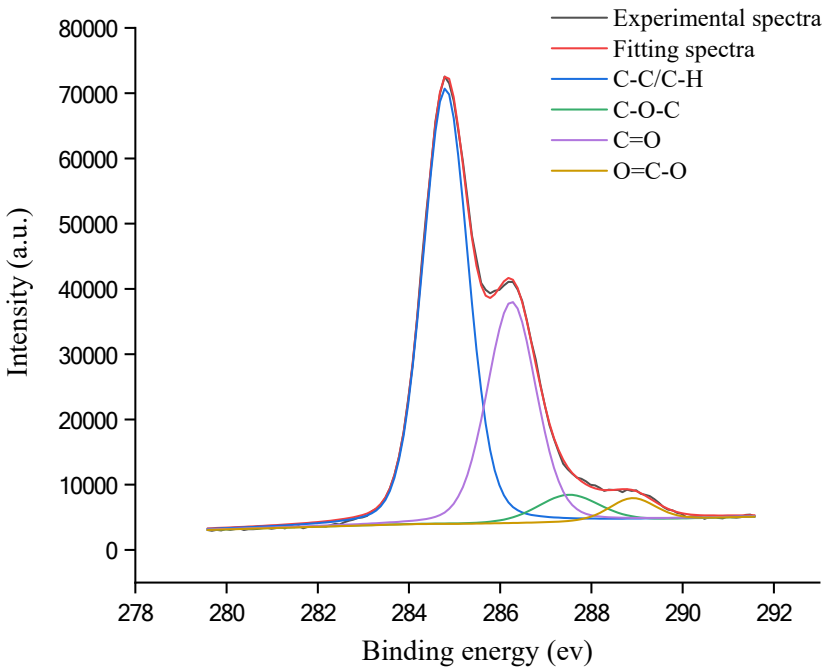


Figure S4 XPS C1s spectra of solid residue after DES-assisted HTT

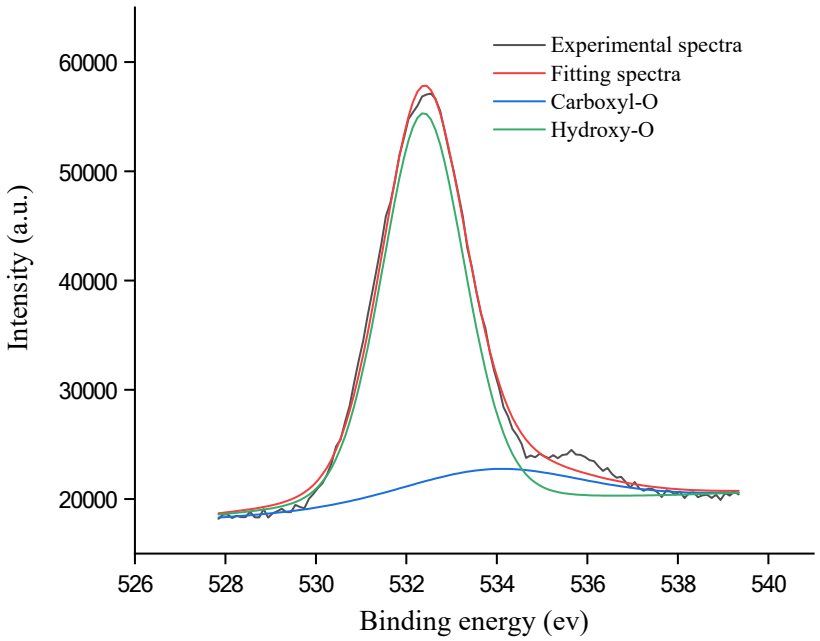


Figure S5 XPS O1s spectra of raw microalgae biomass

