Electronic Supplementary Material (ESI) for Energy & Environmental Science

SUPPLEMENTARY INFORMATION

On the feasibility of producing hydrogen with net carbon fixation by the decomposition of vegetable and microalgal oils

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Appendix A

Table A.1 gathers supporting data on the selected oils. Table A.2 shows the distribution of fatty acids for each of these oils according to literature data.[35-38]

Table A.1. Seed yield, extractable oil content and literature sources for the selected biomass feedstocks

	Sunflower	**Soybean**	**Rapeseed**	**Jatropha**	***B. braunii***	***C. vulgaris***
Seed yield (t/ha/year)	0.5-2.5	0.7-3.6	0.7-3.5	1.5-12.5	12.4-33.8	38.9-50.0
Extractable oil content (%)	40-48	18-20	30-40	34	14-53	12-27
References	[24,25]	[24,25]	[24-26]	[27-29]	[30-33]	[31-34]

Table A.2. Fatty acid composition of the selected oils

Fatty acid	**Formula**	**Molecular weight**	**Mass percentage in:**					
			Sunflower oil	**Soybean oil**	**Rapeseed oil**	**Jatropha oil**	***B. braunii* oil**	***C. vulgaris* oil**
Lauric	$C_{12}H_{24}O_2$	200	-	-	-	-	2.30	2.79
Myristic	$C_{14}H_{28}O_2$	228	-	-	-	-	2.87	0.77
Palmitic	$C_{16}H_{32}O_2$	256	6.40	10.97	5.10	12.94	40.58	19.20
Palmitoleic	$C_{16}H_{30}O_2$	254	-	-	-	-	-	0.87
Margaric	$C_{17}H_{34}O_2$	270	-	-	-	-	-	4.19
Heptadecenoic	$C_{17}H_{32}O_2$	268	-	-	-	-	-	1.25
Stearic	$C_{18}H_{36}O_2$	284	4.40	4.18	1.90	7.38	4.32	14.60
Oleic	$C_{18}H_{34}O_2$	282	26.40	21.41	59.60	45.30	22.28	12.66
Linoleic	$C_{18}H_{32}O_2$	280	61.70	54.83	20.30	34.38	14.45	3.77
Linolenic	$C_{18}H_{30}O_2$	278	0.80	7.83	8.64	-	13.20	26.09
Eicosanoic	$C_{20}H_{40}O_2$	312	0.20	0.52	0.61	-	-	0.36
Eicosenoic	$C_{20}H_{38}O_2$	310	0.10	0.26	1.60	-	-	4.09
Eicosadienoic	$C_{20}H_{36}O_2$	308	-	-	-	-	-	3.91
Dihomo-ɣ-linolenic	$C_{20}H_{34}O_2$	306	-	-	-	-	-	3.30
Eicosapentaenoic	$C_{20}H_{30}O_2$	302	-	-	-	-	-	2.10
Behenic	$C_{22}H_{44}O_2$	340	-	-	0.25	-	-	-
Erucic	$C_{22}H_{42}O_2$	338	-	-	2.00	-	-	0.05

Appendix B

Table B.1 details the computation of the decomposition enthalpy of the different fatty acids contained in the selected oils.

Table B.1. Decomposition enthalpy (ΔH) of the fatty acids considered in the study

