energies

Review

Low Indirect Land Use Change (ILUC) Energy Crops to Bioenergy and Biofuels—A Review

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The transformation systems vary with several factors like the desired biofuel product, composition of biomass, economics, time and operation conditions from an Microalgal-based biofuels can be obtained through chemical (Table S1), biochemical (Table S2, Table S3 and Table S4) and thermochemical (Table S5, Table S6 and Table S7) conversion pathways [1,2].

Table S1. Microalgae raw material studied for chemical conversion (transesterification) pathways towards biofuels.

Transesterification - Biodiesel				
Microalgae	**Reaction**	**Conditions**	**Yield (%)**	**Reference**
Chlorella protothecoides	Acidic transesterification	30°C; 7h; 160 rpm M/O= 45:1	68%	[3]
Schizochytrium limacinum	Bligh & Dyer extraction-transesterification *In situ* transesterification	90°C; 40 min	55.5% FAME content = 66.4% 66.3% FAME content = 66.5%	[4]
Nannochloropsis oculata	Soxhlet extraction-transesterification	50°C; 4 h; 1100 rpm M/O = 30:1	97.5%	[5]
Chlorella pyrenoidosa	*In situ* transesterification	90°C; 2h M/A[1]= 4:1 (v w^{-1})	95% FAME content = 99%	[6]
Nannochloropsis gaditana	*In situ* transesterification	255°C; 50 min; 70 rpm M/A= 10:1 (v w^{-1})	48%	[7]
Nannochloropsis sp.	*In situ* transesterification	50°C; 6 h; 1100 rpm M/A = 3.16:100 (w w^{-1})	95%	[8]
Chlorella vulgaris	1st: acidic esterification (radio frequency heating) + hexane xtraction 2nd: alkali transesterification (radio frequency heating)	Cell disruption: 90°C; 30 min 55°C; 20 min M/A= 2:5 (v w^{-1})	FAME yield: 1st: 58.8% 2nd: 79.5%	[9]
	In situ transesterification using IL[2]	IL: [P4444][For][3] 102.4°C, 4.6 h M/A=9:1 (molar) IL/A=8:1 (molar) Water content: 40.6%	FAME yield: Theoretical: 98.0% Experimental: 98.6%	[10]

[1] M/A - Methanol to biomass (algae) ratio
[2] IL - Ionic liquids
[3] [P4444][For] - Tetrabutylphosphonium formate.

Table S2. Microalgae feedstock applied for biochemical conversion (anaerobic digestion) pathways towards biofuels.

Anaerobic digestion - Biogas					
Microalgae	**Reaction**	**Organism**	**Conditions**	**Yield (%)**	**Reference**
Chlamydomonas reinhardtii	AD	Inoculum: Sludge from a local sewage plant	38°C; 32 d	587 ml biogas g^{-1} VS (66% methane)	[11]
Dunaliella salina	AD	Inoculum: Sludge from a local sewage plant	38°C; 32 d	505 ml biogas g^{-1} VS (64% methane)	[11]
Chlorella vulgaris	AD	Inoculum: Sludge from a tertiary WW treatment pond	35°C; 16-28 d	240 ml methane g^{-1} VSS[1]	[12]
Phaeodactylum tricornutum	AD	Inoculum: Biomass from a full-scale anaerobic digester treating potato-processing WW	33°C; 30 d; I/M[2]= 3:1	360 ml methane g^{-1} VS	[13]
Scenedesmus obliquus	AD	Inoculum: Biomass from a full-scale anaerobic digester treating potato-processing WW	33°C; 30 d; I/M= 3:1	240 ml methane g^{-1} VS	[13]
Scenedesmus sp.-AMDD	AD	Inoculum: Biomass from a UASB[3] digester with apple processing WW	35°C; 34-50 d; 150 rpm; I/M= 3:1	410 ml methane g^{-1} VS	[14]
Isochrysis sp.	AD	Inoculum: Biomass from a UASB digester with apple processing WW	35°C; 34–50 d; 150 rpm; I/M= 3:1	408 ml methane g^{-1} VS	[14]
Arthrospira platensis	Co-digestion with sludge	Inoculum: Digested sludge collected from a lab-scale anaerobic reactor	35°C; 23 d; I/M=2:1; M/S[4]= 2:1	343 ml methane g^{-1} VS	[15]

[1] VSS - Volatile Suspended Solids.
[2] I/M - Inoculum to microalgae ratio.
[3] UASB - Upflow Anaerobic Sludge Blanket.
[4] M/S - Microalgae to sludge ratio.

