energies

MDPI

Supplementary Materials

Hydrothermal Carbonization: Modeling, Final Properties Design and Applications: A Review

Silvia Román, Judy Libra, Nicole Berge, Eduardo Sabio, Kyoung Ro, Liang Li, Beatriz Ledesma, Andrés Álvarez and Sunny Bae

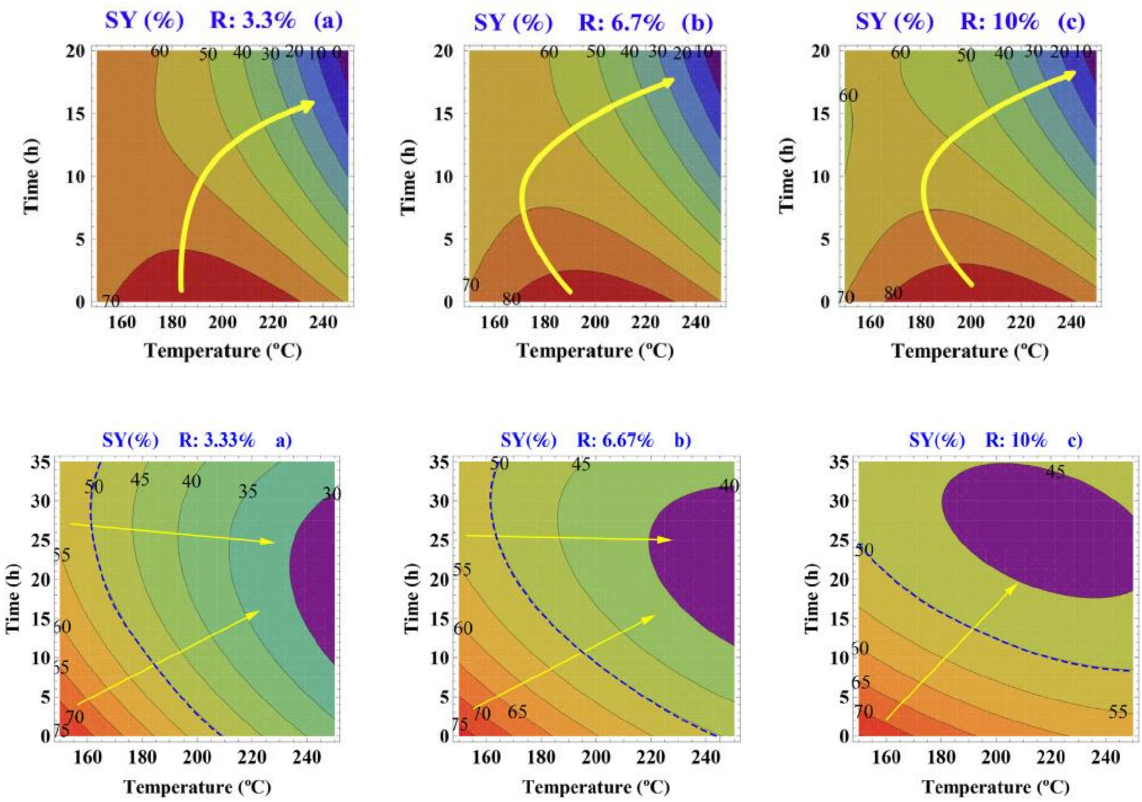

Figure S1. SY level curves (Alvarez Murillo et al., 2015)

Table S1. Percentage of Collected Papers that Report Specific Hydrochar Properties.

Hydrochar Property	% Collected Papers Reporting this Property
Yield (%, db)	70.54
Carbon (%, db)	53.57
Hydrogen (%, db)	46.43
Oxygen (%, db)	38.39
Nitrogen (%, db)	31.25
Sulfur (%, db)	16.07
Energy content (MJ/kg, db)	42.86

Table S2. Influence of changing feedstocks in relevant collected carbonization studies.