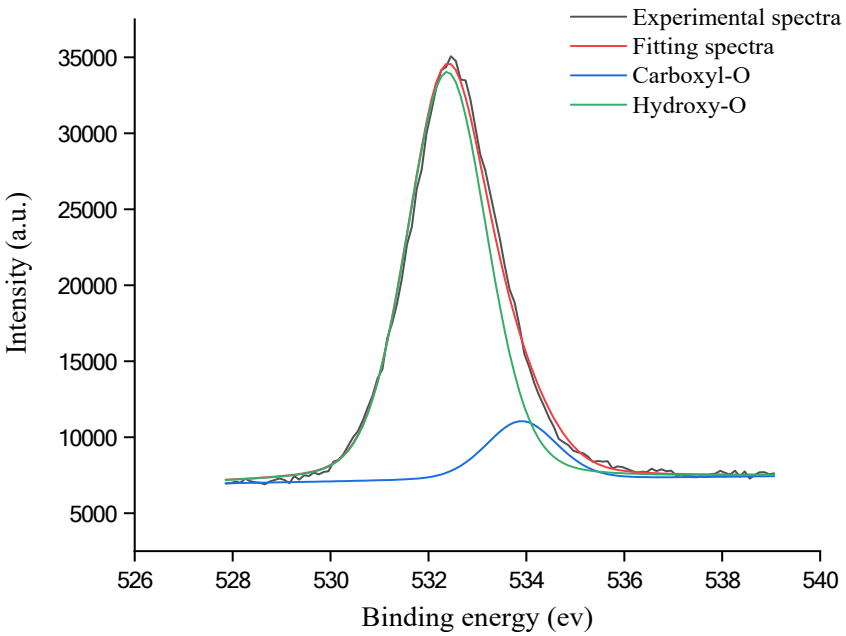


Figure S6 XPS O1s spectra of solid residue after traditional HTT

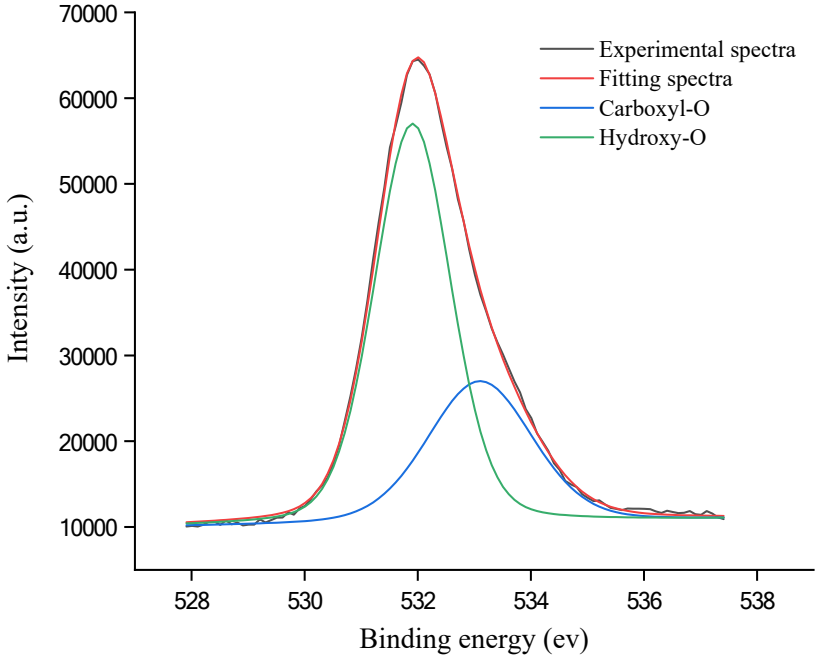