Table S3. Microalgae feedstock studied for biochemical conversion (alcoholic fermentation) pathways towards biofuels.

Alcoholic fermentation - Bioethanol					
Microalgae	**Reaction**	**Organism**	**Conditions**	**Yield (%)**	**Reference**
Chlamydomonas reinhardtii UTEX 90	SHF	*Saccharomyces cerevisiae* S288C	30°C; pH: 5; 24 h; 160 rpm; Yeast: 10 % (v/v)	29.2%	[16]
Chlorococum sp.	SHF	*Saccharomyces bayanus*	30°C; 60 h; 200 rpm; Substrate: 10 g L^{-1}; Yeast: 3% (v/v)	38%	[17]
Chlorella vulgaris	SHF	*Escherichia coli* SJL2526	37°C; pH: 7; 24h; 150 rpm; Substrate: 5 g L^{-1}	40%	[18]

Schizocytrium sp.	SSF	*Escherichia coli* KO11	37°C; 72 h; 150 rpm	5.5%	[19]
Scenedesmus obliquus	SHF	*Kluyveromyces marxianus* IGC 2671 *Saccharomyces carlsbergensis* ATCC 6269 *Saccharomyces bayanus*	30°C; pH: 5.2; 78 h; 150 rpm; Substrate: 500 ml microalga hydrolysate; Yeast: 300 mg dw^{-1} L^{-1}	*K. marxianus:* 11.7 g L^{-1} *S. carlsbergensis:* 11.2 g L^{-1} *S. bayanus:* 9 g L^{-1}	[20]
Chlorella sp.	SHF SSF	*Zymomonas mobilis* ATCC 29191	30°C; 60 h; 200 rpm; Substrate: 20 g L^{-1}; Bacterium: 10% (v v^{-1})	SHF: 17.8% SSF: 21.4%	[21]
Arthrospira platensis	SHF	*Sacharomyces cerevisiae* CAT-1	30°C; 20 h; Substrate: 20 g L^{-1}; Bacterium: 10% (v v^{-1})	83.36% 1.57 g L^{-1} h^{-1} (16h)	[22]
Arthrospira sp.	SHF	*Sacharomyces cerevisiae* ATCC 26603	30°C; 24 h; B/M[1]: 25% (v v^{-1}); Bacterium: 10% (v v^{-1})	78.9% 0.72 g L^{-1} h^{-1}	[23]
Arthrospira sp.	SSF	Sacharomyces cerevisiae CAT-1	30°C; 72 h; 130 rpm; Substrate: 20 % (15% corn starch + 5% alga) (w v^{-1}); Bacterium: 10% (v v^{-1})	55 g L^{-1}	[24]

[1] B/M - Biomass to molasses ratio.

Table S4. Microalgae feedstock applied for biochemical conversion (biological H_2 production) pathways towards biofuels.

Biological H_2 production - Biohydrogen					
Microalgae	**Reaction**	**Organism**	**Conditions**	**Yield (%)**	**Reference**
Chlamydomonas reinhardtii 137c	Biophotolysis (S deprivation)	-	25°C; pH: 7.2; 120 h; I[1]: 110 µmol m^{-2} s^{-1}	2.5 ml H_2 L^{-1} culture h^{-1}	[25]
Chlorella sorokiniana Ce	Biophotolysis (S deprivation)	-	30°C; pH: 7.2; 220 h I: 120 µmol m^{-2} s^{-1}	1.35 ml H_2 L^{-1} culture h^{-1}	[26]
Chlamydomonas reinhardtii	Biophotolysis (S deprivation)	-	120 h I: 100 µmol m^{-2} s^{-1}	5.2 ml H_2 L^{-1} culture	[27]
Chlorella vulgaris	Biophotolysis (S deprivation)	-	27°C; 52 h I: 120 µmol m^{-2} s^{-1} 24 h light/48 h dark	530 ml H_2 L^{-1} culture 34.8 ml H_2 L^{-1} culture h^{-1}	[28]
Chlorella vulgaris	DF	*Clostridium butyricum*	37°C; 30 h; 220 rpm; Substrate: 5 g L^{-1}; Bacterium: 20%	81 ml H_2 g^{-1} (dw)	[29]