Feedstock	Washed Solids?	Process Conditions Evaluated			General carbonization product trends associated with changing process conditions	Ref.
		% Solids	Temp. (°C)	Time (min)*		
Anaerobically digested sludge, Industrial sludge	Yes	2.47, 2.67	200	1440	Feedstock types influence the %C in char	(Alatalo et al., 2013)
Glucose, lactose, olive waste, hazel nutshell	Yes	4.77	180	240	Solids generated from saccharides have different chemical structure than those generated from glucose or lactose. Chars from glucose and lactose have furanic chains; chars from olive oil waste and hazel nutshells have mainly an aromatic structure.	(Aydincak et al., 2012)
Paper, food, mixed MSW, anaerobic digestion solids	No	20	250	1200	Feedstock composition influences product composition Higher solid-phase carbon contents were found in hydrochar formed from food waste than other feedstocks evaluated	(Berge et al., 2011)
Wood chips, Digestate, Straw, Grass	No	10	180	480	Feedstock types influence the %C in char	(Eibisch et al., 2013)
Straw, Digestate	No	5	230	522.5	Feedstock types influence the char carbon	(Funke et al., 2013b)
Wheat straw, rice straw, cotton stem, water hyacinth, pine sawdust	No	3.5	240	240	Feedstock type influences the solid yields, char carbon and energy content of recovered solids	(Gao et al., 2016)
Cellulose, saw dust, lignin, rice husk	Yes	14.31	280	102	Feedstock type influences gas composition.	(Karagöz et al., 2005)
Sawdust from pine	Yes	14.29, 25	280	100	Initial solids concentration has an important effect on product distribution and composition of oil products. Solids yields increases with initial solids concentration.	(Karagöz et al., 2006)
Food waste, yard waste, paper	No	20	250	120-1440	Feedstock type influences the carbon distribution in different phases Feedstock type influences the solid yields, char carbon and energy content of recovered solids	(Li et al., 2014)
Coconut fibers, Eucalyptus leaves	No	9.11	250	30	Feedstock types influence the solids yield and energy content of recovered solids	(Liu & Balasubramanian, 2013)
Japanese MSW, Indian MSW	No	50	220	30	Energy densities increase as a result of carbonization.	(Lu et al., 2011)
Cellulose, glucose, starch, xylose, lignin, corn, paper, pine wood	No	20	250	30-5760	Feedstock types influences the char yields and product distribution	(Lu & Berge, 2014)
Agricultural Residues, Industrial Organic Waste, Agricultural Residues	No	15	220	390	Feedstock type influences the solid yields and energy content of recovered solids	(Oliveira et al., 2013)
Sewage sludge, Low rank	Yes	4.05, 9.09	250	15	Feedstock types influence the char carbon and energy content of recovered solids	(Parshetti et al., 2013b)

Indonesian coal						
Eucalyptus sawdust, barley straw	Yes	13.82	250	176.25	Chemical composition of collected hydrochars was similar	(Sevilla et al., 2011)
Beech wood chips	No	47.12	210	240	Chemical composition of the hydrochars generated from these feedstocks was similar	(Tremel et al., 2012)
Corn stalk, tamarix ramosissima	Yes	9.11	250	296.25	Recovered solids composition is similar. Liquid composition differs slightly form the different feedstocks.	(Xiao et al., 2012)

*reaction times in this table have been corrected to include the heating time; unless otherwise noted, a time = 0 represents the time when heating commences

Table S3. Influence of process related parameters in relevant collected carbonization studies.

