Electronic Supplementary Material (ESI) for Green Chemistry.

Life cycle inventory and system boundary of biomass-to-chemical production

Input-output data pertaining to corn, wheat and rice production are displayed as tables A1, A2, A3 respectively. Details of sugarcane plantation and sugar milling, including the generation of bagasse, are compiled in Table A4. All CO_2 intake by crops during photosynthesis are allocated by mass to the respective agricultural residues.

Information for biotechnologies for biomass to formic acid and methanol production are contained in Tables B1 – B3. The LCA system boundary for rice straw to methanol or rice straw to bio-acetone is displayed in Fig. A; and for wheat straw to bio-formic acid or acetone, Fig. B.

Data relating to P and N fertilizers vs. Crop yield for corn, wheat, rice and sugarcane, are compiled in Table C.

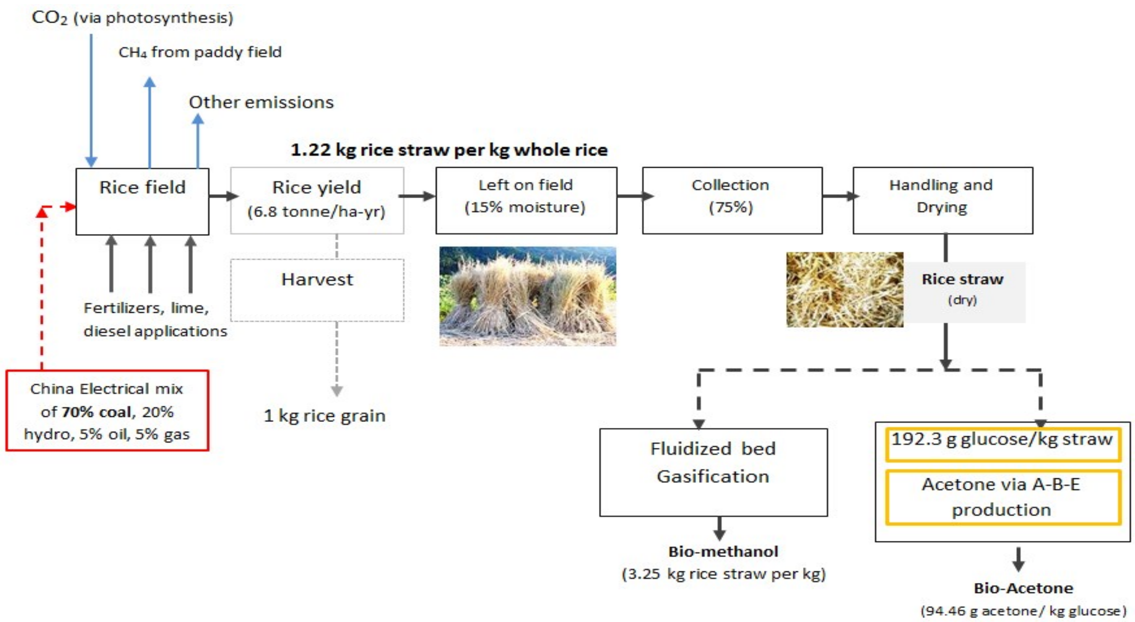

Figure A. LCA system of rice cultivation and rice straw collection to produce: i) bio-methanol; or ii) acetone (via A-B-E process)