			(v v^{-1})		
Nannochloropsis sp.	DF	*Enterobacter aerogenes*	30°C; 6 h; 220 rpm; Substrate: 2.5 g L^{-1}; Bacterium: 10% (v v^{-1})	60.6 ml H_2 g^{-1} (dw)	[30]
Chlorella pyrenoidosa	DF	Hydrogen producing and photosynthetic bacteria	DF: 35°C; pH: 6; 48 h; Substrate: 20 g L^{-1}; PF[2]: 30°C; pH: 8; 96 h; Substrate: 15 mM SMPs[3]; I: 120 μmol m^{-2} s^{-1}	198.3 ml g^{-1} TVS	[31]
Scenedesmus obliquus	DF	*Enterobacter aerogenes*	30°C; 6 h; 220 rpm; Substrate: 2.5 g L^{-1}; Bacterium: 10% (v v^{-1})	57.6 ml H_2 g^{-1} VS (wet biomass)	[32]
Scenedesmus obliquus	DF	*Clostridium butyricum*	37°C; 48 h; 150 rpm; Substrate: 50 g L^{-1}; Bacterium: 1% (v v^{-1})	113.1 ml H_2 g^{-1} VS (dried biomass)	[32]
Scenedesmus obliquus	DF	*Clostridium butyricum*	37°C; 96 h; 150 rpm; Substrate: 50 g L^{-1} (dw); Bacterium: 1% (v v^{-1})	116.3 ml H_2 g^{-1} alga	[33]
Spirogyra sp.	DF	*Clostridium butyricum* DSM 10702	37°C; 144 h; 150 rpm; Substrate: 10 g L^{-1} (dw); Bacterium: 1% (v v^{-1})	47 ml H_2 g^{-1} $alga_{dw}$ 156 ml H_2 $g^{-1}_{total\ sugars}$	[34]
Spirogyra sp.	DF (SBR[4])	*Clostridium butyricum* DSM 10702	37°C; 10-14 h; 150 rpm; Substrate: 10 g_{sugar} L^{-1}; Bacterium: 10% (v v^{-1})	324 ml H_2 L^{-1} h^{-1} 4.4 L H_2 L^{-1} FM	[35]
Chlorella sp.	DF	Mixed acidogenic bacteria	35°C; 150 h; pH 7; 150 rpm; Substrate: 80-100 g_{VS} L^{-1}; Bacteria: 25% (v v^{-1})	22 ml H_2 g^{-1} VS	[36]
Chlorella vulgaris	Biophotolysis (S deprivation)	-	30°C; 120 h; pH 7.5; I (purple light): 140 μmol m^{-2} s^{-1}	60.4 ml H_2 L^{-1} 39.18 ml H_2 L^{-1} d^{-1}	[37]
Scenedesmus obliquus	Biophotolysis (S deprivation)	-	30°C; 120 h; pH 7.5; I (purple light): 140 μmol m^{-2} s^{-1}	128 ml H_2 L^{-1} 204 ml H_2 L^{-1} d^{-1}	[37]

[1] I - Light Intensity.
[2] PF - Photo-Fermentation.
[3] SMPs - Soluble Metabolite Products.
[4] SBR - Sequential Batch Reactor.

Table S5. Microalgae raw material studied for thermochemical conversion (gasification) pathways towards biofuels.

Gasification - Syngas				
Microalgae	**Reaction**	**Conditions**	**Yield**	**Reference**
Chlorella vulgaris	Supercritical water gasification	600°C; 240 bar; 2 min; 7.3 wt% loading	53%	[38]
Nannochloropsis sp.	Supercritical water gasification	450°C; 40 min; 4.8 wt% loading	16.3 mmol H_2 g^{-1} 5.1 mmol methane g^{-1}	[39]
Chlorella vulgaris	Supercritical water gasification	500°C; 36 MPa; 30 min; Catalyst: 1.67M NaOH	12 mmol H_2 g^{-1}	[40]
Nannochloropsis oculata	Steam gasification	700°C; 30 min; Catalyst: Fe_2O_3-CeO_2	413 cm^3 H_2 g^{-1} 278 cm^3 CO_2 g^{-1}	[41]
Nannochloropsis gaditana	Supercritical water gasification	663°C; 24 MPa; 128 s; 3-5 wt% loading	73-97%	[42]
Chlorella vulgaris	Steam gasification	800°C; 10 min	61.7%	[43]
Chlorella vulgaris	Chemical looping gasification (CLG)	800°C; 10 min; Oxygen carrier: Fe_2O_3	81.6% 1.05 Nm^3 syngas kg^{-1}	[43]
Chlorella pyrenoidosa	Supercritical water gasification	430°C; 2-13 MPa; 60 min	5.6 mmol H_2 g^{-1} 8.2 mmol methane g^{-1}	[44]
Chlorella vulgaris	Supercritical water gasification	385°C; 26 MPa; 30 min; Catalyst: Ru/charcoal	87% C gasification	[45]
Chlorella vulgaris (lipid-extracted) *Arthrospira platensis* (lipid-extracted)	Steam gasification	800°C; 10°C min^{-1}; Catalyst: Ni-CaO	Yield: 497.29 ml H_2 g^{-1} Purity: 63.15% Yield: 435 ml H_2 g^{-1} Purity: 45.78%	[46]