Feedstock	Washed Solids?	Process Conditions Evaluated			General carbonization product trends associated with changing process conditions	Ref.
		% Solids	Temp. (ºC)	Time (min)*		
Cherry Stones	Yes	9.11	200-300	0-30	• Solid yields decrease with increases in temperature and time; time influences product distribution • The energy content of residuals increased with reaction temperature at the same reaction time	(Akalın et al., 2012)
Olive stone	No	6.25	200-250	192-2208	• Solid yields decrease with increasing time • Energy content increases with increasing temperature and time	(Álvarez-Murillo et al., 2015)
Fructose	No	0.89	200-300	0.5-15	• Temperature has a strong influence on liquid product composition • Reaction time also influenced product composition	(Asghari & Yoshida, 2006)
Digestate, Wheat Straw, and Pine, Poplar, Masanduba, and Garapa Wood	No	5.06	190-270	453-469	• Solid yields decrease with increasing temperature and time	(Becker et al., 2013)
Fresh olive mill waste, fresh orange juice waste	No	20.59, 29.29	200-250	120-1440	• Solid yields decrease with increasing temperature and time • Char carbon increases with temperature and time • Energy content increases with temperature and time	(Benavente et al., 2015)
Grape marc	No	16	180-250	77.5-497.5	• Solid yields decrease with increasing temperature and time • Energy content increases with temperature and time	(Basso et al., 2016)
Sugar beet pulp, Bark mulch	No	20	200-250	205-1228	• Temperature has more influence on hydrochar characteristics than time • %C in char increases with temperature and time	(Cao et al., 2013)
Eucalyptus wood	Yes	10	180-190	17.5	• Solid yields decrease with increasing temperature	(Chang et al., 2013)

Sugarcane Bagasse	Yes	9.11	180	5-30	• The energy density of the hydrochar increases with reaction time	(Chen et al., 2012)
Algae (C. fragile)	Yes	6.52	180-240	10	• Reaction time and temperature influence the liquid composition and product distribution/composition	(Daneshvar et al., 2012)
Primary sewage sludge	No	4-25	190-200	45-255	• Energy content of the solids increases with temperature and time • Solid yields increase with the solid concentration	(Danso-Boateng et al., 2013)
Algae	Yes	20	200, 225	10-60	• Solid yields decrease with reaction temperature and time	(Du et al., 2012)
Sewage sludge	No	22, 9	190-220	300, 420	• Increases in reaction time may result in higher heating values	(Escala et al., 2013)
Glucose, cellulose, rye straw, pure alcell lignin	Yes	9.11	180-280	1440	• Solid yields decrease and carbon content of the hydrochar increase with increasing temperature • Solids oxygen content decreases with reaction temp.	(Falco et al., 2011a)
Carbonized wood materials	No	25	200, 300	1200	• Solid yields decrease with increasing temperature	(Fujino et al., 2002)
Fresh wheat straw, Digestated wheat straw	Yes	5.8, 5.5	190-250	415-435	• Solid yields decrease with increasing temperature • Feedstock types influence the solid yields	(Funke et al., 2013a)
Water hyacinth	Yes	5.66	240	143-1513	• Energy content of recovered solids increases with time	(Gao et al., 2013)
Rabbit food	Yes	NR	250, 300	0.33-2.5	• Solid yields decrease with increasing temperature • HMF yields increase with time	(Goto et al., 2004)
Sewage sludge	Yes	14.3	200	240-720	• Carbon content of the hydrochar decreases with time	(He et al., 2013)
Various microalgae	Yes	5-12.5	190-213	75-180	• Solids concentration is statistically significant • Solid yields increase with increasing initial solids concentration and decrease with increasing time and temperature	(Heilmann et al., 2010)
Corn distiller's grains	Yes	5-25	190-210	75-150	• Solid yields increase with initial solids concentration and decrease with increasing temperature • Carbon content of the hydrochar increases with reaction time	(Heilmann et al., 2011)