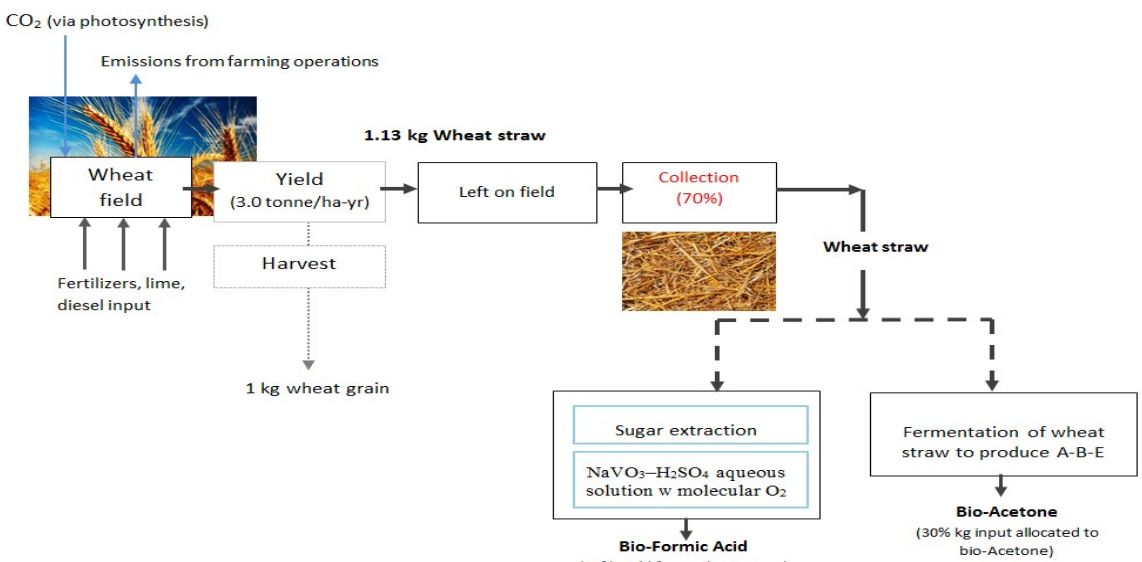

Figure B. LCA system of wheat plantation and wheat straw generation to produce: i) formic acid; or ii) acetone via (A-B-E)

Table A1. Input-output LCI data for corn stover [a]

Input (corn agriculture)			
Flow	**Unit**	**Amount**	**Comments**
Carbon dioxide	kg	1.49	Photosynthesis during biomass growth
Diesel, combusted in industrial equipment	l	6.86×10^{-3}	Farm energy input
Agrochemicals	kg	2.88×10^{-4}	Pesticides consumption
Phosphorous Fertilizer (P_2O_5)	kg	5.84×10^{-3}	Fertilizers
Electricity	kWh	0.0122	Energy consumption
Gasoline, combusted in farm equipment	l	1.88×10^{-3}	For farm tractor
Liquefied petroleum gas, combusted in industrial boiler	l	4.87×10^{-3}	Energy consumption
Natural gas, combusted in industrial boiler	m^3	3.05×10^{-3}	Energy consumption
Nitrogen fertilizer	kg	0.0169	Fertilizers
Quicklime, at plant	kg	0.0305	
Water (total)	l	32.6	Water for irrigation
Output			
Flow	**Unit**	**Amount**	**Comments**
Corn stover, at field	**kg**	**1.00**	62% collection for use as lignocellulose feedstock; the rest left on field to prevent soil erosion
Corn	kg	1.00	For food
N_2O	kg	5.26×10^{-4}	Greenhouse gas
NOx	kg	2.97×10^{-3}	Contribution to acidification potential
Particulates, unspecified	kg	3.45 x 10-7	Particulate emissions
Hydrocarbons, unspecified	kg	1.73×10^{-4}	Due to use of pesticides
Nitrogen, total	kg	2.10×10^{-3}	Runoff/leaching of fertilizers to water body
Phosphorus compounds, unspecified	kg	3.80×10^{-5}	Runoff/leaching of fertilizers to water body
Suspended solids, unspecified	kg	0.822	Erosion leading to water pollution

[a]NREL, Crop production – corn farming, quantitative reference: corn stover at field, 2001.

Table A2. Input-output LCI data for wheat straw[b]

Input (wheat agriculture)

Flow	Unit	Amount	Comments
Carbon dioxide	kg	1.51	Photosynthesis during biomass growth
Diesel, combusted in industrial equipment	l	0.0172	Farm energy input
Agrochemicals	kg	1.71×10^{-4}	Pesticides consumption
Phosphorous Fertilizer (P_2O_5)	kg	0.0103	Fertilizers
Gasoline, combusted in farm equipment	l	3.90×10^{-3}	For farm tractor
Nitrogen fertilizer, production mix	kg	0.0285	Fertilizers
Quicklime	kg	0.0187	
Water (total)	m^3	0.0595	Water for irrigation
Output			
Flow	**Unit**	**Amount**	**Comments**
Wheat straw, at field	**kg**	**1.30**	70% collection for use as lignocellulose feedstock; the rest left on field to prevent soil erosion
Wheat grain	kg	1.00	For food
N_2O	kg	8.37×10^{-4}	Greenhouse gas
NOx	kg	4.64×10^{-3}	Contribution to acidification potential
Particulates, unspecified	kg	1.22×10^{-6}	Particulate emissions
Hydrocarbons, unspecified	kg	1.03×10^{-4}	Due to use of pesticides
Nitrogen, total	kg	3.48×10^{-3}	Runoff/leaching of fertilizers to water body
Phosphate	kg	6.07×10^{-5}	Runoff/leaching of fertilizers to water body
Suspended solids, unspecified	kg	2.90	Erosion leading to water pollution