Table S6. Microalgae feedstock studied for thermochemical conversion (pyrolysis) pathways towards biofuels.

Pyrolysis - Bio-oil, biochar, biogas				
Microalgae	**Reaction**	**Conditions**	**Yield**	**Reference**
Chlorella protothecoides	Slow pyrolysis	500°C; 5 min	Bio-oil: 52%	[47]
Chlorella protothecoides	Fast pyrolysis	450°C; 2-3 s; N_2 Flow = 0.4 m^3 h^{-1}	Bio-oil (Autotrophic): 16.6%; Bio-oil (Heterotrophic): 57.9	[48]
Nannochloropsis sp.	Slow pyrolysis	400°C; 120 min; N_2 Flow: 30 ml min^{-1}	Bio-oil: 31% Biochar: 28% Biogas: 25%	[49]
Chlorella sp.	Microwave-assisted	750 W; 20 min;	Bio-oil: 28.6%	[50]

	pyrolysis	N_2 Flow: 500 ml min^{-1}; Biomass/Char= 1:5 (w w^{-1})		
Chlorella sp.	Slow pyrolysis	450°C; 30 min; Air Flow: 100 ml min^{-1}	Bio-oil: 55% (40% energy recovery) Biochar: 30% Biogas: 15%	[51]
Chlorella vulgaris	Microwave-assisted pyrolysis	1500 W; 20 min; N_2 Flow: 300 ml min^{-1}	Bio-oil: 35.83% Biochar: 29.87% Biogas: 33%	[52]
Chlorella vulgaris (lipid-extracted)	Fast pyrolysis	500°C	Bio-oil: 53% Biochar: 31% Biogas: 10%	[53]
Scenedesmus obliquus	Slow pyrolysis	475°C; 30 min; N_2 Flow: 200 ml min^{-1}	Bio-oil: 57.6% Bio-char: 25.6% Biogas: 16.8%	[54]
Arthrospira platensis	Slow pyrolysis	550°C; 60 min	Bio-oil: 35% Biochar: 32% Biogas: 12%	[55]
Nannochloropsis sp. *Tetraselmis* sp. *Isochrysis galbana*	Fast pyrolysis	500°C; N_2 Flow: 3500 ml min^{-1}	Bio-oil: 58-66% Biochar: 21-30% Biogas: 13%	[56]
Chlorella sp.	Slow pyrolysis	550°C; 240 min	Bio-oil: 42.81% Biochar: 55% Biogas: 1.14%	[57]

Table S7. Microalgae raw material studied for thermochemical conversion (hydrothermal liquefaction) pathways towards biofuels.

Hydrothermal liquefaction - Bio-oil				
Microalgae	**Reaction**	**Conditions**	**Yield**	**Reference**
Botyrococcus braunii	Liquefaction	300°C; 60 min	57%	[58]
Dunaliella tertiolecta	Liquefaction	300°C; 5 min	43.8% (organic basis)	[59]
Nannochloropsis sp.	Liquefaction	350°C; 60 min	43 wt%	[60]
Nannochloropsis sp.	Liquefaction	350°C; 60 min	57%	[61]
Chlorella vulgaris *Nannochloropsis oculata* *Porpyridium creuntum* *Arthrospira* sp.	Liquefaction	350°C; 60 min	35.8% daf[1] 34.3% daf 21% daf 29% daf	[62]
Desmodesmus sp.	Liquefaction	375°C; 5 min	49%	[63]
Nannochloropsis sp.	Liquefaction	600°C; 1 min	66%	[64]
Chlorella sp.	Liquefaction	350°C; 1.4 min	39.7% daf	[65]
Scenedesmus obliquus	Liquefaction	300°C; 15 min	44% daf	[66]
Tetraselmis sp.	Liquefaction	350°C; 30 min	31%	[67]
Haematococcus pluvialis	Liquefaction	200°C; 150 min	54.2%	[68]

[1] daf - dry ash free basis.

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