Fatty acid	Formula	Molecular weight	χ	ΔH_f^0 (kJ/mol)	ΔH (kJ/mol)	ΔH (MJ/kg)
Lauric	$C_{12}H_{24}O_2$	200	6.77	-759.41	365.91	1.83
Myristic	$C_{14}H_{28}O_2$	228	7.77	-826.27	432.77	1.90
Palmitic	$C_{16}H_{32}O_2$	256	8.77	-897.27	503.77	1.97
Palmitoleic	$C_{16}H_{30}O_2$	254	8.42	-871.95	478.45	1.88
Margaric	$C_{17}H_{34}O_2$	270	9.475	-949.83	556.33	2.06
Heptadecenoic	$C_{17}H_{32}O_2$	268	9.27	-934.33	540.83	2.02
Stearic	$C_{18}H_{36}O_2$	284	9.77	-972.43	578.93	2.04
Oleic	$C_{18}H_{34}O_2$	282	9.42	-945.65	552.15	1.96
Linoleic	$C_{18}H_{32}O_2$	280	9.07	-919.39	525.89	1.88
Linolenic	$C_{18}H_{30}O_2$	278	8.72	-893.63	500.13	1.80
Eicosanoic	$C_{20}H_{40}O_2$	312	10.77	-1,051.73	658.23	2.11
Eicosenoic	$C_{20}H_{38}O_2$	310	10.42	-1,023.50	630.00	2.03
Eicosadienoic	$C_{20}H_{36}O_2$	308	10.275	-1,011.96	618.46	2.01
Dihomo-ɣ-linolenic	$C_{20}H_{34}O_2$	306	9.925	-984.45	590.95	1.93
Eicosapentaenoic	$C_{20}H_{30}O_2$	302	9.224	-930.88	537.38	1.78
Behenic	$C_{22}H_{44}O_2$	340	11.77	-1,135.17	741.67	2.18
Erucic	$C_{22}H_{42}O_2$	338	11.42	-1,105.50	712.00	2.11

Appendix C

The computation of the energy and CO_2 balances for each of the three scenarios is detailed in Tables C.1 and C.2, respectively.

Table C.1. Estimation of the energy surpluses for each scenario (favourable energy surpluses in bold)

	SF2	SB2	RS2	RS3	J1	J2	BB1	BB2
SCENARIO 1								
Available C energy (MJ/kg oil)	19.03	19.02	19.03	19.03	18.95	18.95	18.75	18.75
Energy demand (MJ/kg oil)	17.07	24.54	20.20	14.04	19.64	11.47	29.72	15.80
SURPLUS:								
1. Energy (MJ/kg oil)	**1.96**	-5.52	-1.17	**4.99**	-0.69	**7.49**	-10.96	**2.95**
2. Hydrogen (kg/kg oil)	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
SCENARIO 2								
Available H_2 energy (MJ/kg oil)	3.54	3.54	3.59	3.59	3.61	3.61	3.63	3.63
Available C energy (MJ/kg oil)	19.03	19.02	19.03	19.03	18.95	18.95	18.75	18.75
Energy demand (MJ/kg oil)	17.07	24.54	20.20	14.04	19.64	11.47	29.72	15.80
SURPLUS:								
1. Energy (MJ/kg oil)	**5.50**	-1.99	**2.42**	**8.58**	**2.93**	**11.10**	-7.33	**6.58**
2. Hydrogen (kg/kg oil)	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
SCENARIO 3								
Available C energy (MJ/kg oil)	19.03	19.02	19.03	19.03	18.95	18.95	18.75	18.75
Available H_2 energy (MJ/kg oil)	0.00	5.52	1.17	0.00	0.69	0.00	7.26	0.00
Energy demand (MJ/kg oil)	17.07	24.54	20.20	14.04	19.64	11.47	29.72	15.80
SURPLUS:								
1. Energy (MJ/kg oil)	**1.96**	**0.00**	**0.00**	**4.99**	**0.00**	**7.49**	-3.70	**2.95**
2. Hydrogen (kg/kg oil)	0.12	0.03	0.10	0.12	0.11	0.12	0.00	0.12

Table C.2. Calculation of the CO_2 balances of those case studies with a favourable energy surplus (negative balances in bold)

