Integrating Anaerobic Digestion with Algal Cultivation Systems: Enhancement of Biomethane Production Through Thermochemical Pretreatment

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ABSTRACT

Integration of algal biofuel production with anaerobic digestion (AD) provides opportunities to improve biofuel production economy and sustainability. Technological roadblocks need to be resolved to make the process economically viable e.g., incomplete lysis and hydrolysis of algal cells in a digester due to the presence in some species of rigid cell walls. We address this limitation by thermal, chemical and thermochemical pretreatment of algal biomass prior to AD.

INTRODUCTION

AD converts to biofuel all classes of organic matter. A large fraction of the energy stored as carbohydrates and proteins is lost as low-value by-products (Fig. 1); **Algal lipids content is less critical.** Local robust fast-growing strains can be used for integrated biofuel production and wastewater treatment.

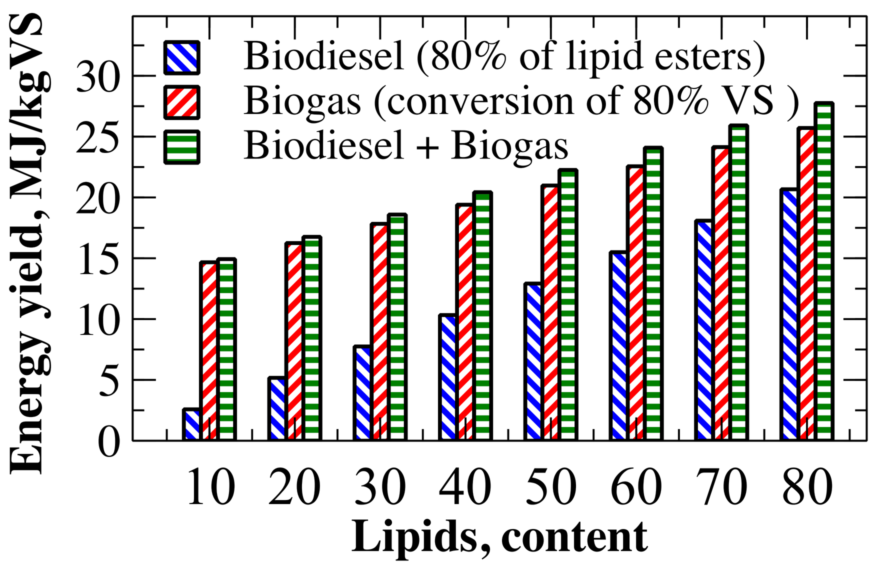

Fig. 1. Potential energy yield from algal biomass

PROJECT GOALS

(1) to improve methane yield through algal cell lysis and hydrolysis using chemical, thermal or thermochemical pretreatments;

(2) to determine the influence of algal cell wall structure on methane and biogas yields.

MATERIALS AND METHODS

Algal biomass pretreatment procedure:

- Algal solutions (26-27 gVS/L) were prepared from stock algal solutions (<18% dw) purchased from Reed Mariculture Inc.
- NaOH (50%) was added to 300 ml of algal solutions to a final concentration ranging from 0 to 21 g NaOH/L.
- Samples for thermal and thermochemical pretreatments were autoclaved at 121°C for 30 min.
- Treated samples were cooled to the ambient temperature during ~1.5 hrs; pH was measured and corrected to the neutral (7.2±0.15) level by addition of 50% HCl.
- All samples were centrifuged at 5,200 rpm × 10 min at 4°C, the liquid phase was separated.
- The "solubilization" of algal biomass was measured as a fraction of Chemical Oxygen Demand (COD) in a liquid phase after centrifugation.

Tested algal species and their characteristics:

(A) Chlorella sp. has rigid cell wall composed of polysaccharides;

(B) Nannochloropsis salina has thick, multilayered cell wall composed of polysaccharides;

(C) *Thalassiosira weissflogii* (CCMP105) has cell wall made of silica;

(D) *Tetraselmis sp.* has cell wall composed of glycoproteins;

(E) *Pavlova_cf sp.* (CCMP459) – no distinct cell wall.