Mixture of Jeffrey pine and white fir	Yes	11.11	215-295	65-120	• Increases in temperature and time increase gas and liquid products; solid yields decrease • Energy density of the char increases with reaction severity (e.g., time and temp)	(Hoekman et al., 2011)
Paper, dog food, wood, plastics	No	25.04	234, 295	80	• Carbon and energy content of the char increases as temperature increases; solid yields also increase	(Hwang et al., 2012)
Empty fruit bunches	Yes	6.25	180-220	100-1420	• Energy and carbon content of the solids increase with time • Carbon content of the solids increases with increasing temperature, while the oxygen content of the solids decrease with increasing temperature	(Jamari & Howse, 2012)
Miscanthus	No	6.91, 12.90	190-260	5-30	• Solid yields decrease with increasing time and decreasing concentration • Energy content increases with time	(Kambo & Dutta, 2015)
Black liquor solids, lignin, cellulose, D-xylose, pine wood meal	No	20, 25	220-285	480, 1200	• Solid yields decrease with increasing temperature • Feedstock composition influences yields: lignin > WM > cellulose > D- xylose	(Kang et al., 2012a; Kang et al., 2012b)
Coconut meal	No	9.09	200-250	17-252	• Solid yields increase with increasing time and temperature	(Khuwijitjaru et al., 2012)
Glucose	Yes	3.5-16.5	300, 350	5-10,000	• Time and temp influence product distribution; time plays a more important role during early times. • Solid yields decrease with increasing time and temperature	(Knežević et al., 2009)
Glucose, wood, pyrolysis oil, sawdust	Yes	3.6-43	250-350	2-60	• Time and temp influence product distribution; Time plays a more important role during early times. • Solid yields decrease with increasing time and temp.	(Knežević et al., 2010)
Wood slurry	Yes	10	200-300	21	• Product distribution depends on reaction temperature; carbon content increases with increasing temp., while the oxygen content decreases with increasing temperature	(Kobayashi et al., 2008)

Micro crystalline cellulose	No	1.94	250-350	2	• Carbon and energy content of the char increases with temperature	(Kong et al., 2013)
Baker's yeast	No	10	200, 250	5-30	• Solid yields decrease with increasing temperature and time	(Lamoolphak et al., 2006)
Silk fibroin fiber	No	1 - 5	180-250	10-60	• Solid yields decrease with increasing reaction temp and time	(Lamoolphak et al., 2008)
Food waste, packaging materials	No	5-41	225-275	30-5760	• Initial solids concentration and time influence carbon distribution • Temperature has a small influence on carbon distribution when carbonizing food • Presence of packaging materials greatly influences hydrochar energy content and carbon distribution	(Li et al., 2013)
Food waste, yard waste, paper	No	20	250	120-1440	• Solid yields decrease with increasing time	(Li et al., 2014)
Seaweed, horse manure	No	NR	205	1350, 1430	• Feedstock type influences energy content of recovered solids	(Lilliestråle, 2007)
Cypress	Yes	9.09	260	69-99	• Percent carbon and energy content of solids increase with time	(Liu et al., 2013a)
Coconut fiber, eucalyptus leaves	No	9.09	200-350	30	• Energy density increases with increasing temperature, while the solid yields decrease	(Liu et al., 2013b)
Cellulose	No	20	225-275	30-5760	• Temperature and time have great influence on cellulose carbonization at early times • Reaction time influences the composition of gas-phase and liquid-phase	(Lu et al., 2013)
Paper, food, MSW,	No	20	250	120-7200	• Product distribution changes with time: solid yields decrease until reaching a stable level; gas carbon increases with increasing time, while the liquid increases and then decreases	(Lu et al., 2012)
Cellulose, glucose, starch, xylose, lignin, corn, paper, pine wood	No	20	250	30-5760	• Reaction time influences the composition of gas-phase, liquid-phase and solid phase • Reaction time influences solid yields, char carbon and energy content of recovered solids	(Lu & Berge, 2014)