[b]NREL, Crop production – wheat farming, quantitative reference: wheat straw at field, 2000.

Table A3. Input-output LCI data for rice straw[c]

Input (rice agriculture)			
Flow	**Unit**	**Amount**	**Comments**
Carbon dioxide	kg	1.27	Photosynthesis during biomass growth
Diesel, combusted in	l	4.86×10^{-2}	Farm energy input

industrial equipment			
Agrochemicals	kg	9.21×10^{-4}	Pesticides consumption
Phosphorous Fertilizer (P_2O_5)	kg	5.17×10^{-3}	Fertilizers
Electricity	kWh	0.0501	Energy consumption
Liquefied petroleum gas, combusted in industrial boiler	l	2.83×10^{-3}	Energy consumption
Natural gas, combusted in industrial boiler	m^3	5.37×10^{-3}	Energy consumption
Nitrogen fertilizer	kg	2.38×10^{-2}	Fertilizers
Quicklime, at plant	kg	6.89×10^{-3}	
Water (total)	l	668.0	Water for irrigation
Output			
Flow	**Unit**	**Amount**	**Comments**
Rice straw, at field	**kg**	**1.22**	75% collection for use as lignocellulose feedstock; the rest left on field to prevent soil erosion
Rice grain, at field	kg	1	For food
CO	kg	7.22×10^{-3}	Greenhouse gas
CH_4	kg	0.0446	Greenhouse gas
N_2O	kg	7.43×10^{-4}	Greenhouse gas
NOx	kg	4.26×10^{-3}	Contribution to acidification potential
Ammonia	kg	1.43×10^{-3}	Due to use of pesticides
Hydrocarbons, unspecified	kg	5.53×10^{-4}	Due to use of pesticides
Nitrogen, total	kg	2.90×10^{-3}	Runoff/leaching of fertilizers to water body
Phosphorus compounds	kg	3.05×10^{-5}	Runoff/leaching of fertilizers to water body
Suspended solids	kg	1.07	Erosion leading to water pollution
Copper ions	kg	2.41×10^{-6}	Water pollution due to use of pesticides

[c]NREL, Crop production – rice farming, quantitative reference: rice straw at field, 2001.

Table A4. Input-output LCI data for bagasse[d]

Input (sugarcane plantation)			
Flow	**Unit**	**Amount**	**Comments**
Carbon dioxide	kg	0.44	Photosynthesis during biomass growth (per kg sugarcane)[e]
Diesel	l	0.03	Farm energy input
Herbicide	kg	2.1×10^{-4}	Pesticides consumption
Phosphorous Fertilizer (P_2O_5)	kg	0.012	Fertilizers

Nitrogen fertilizer	kg	4.5×10^{-4}	Fertilizers
Insecticide	kg	1.53×10^{-3}	
Water (total)	m^3	0.042	Water for irrigation[e]
Output (from sugarcane plantation)			
Flow	**Unit**	**Amount**	**Comments**
Sugarcane	**kg**	**8.3**	**Required per 1.66 kg (dry) bagasse at Mill**
CH_4 total	kg	2.77×10^{-4}	Greenhouse gas due to traditional harvesting
N_2O total	kg	1.64×10^{-3}	Greenhouse gas due to traditional harvesting
NOx	kg	3.71×10^{-3}	Contribution to acidification potential
Particulates, unspecified	kg	3.20×10^{-5}	Particulate emissions
Nitrate	g	7.03×10^{-5}	Due to use of pesticides
Ammonium	g	2.2×10^{-4}	
Ammonia	g	0.429	Due to volatization
Input (Sugar Mill)			
Flow	**Unit**	**Amount**	**Comments**
Sugarcane	kg	8.3	From plantation
Steam	MJ	1.3	Energy input for milling process; operating temperature 260 – 300 °C, pressure 1.9 – 2.1 MPa
Output (Sugar Mill)			
Bagasse (dry)	**kg**	**1.66**	**As input per kg methanol**
Other by-products not taken into account			