Theoretical CH_4 yield was estimated by the Bushwell equation (1):

$$C_cH_hO_oN_nS_s + y(H_2O) \rightarrow x(CH_4) + (c-x)CO_2 + d(NH_3) + eH_2S$$

where: $x = (4c + b - 2o - 3n - 2s)/8$ and $y = (4c - b - 2o + 3n + 2s)/4$

Methane and biogas yield and analysis.

- Methane and biogas yields were measured through the Biomethane Potential Test (2,3).
- Assays were performed in 150 ml serum bottles. The organic load was 0.9gCOD/L in the final media.
- Anaerobic sludge from the digester treating sewage sludge at the Back River WWTP, Baltimore, MD was applied as inoculum.
- Samples were incubated at 35°C during 94-95 days.
- Shimadzu GC-TCD equipped with the Hayes Q 80/100 column was used for biogas composition analysis. The helium was used as a gas carrier at the 2 bar pressure. The Inj/Det temperature was 130°C and column current 80 mA.

RESULTS AND DISCUSSION

Table 1. Theoretical and observed methane yields from raw algal biomass

Algal strain	Chemical formula	Theoretical yield		Observed yield		CH_4 yield from theor., %
		CH_4, L/gVS	CH_4, %	CH_4, L/gVS	CH_4, %	
Chlorella sp.	$C_{7.02}H_{12.47}O_{3.11}N$	0.55	55.8	0.338±0.016	73.6	61.4
N.salina	$C_{8.74}H_{15.0}O_{2.95}N$	0.63	58.6	0.355±0.012	71.6	56.3
T. weissflogii	$C_{8.17}H_{13.33}O_{4.56}N$	0.48	51.8	0.378±0.003	74.4	78.7
Tetraselmis sp.	$C_{7.00}H_{12.48}O_{3.14}N$	0.54	55.7	0.421±0.001	78.8	78.0
Pavlova_cf sp.	$C_{10.8}H_{17.6}O_{2.54}N$	0.73	61.0	0.511±0.009	72.8	70.0

- The lowest methane yield was observed for *N.salina* and *Chlorella sp.* (strong polysaccharide cell walls). The observed CH_4 yield was only 56 and 61% from theoretical.
- Thermochemical pretreatment had a dramatic effect on *Chlorella* and *Nannochloropsis* biomass solubilization. sCOD increased up to 500% and 300% and reached 83% and 95% from total COD, respectively (Fig. 2).
- sCOD for *Pavlova_cf sp.* and *Tetraselmis sp.* reached 95% and the observed improvement was only about 50-100% compared to the non-treated samples.
- All pretreatments did not affect the solubilization of *Thalassiosira weissflogii* biomass.