Water lettuce	Yes	5.4	200, 250	30, 60	• Greater solids hydrolysis occurs when the reactions were conducted at a higher temperatures or longer times; protein solubility in water increases with increasing temp	(Luo et al., 2011)
Cellulose	Yes	0.99	185	25-110	• Carbon content in the liquid increases and then decreases with reaction time	(Möller et al., 2013)
Starch	Yes	9.11	180-240	11 - 12	• Solid yields increase with increasing temperature and decrease with increasing time	(Nagamori & Funazukuri, 2004)
Empty fruit bunch	Yes	9.09	250, 350	20	• Percent carbon and energy content of solids increase with temperature • Solid yields decrease with increasing temperature	(Parshetti et al., 2013a)
Cellulose	Yes	9.09	220-350	25-91	• Temperature influences the product distribution • Solid yields decrease with increasing time	(Pavlovic et al., 2013)
Alkali lignin	Yes	5	280	26 -266	• Increasing temperature and time increase secondary reactions	(Pinkowska et al., 2012)
Rice bran	Yes	14.29	180-320	5	• Temperature influences liquid composition; more feedstock is solubilized at higher temperatures	(Pourali et al., 2009)
Japonica-type rice	Yes	14.29	200-340	22 - 50	• Total phenolic content and antioxidant activity increases with temperature and time	(Pourali et al., 2010)
Corn stover, Miscanthus, Switch grass, Rice hull	No	16.7	200-260	44	• Energy content of solids increases with temperature, while the solid yields decrease with increasing temperature	(Reza et al., 2013a)
Loblolly pine	Yes	1.96	200-260	25-310	• Energy content of recovered solids increases with increasing temperature and time • Solid yields decrease with increasing temperature and time	(Reza et al., 2013b)
Maize silage	No	6.70	200-250	78.3-435	• Solid yields decrease with increasing time • Energy content of recovered solids increases with increasing time	(Reza et al., 2014)
Walnut shell, sunflower stem	Yes	3.23-4.77	190, 230	1200, 2700	• Temperature and initial solids concentration were more influential on product formation than time	(Román et al., 2012)

					• Higher temperature results in greater energy content of the solids • Greater ratio of feedstock to water results in lower solid yields • Sunflower stem was more reactive than walnut shell	
Tomato peel	No	1.09-10.09	200, 230	96-1104	• Solid yields and energy content increase with initial solid concentration	(Sabio et al., 2016)
Onion bulbs, Onion skins	Yes	4.62, 9.09	180-290	5	• Temperature influences liquid composition • Char carbon content increases with temperature	(Salak et al., 2013)
Glucose, sucrose, starch	Yes	1.58-15.28	180-240	84-940	• Solid yields increase with reaction temperature and initial solids concentration	(Sevilla & Fuertes, 2009)
Cellulose	Yes	3.85-24.28	230,250	120, 240	• Solid carbon and yield increase with reaction temperature	(Sevilla & Fuertes, 2009)
Paulowina	Yes	14.31	280-340	62-78	• Temperature significantly influences the process of biomass liquefaction	(Sun et al., 2011)
Tofu waste	No	1.64-14.29	200-350	30	• Temperature was the most significant parameter • Gas yields increase with increasing temperature	(Tian et al., 2012)
Spirulina, Nannochloropsis salina	No	25	220-350	90-180	• Solid yields decrease with the increase of temperature • Feedstock type influences the solid yields and energy content of the recovered solids	(Toor et al., 2013)
Tamarix ramosissima	Yes	9	180-240	30-40	• Solid yields decrease with increasing temperature	(Xiao et al., 2013)
Loblolly pine	No	16.7	200-260	20-35	• Increasing temperature results in decreased mass yield and increased energy densification • Solids carbon content increases with temperature, while the oxygen content decreases	(Yan et al., 2009)
Cellulose	No	3.23	275-320	57-87	• HMF yields increase and decrease with increasing temperature • Solids yields decrease with increasing time	(Yin et al., 2011)

Corncob residues	No	9.09	190-350	60-360	• Solid yields decrease with increasing temperature • Char carbon content increases with temperature and time • Energy content increases with temperature and time	(Zhang et al., 2015)

*reaction times in this table have been corrected to include the heating time; unless otherwise noted, a time = 0 represents the time when heating commences

Table S4. Influence of changing feedstocks in relevant collected carbonization studies.