[d] Extracted from M.L.G. Renó et al., 20th International Congress on Mechanical Engineering, 2009.
[e] Supplemented by EcoInvent

Table B1. Input-output LCI data for biomass (stover) to formic acid

Input (stover)			
Flow	**Unit**	**Amount**	**Comments**
Biomass	kg	1.7	Material input are all allocated by mass based on Biofine process[f]
Water	kg	2.49	with additional information from Fitzpatrick[g]
Sulphuric Acid	kg	-	Assume 100% recovery
Biochar for steam generation	kg	0.35	Net amount; allocated by mass
Output (formic acid)			
Formic Acid	**kg**	**1**	**Functional unit**
CO_2	kg	1.08	Estimated based on composition of carbon, nitrogen and sulphur in
NOx	kg	0.03	biochar [h] (99% scrubber efficiency)

SO_2	kg	7.8×10^{-6}

[f] D.J. Hayes et al., Biorefineries – Industrial processes and Products, 2006.
[g] S.W. Fitzpatrick, Commercialization of the Biofine technology for levulinic acid production from paper sludge, United States: US Department of Energy, 2002.
[h] J. Lehmann, S. Joseph, Biochar for Environmental Management: Science, Technology and Implementation, Taylor & Francis, 2015.

Table B2. Input-output LCI data for biomass (bagasse) to methanol [i]

		Input (bagasse)	
Flow	**Unit**	**Amount**	**Comments**
Biomass	kg	1.66	Pre-treated, dry
Steam	kg	2.3	
Electricity	MJ	0.38	
		Output (Methanol)	
Bio-Methanol	**kg**	**1**	**Functional unit**
CO	kg	2.5×10^{-5}	
CH_3OH (VOC)	kg	6.58×10^{-5}	
HCN	kg	3.60×10^{-4}	Fugitive emissions
H_2S	kg	9.96×10^{-5}	
NH_3	kg	3.60×10^{-4}	

[i] Extracted from M.L.G. Renó et al., 20th International Congress on Mechanical Engineering, 2009.

Table B3. Input-output LCI data for biomass (rice straw) to methanol [j]

Input (bagasse)			
Flow	**Unit**	**Amount**	**Comments**
Biomass	kg	3.25	Pre-treated, dry
Energy	MJ	0	Energy are provided by combustion of flue gas, hot/cold process fluid
Output (Methanol)			
Methanol	**kg**	**1**	**Functional unit**
CO_2	kg	1.83	
CO	kg	1.12×10^{-3}	Greenhouse gas
CH_4	kg	2.34×10^{-4}	
NO_x	kg	9.28×10^{-4}	Contribution to acidification potential
SO_2	kg	5.24×10^{-4}	
PM_{10}	kg	9.30×10^{-4}	Dusts/particulates

[j] Extracted from J. Xiao et al., *Ind. Eng. Chem. Res.*, 48, 999, 2009.

Table C. N and P fertilizer input vs. Crop yield

Corn (kg/ha)[†]			Wheat (kg/ha)[α]			Rice (kg/ha)[β]			Sugarcane (kg/ha)[δ]		
N	**P**	**Yield**	**N**	**P**	**Yield**	**N**	**P**	**Yield**	**N**	**P**	**Yield**
44.6	45.7	6797	79.8	34.5	2846	200	51	6300	31	30	53936
46.6	48	6928	78.6	32.8	2213	157	50	5290	61	57	76640
45.8	47	6949	80.7	34.5	2539	160	48	6030	57	60	75310
47	48	7102	82.6	34.2	3145	196	58	7050	76	45	73557

[†] Extracted from S. Gul et al., *Scientifica*, 1, 2015.

[α] Extracted from R. Carew et al., *J. Agri. & Applied Econs.*, 41, 625, 2009.

[β] Extracted from J.Y. Jin et al., *Better Crops International*, 2002.

[δ] FAO, *Fertilizer by Crop in Brazil*, 2004.