Figure S7 XPS O1s spectra of solid residue after acid-assisted HTT

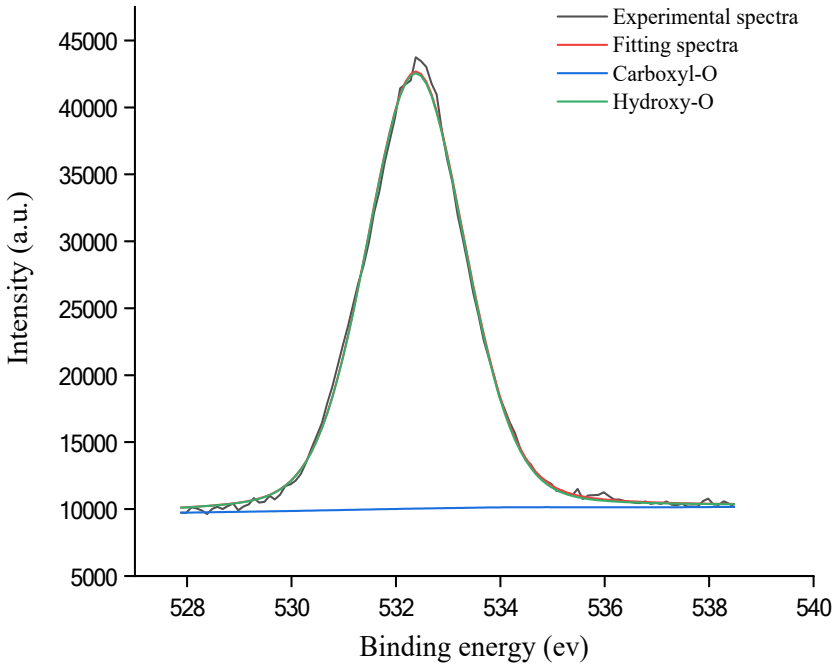
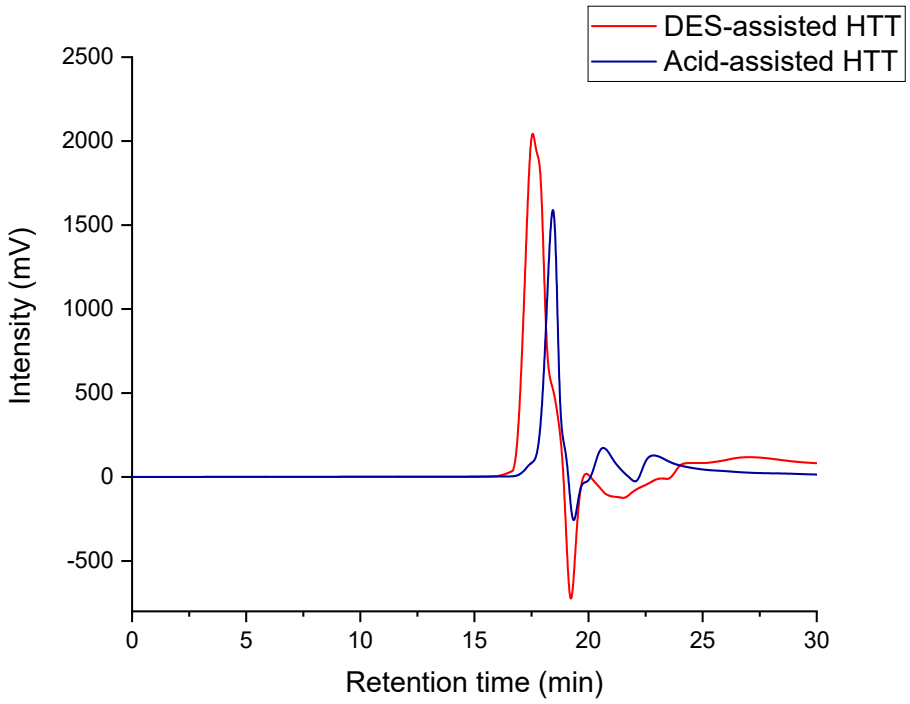
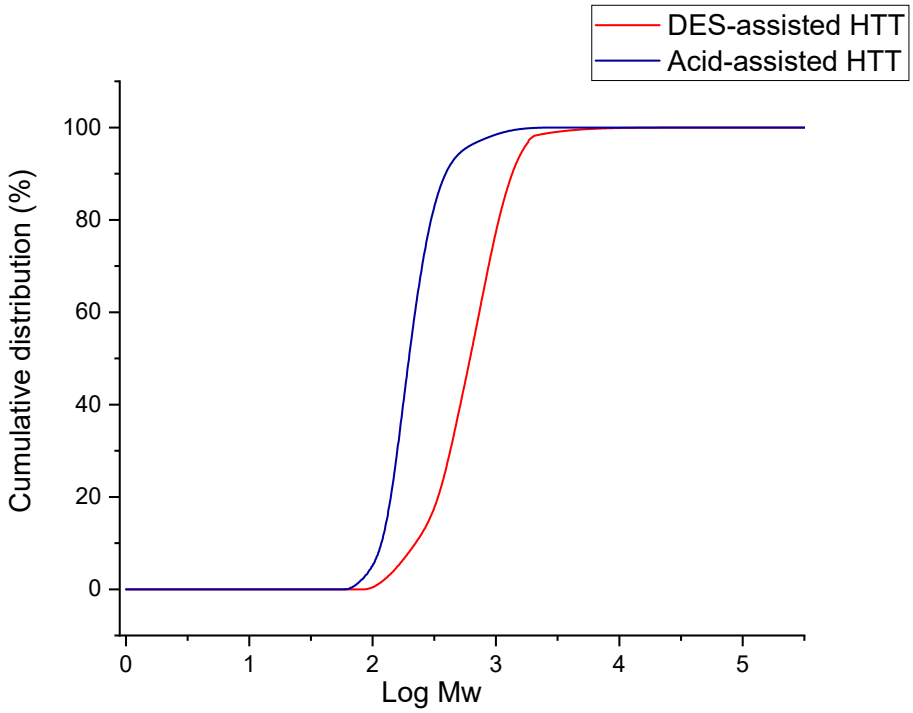