Feedstock	Washed Solids?	Process Conditions Evaluated			General carbonization product trends associated with changing process conditions	Ref.
		% Solids	**Temp. (ºC)**	**Time (min)***		
Anaerobically digested sludge, Industrial sludge	Yes	2.47, 2.67	200	1440	• Feedstock types influence the %C in char	(Alatalo et al., 2013)
Glucose, lactose, olive waste, hazel nutshell	Yes	4.77	180	240	• Solids generated from saccharides have different chemical structure than those generated from glucose or lactose. • Chars from glucose and lactose have furanic chains; chars from olive oil waste and hazel nutshells have mainly an aromatic structure.	(Aydıncak et al., 2012)
Paper, food, mixed MSW, anaerobic digestion solids	No	20	250	1200	• Feedstock composition influences product composition • Higher solid-phase carbon contents were found in hydrochar formed from food waste than other feedstocks evaluated	(Berge et al., 2011)
Wood chips, Digestate, Straw, Grass	No	10	180	480	• Feedstock types influence the %C in char	(Eibisch et al., 2013)
Straw, Digestate	No	5	230	522.5	• Feedstock types influence the char carbon	(Funke et al., 2013b)
Wheat straw, rice straw, cotton stem, water hyacinth, pine sawdust	No	3.5	240	240	• Feedstock type influences the solid yields, char carbon and energy content of recovered solids	(Gao et al., 2016)

Cellulose, saw dust, lignin, rice husk	Yes	14.31	280	102	• Feedstock type influences gas composition.	(Karagöz et al., 2005)
Sawdust from pine	Yes	14.29, 25	280	100	• Initial solids concentration has an important effect on product distribution and composition of oil products. Solids yields increases with initial solids concentration.	(Karagöz et al., 2006)
Food waste, yard waste, paper	No	20	250	120-1440	• Feedstock type influences the carbon distribution in different phases • Feedstock type influences the solid yields, char carbon and energy content of recovered solids	(Li et al., 2014)
Coconut fibers, Eucalyptus leaves	No	9.11	250	30	• Feedstock types influence the solids yield and energy content of recovered solids	(Liu & Balasubramanian, 2013)
Holocellulose, wood powder	Yes	1.64	210	540	• Feedstock type influences the char carbon and energy content of recovered solids	(Liu et al., 2015)
Japanese MSW, Indian MSW	No	50	220	30	• Energy densities increase as a result of carbonization.	(Lu et al., 2011)
Cellulose, glucose, starch, xylose, lignin, corn, paper, pine wood	No	20	250	30-5760	• Feedstock types influences the char yields and product distribution	(Lu & Berge, 2014)
Agricultural Residues, Industrial Organic Waste, Agricultural Residues	No	15	220	390	• Feedstock type influences the solid yields and energy content of recovered solids	(Oliveira et al., 2013)
Sewage sludge, Low rank Indonesian coal	Yes	4.05, 9.09	250	15	• Feedstock types influence the char carbon and energy content of recovered solids	(Parshetti et al., 2013b)
Eucalyptus sawdust, barley straw	Yes	13.82	250	176.25	• Chemical composition of collected hydrochars was similar	(Sevilla et al., 2011)
Beech wood chips	No	47.12	210	240	• Chemical composition of the hydrochars generated from these feedstocks was similar	(Tremel et al., 2012)
Corn stalk, tamarix ramosissima	Yes	9.11	250	296.25	• Recovered solids composition is similar.	(Xiao et al., 2012)

					• Liquid composition differs slightly form the different feedstocks.	

*reaction times in this table have been corrected to include the heating time; unless otherwise noted, a time = 0 represents the time when heating commences