	SF2	**SB2**	**RS2**	**RS3**	**J1**	**J2**	**BB2**
SCENARIO 1							
C-energy use (kg/kg oil)	0.65	-	-	0.53	-	0.44	0.60
C-fixed (kg/kg oil)	0.07	-	-	0.19	-	0.29	0.11
CO_2-input (kg/kg oil)	2.82	-	-	2.81	-	2.81	2.79
CO_2-output (kg/kg oil)	2.54	-	-	2.12	-	1.76	2.37
CO_2-balance (kg/kg oil)	**-0.27**	-	-	**-0.70**	-	**-1.05**	**-0.41**
SCENARIO 2							
C-energy use (kg/kg oil)	0.52	-	0.63	0.40	0.61	0.30	0.46
C-fixed (kg/kg oil)	0.21	-	0.09	0.33	0.11	0.42	0.25
CO_2-input (kg/kg oil)	2.82	-	2.81	2.81	2.81	2.81	2.79
CO_2-output (kg/kg oil)	2.05	-	2.48	1.62	2.40	1.26	1.87
CO_2-balance (kg/kg oil)	**-0.77**	-	**-0.34**	**-1.20**	**-0.41**	**-1.55**	**-0.92**
SCENARIO 3							
C-energy use (kg/kg oil)	0.65	0.72	0.72	0.53	0.72	0.44	0.60
C-fixed (kg/kg oil)	0.07	0.00	0.00	0.19	0.00	0.29	0.11
CO_2-input (kg/kg oil)	2.82	2.82	2.81	2.81	2.81	2.81	2.79
CO_2-output (kg/kg oil)	2.54	2.82	2.81	2.12	2.81	1.76	2.37
CO_2-balance (kg/kg oil)	**-0.27**	0.00	0.00	**-0.70**	0.00	**-1.05**	**-0.41**

Appendix D

Table D.1 details the computation of the energy balances for the decarbonization and transesterification systems in the context of the comparative analysis conducted in section 3.4.

Table D.1. Computation of the energy balances for the oil decarbonization and transesterification systems (favourable balances in bold)

	SF1	SF2	SF3	SB1	SB2	RS1	RS2	RS3	J1	J2	BB1	BB2	CV1	CV2
Energy input (MJ/kg oil)														
Cultivation	100.00	10.67	38.00	107.14	15.16	46.43	11.49	5.33	12.46	4.29	23.19	9.28	33.70	6.60
Extraction	3.15	3.15	3.15	5.90	5.90	5.42	5.42	5.42	3.81	3.81	3.17	3.17	92.98	42.21
Decomposition	3.26	3.26	3.26	3.48	3.48	3.29	3.29	3.29	3.38	3.38	3.36	3.36	3.36	3.36
Refining and transesterification	1.90	1.90	1.90	1.90	1.90	1.90	1.90	1.90	1.90	1.90	0.85	0.85	0.85	0.85
Total energy demand (decarbonization system)	106.41	17.07	44.41	116.52	24.54	55.13	20.20	14.04	19.64	11.47	29.72	15.80	130.04	52.16
Total energy demand (transesterification system)	105.05	15.71	43.05	114.94	22.96	53.74	18.81	12.65	18.16	9.99	27.21	13.29	127.53	49.65
Energy output (MJ/kg oil)														
Carbon and hydrogen (decarbonization system)	37.97	37.97	37.97	37.92	37.92	38.15	38.15	38.15	38.14	38.14	37.97	37.97	37.97	37.97
Biodiesel (transesterification system)	37.63	37.63	37.63	37.63	37.63	37.63	37.63	37.63	37.63	37.63	36.19	36.19	36.19	36.19
Energy surplus (MJ/kg oil)														
Decarbonization system	-68.44	**20.89**	-6.44	-78.60	**13.38**	-16.99	**17.95**	**24.11**	**18.50**	**26.67**	**8.26**	**22.17**	-92.07	-14.20
Transesterification system	-67.41	**21.92**	-5.41	-77.30	**14.67**	-16.11	**18.83**	**24.99**	**19.47**	**27.65**	**8.98**	**22.90**	-91.34	-13.46