Figure S8 XPS O1s spectra of solid residue after DES-assisted HTT



(a) Gel permeation chromatography curve



(b) molar mass distribution

Figure S9 Gel permeation chromatography (GPC) of aqueous phases after acid-assisted HTT hydrothermal

Table S1 Compositions of lipids extracted from wet microalgal biomass after DES-assisted hydrothermal treatment

Compositions of lipids	Lipid extraction after disintegration of wet microalgae biomass by DES-assisted hydrothermal treatment (%)	Conventional lipid extraction from microalgae through Bligh & Dyer method (%)
C14:0	5.04	5.45
C16:0	22.62	22.37
C16:1	28.74	29.32
C18:0	0.82	0.51
C18:1	7.42	7.07
C18:2	3.05	3.2
C20:0	0.02	0.04
C20:5	26.29	26.03

Text S1 Energy Balance Calculations

The energy balances of two different processes, including dried biomass treated with DES at room temperature and wet microalgae disintegrated with DES-assisted hydrothermal treatment, were calculated. The net energy ratio (NER) was employed to quantify the energy balance as following:

$$\text{NER} = \frac{\text{Energy input}}{\text{Energy output}}$$

A lower NER indicates that greater energy outputs can be obtained from lower energy inputs.

1. Energy input.

Since the main differences for the two processes lies in the treatment temperature and the requirement for the water content of the microalgae biomass, the energy consumed by heating and drying microalgae biomass is mainly considered when calculating the energy input. Energy input for processing 1 kg of wet microalgae with a moisture content of 90% is calculated as follows:

(1) Energy input for dried microalgae biomass treated with DES at room temperature was calculated as following:

$$E_{Input-dry} = m_{water} \times (h_{vap} - h_{npt})$$

$$= 0.9\ kg \times (2674.94kJ/kg - 104.93kJ/kg)$$

$$= 2313.01kJ$$

Where $E_{Input-dry}$ is the energy input for dried microalgae biomass treated with DES; m_{water} is the mass of water contained in the wet microalgae biomass; h_{vap} is the specific enthalpy for water vapor at atmospheric pressure; $h_{npt}$is specific enthalpy for

water at temperature of 25°C and pressure of 1 atm.

(2) Energy input for wet microalgae disintegrated with DES-assisted hydrothermal treatment was calculated as following:

a) Without heat recovery:

$$E_{Input-HTT-N} = m_{biomass} \times (h_{HTT} - h_{npt})$$

$$= 1\ kg \times (675.57kJ/kg - 104.93kJ/kg)$$

$$= 570.64kJ$$

Where $E_{Input-HTT-N}$ is the energy input for wet microalgae disintegrated with DES-assisted hydrothermal treatment without heat recovery; $m_{biomass}$ is the mass of wet microalgae biomass; h_{HTT} is the specific enthalpy for water during hydrothermal treatment(temperature of 160°C and pressure of 0.62Mpa); $h_{npt}$is specific enthalpy for water at temperature of 25°C and pressure of 1 atm.

b) With heat recovery:

$$E_{Input-HTT-Y} = m_{biomass} \times (h_{HTT} - h_{npt}) \times (1 - \varphi)$$

$$= 1\ kg \times (675.57kJ/kg - 104.93kJ/kg) \times (1 - 74.2\%)$$

$$= 114.13kJ$$

Where $E_{Input-HTT-N}$ is the energy input for wet microalgae disintegrated with DES-assisted hydrothermal treatment with heat recovery; $m_{biomass}$ is the mass of wet microalgae biomass; h_{HTT} is the specific enthalpy for water during hydrothermal treatment(temperature of 25°C and pressure of 0.62Mpa); $h_{npt}$is specific enthalpy for water at temperature of 25°C and pressure of 1 atm. φ is the heat recovery for hydrothermal treatment of microalgae reported by Anastasakis et al. [1].