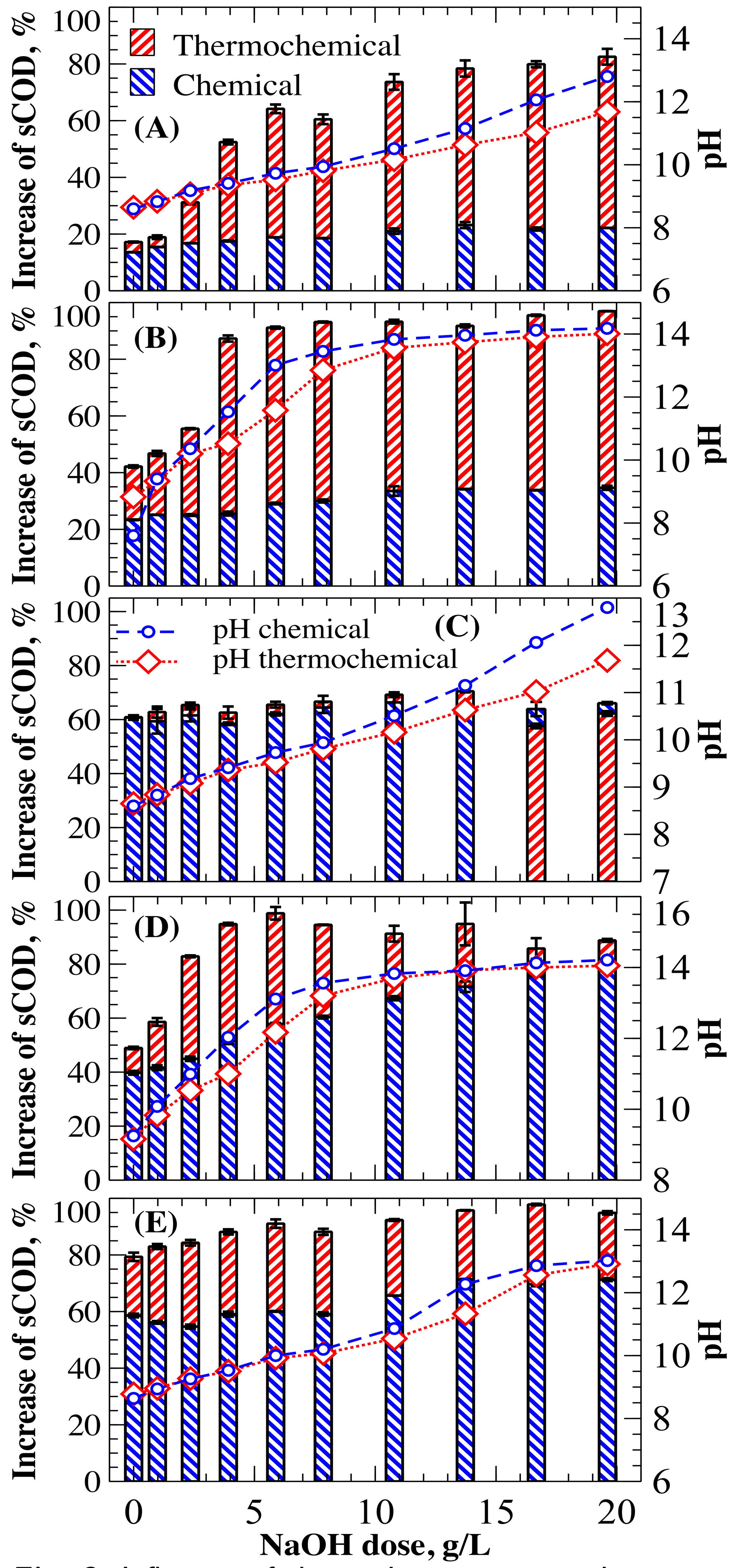

Fig. 2. Influence of chemical pretreatment alone (blue bars) and thermochemical pretreatment (red bars) on algal organic matter solubilization