2. Energy output.

The energy output was calculated from the yield and heating values of extracted lipid as following:

(1) Energy output for dried microalgae biomass treated with DES at room temperature was calculated as following:

$$E_{Output-dry} = m_{dried-biomass} \times \theta \times \emptyset_d \times HHV$$

$$= 100g \times 240.12mg/g \times 80.9\% \times 36.97J/mg$$

$$= 718168.42J$$

$$= 718.17KJ$$

Where $E_{Output-dry}$ is the energy output for dried microalgae biomass treated with DES at room temperature; $m_{dried-biomass}$ is the mass of dried biomass contained in 1 kg of wet microalgae with a moisture content of 90%; θ is the lipid content of dried microalgae biomass; $\emptyset_d$ is the lipid extraction efficiency of dried microalgae biomass treated with DES at room temperature. HHV is the higher heating value of the extracted lipid according to reference[2].

(2) Energy output for wet microalgae disintegrated with DES-assisted hydrothermal treatment was calculated as following:

$$E_{Output-HTT} = m_{dried-biomass} \times \theta \times \emptyset_{HTT} \times HHV$$

$$= 100g \times 240.12mg/g \times 95.8\% \times 36.97J/mg$$

$$= 850439.25J$$

$$= 850.44KJ$$

Where $E_{Output-HTT}$ is the energy output for wet microalgae disintegrated with DES-assisted hydrothermal treatment; $m_{dried-biomass}$ is the mass of dried biomass contained in 1 kg of wet microalgae with a moisture content of 90%; θ is the lipid content of dried microalgae biomass; $\emptyset_{HTT}$ is the lipid extraction efficiency of wet microalgae disintegrated with DES-assisted hydrothermal treatment. HHV is the higher heating value of the extracted lipid according to reference[2].

3. Net energy ratio (NER).

The NER for dried microalgae biomass treated with DES at room temperature was calculated as following:

$$NER_{dry} = \frac{E_{Input-dry}}{E_{Output-dry}} = \frac{2313.01kJ}{718.17kJ} = 3.22$$

The NER for wet microalgae disintegrated with DES-assisted hydrothermal treatment without heat recovery was calculated as following:

$$NER_{HTT-N} = \frac{E_{Input-HTT-N}}{E_{Output-HTT}} = \frac{570.64kJ}{850.44kJ} = 0.67$$

The NER for wet microalgae disintegrated with DES-assisted hydrothermal treatment with heat recovery of 74.2% was calculated as following:

$$NER_{HTT-Y} = \frac{E_{Input-HTT-Y}}{E_{Output-HTT}} = \frac{114.13kJ}{850.44kJ} = 0.13$$

Both the NERs for wet microalgae disintegrated with DES-assisted hydrothermal treatment without heat recovery (0.67) and with heat recovery (0.13) were lower than NER (3.22) for dried microalgae biomass treated with DES at room temperature. This indicated that wet microalgae disintegrated with DES-assisted hydrothermal treatment

for lipid extraction is more energetic effectiveness than dried microalgae biomass treated with DES at room temperature.

References:

[1] K. Anastasakis, P. Biller, R.B. Madsen, M. Glasius, I. Johannsen, Continuous hydrothermal liquefaction of biomass in a novel pilot plant with heat recovery and hydraulic oscillation, Energies 11(10) (2018) 2695.
[2] R. Huang, J. Cheng, Y. Qiu, Z. Zhang, J. Zhou, K. Cen, Solvent-free lipid extraction from microalgal biomass with subcritical water in a continuous flow reactor for acid-catalyzed biodiesel production, Fuel 253 (2019) 90-94.