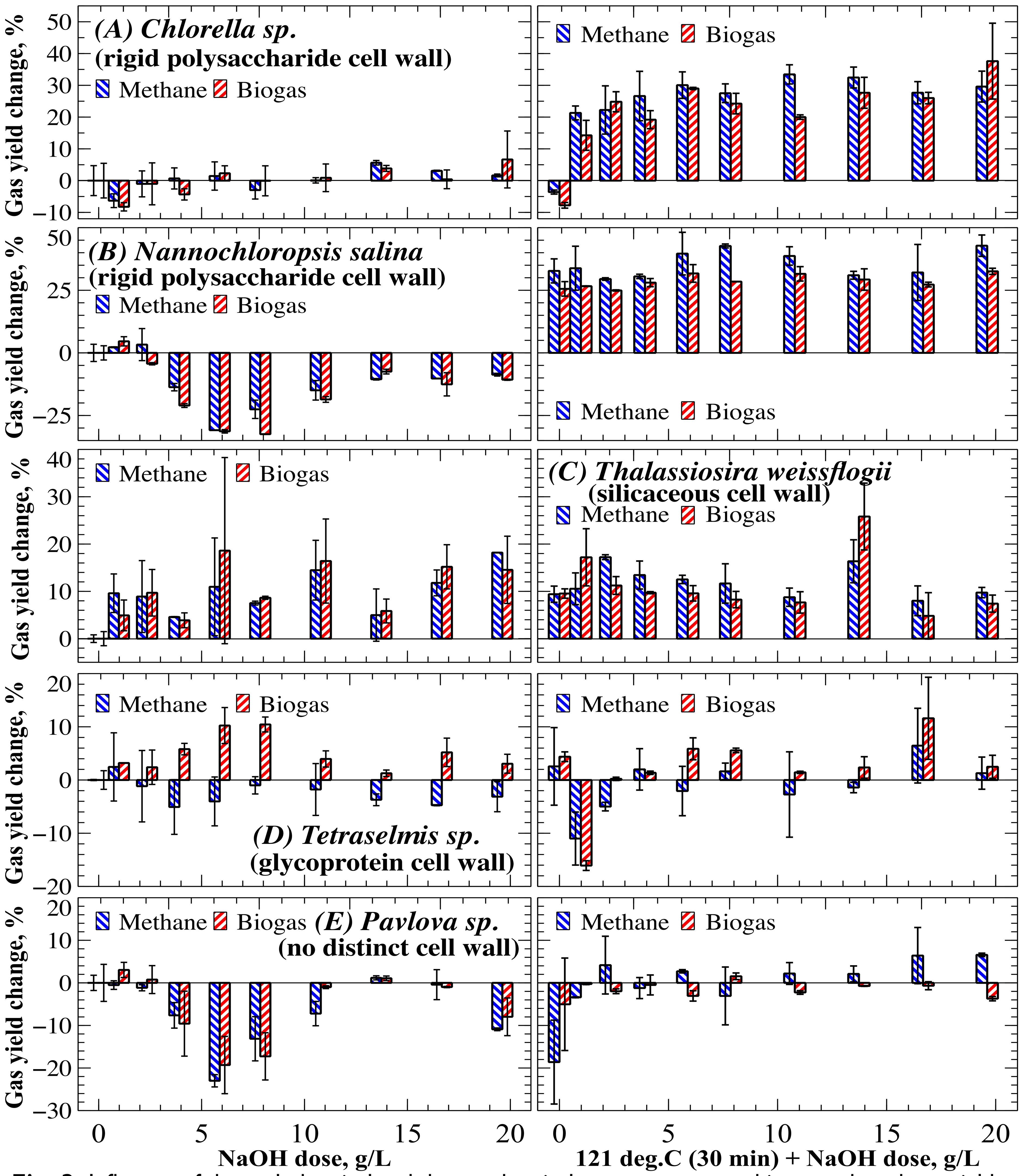

Fig. 3. Influence of thermal, chemical and thermochemical pretreatments on biogas and methane yield

- The pretreatment had a dissimilar effect on CH_4 and biogas yields from different species and was the most distinctly apparent with *Chlorella* and *Nannochloropsis* (Fig. 3);
- The thermochemical hydrolysis of organic matter improved CH_4 yield up to 40 and 30% for *Nannochloropsis* and *Chlorella*, respectively (Fig. 3A, B);
- Chemical pretreatment had a negative or no effect effect on both species.
- Thermal treatment was found to be beneficial for CH_4 production from *Nannochloropsis* but disadvantageous for *Chlorella*.
- All pretreatments had a slightly positive effect on CH_4 yield from *T. weissflogii* biomass (Fig. 3C);
- The pretreatment decreased or did not change the CH_4 yield from *Tetraselmis sp.* and *Pavlova_cf sp.* (Fig. 3D, E).

CONCLUSIONS

1. Thermochemical pretreatment with NaOH was found to be the most effective method for organic mater solubilization. sCOD level reached up to 80-95% for all species with organic cell walls.

2. Hydrolysis of the organic matter improved methane yield but only for species with a strong carbohydrate-base cell wall (up to 40% and 30% for *Nannochloropsis* and *Chlorella*, respectively).

3. Our findings confirm that presence of a strong polysaccharide cell wall limits biomass biodegradability and methane yield, but it can be overcome through thermochemical pretreatment.

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