Supplementary Material to

The role of renewable-derived plastics in the analysis of waste management schemes: A time-dependent carbon cycle assessment

Cristina Aracil, Jacopo Giuntoli, Jorge Cristobal , Ángel L Villanueva Perales, Pedro Haro*

CONTENT

1. Composition and biogenic fraction of RDF 2
2. Modeling of the BAU system 3
3. Modeling of the BIO system 4
4. Attributional carbon cycle assessment: GHG balance and GHG impact 14
5. Modeling of time-dependent GHG emissions 20
6. Summary of assumptions for the study 24
7. Additional results 27

1. Composition and biogenic fraction of RDF

Table S1. Composition of RDF in Spain and Sweden in % mass basis. The values in brackets are expressed in % carbon basis (IEA 2012, Jones *et al* 2013) (see Aracil *et al*, 2017 for additional details).

	Total carbon	Biogenic fraction (α)	RDF composition		Biogenic carbon	
			Spain	Sweden	Spain	Sweden
Organic matter	48	(100)	45	31	22	15
Paper-cardboard	44	(99)	14	23	6	10
Plastics	60	(0)	12	14	0	-
Textiles	55	(50)	6	12	2	3
Wood	50	(100)	2	-	1	-
Hygiene products	50	(36)	-	12	-	2
Inert waste	3	(0)	21	8	0	-
Total					**31 (76)**	**31 (66)**

2. Modeling of the BAU system

Two European countries (Spain and Sweden) have been selected as representative of the two main waste management schemes in Europe. Sweden represents the case of Northern and Central Europe, where incineration with energy recovery (heat and electricity) is dominant and landfilling is negligible. Spain is representative of the Southern and Eastern European case, where landfilling is dominant and energy recovery is focused on electricity production using landfill gas. As a result of the differences between these countries, the RDF composition is also different (Table S1) and the heat production is only taken into account for the Swedish case study since for the Spanish case heat production is negligible. Figure S2 shows a comparison of the conventional waste management scheme of the MSW refuse in both countries. In Spain, a higher fraction of MSW refuse is produced since the recycling ratio is lower than in Sweden (Fischer *et al* 2013, European Compost Network 2010, Vandecasteele *et al* 2016).

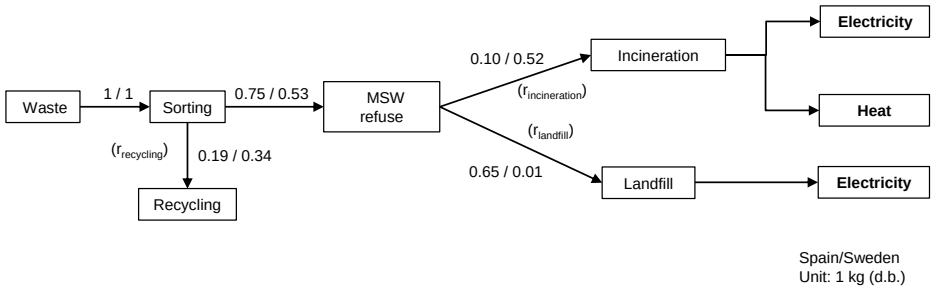


Fig S1. Conventional management of MSW refuse for the selected countries in the study (Spain and Sweden). Final products are shown in bold. Values are in dry mass basis considering 1 kg of MSW refuse as input (Fischer *et al* 2013, European Compost Network 2010).

For the substitution of plastic materials analyzed in this study, the four most demanded plastics in Europe were selected: low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP) and poly-vinyl chloride (PVC). These polymers represent almost 60% of the European plastics net consumption (Plastics Europe 2015). LDPE is used in food packaging and in light and flexible products like plastics bags; HDPE is used in the production of more resistant materials like house pipes or plastic toys; PP is

present in durable products like car bumpers or office folders; finally, PVC can be found in window frames or wellington boots (Plastics Europe 2015).

The GHG impact of the BAU system (E_{BAU}) is calculated by integrating the emissions from the different processes involved (cradle-to-grave) in g of CO_2 eq. MJ^{-1} of total products, see Eq. S1. E_{BAU} is calculated from emissions associated with landfilling and incineration (waste management) and the impact of the background processes (emission factors, see Table S5) for transportation fossil fuels (EF_{fuel}) and plastics ($EF_{PE/PP}$ and EF_{PVC}). Since emissions factors do not depend on the size plant, they have been used as an input for analyzing the fossil production of plastics. $E_{landfill}$ represents the GHG emissions from the landfill, which depend on the behavior of landfilled materials. Although IPCC and EPA establish default values, some parameters are country-specific and even vary between regions (Penman *et al* 2006, EPA 2014). $E_{incineration}$ represents the GHG emissions from MSW refuse incineration with energy recovery. The current EF value for fossil transportation fuels in Europe is used even though it is expected to increase in the short term (Parliament 2004, COM 2016).

$$E_{BAU} = (E_{landfill} \cdot r_{landfill} + E_{incineration} \cdot r_{incineration}) \cdot (x_1 + y_1 + y_2) + EF_{fuel} \cdot z + (EF_{PE/PP} \cdot p_{PE} + EF_{PE/PP} \cdot p_{PP} + EF_{PVC} \cdot p_{PVC}) \cdot w \quad \text{(Eq. S1)}$$

3. Modeling of the BIO system

For the production of renewable-derived drop-in plastics, the MSW refuse has to be pretreated and converted into refuse derived fuel (RDF), a medium-quality solid fuel which is then further processed in the thermochemical biorefinery (further details in Table S1) (Aracil *et al* 2017). This pretreatment can vary depending on the characteristics of the MSW refuse. In spite of this, RDF production increases the lower heating value (LHV) of MSW refuse up to around 16 MJ kg^{-1} (Arena *et al* 2015, Onel *et al* 2014, Patel *et al* 2012, Yassin *et al* 2009). Like for other assessments of biomass residues, there are no upstream emissions (e.g. associated with cultivation, harvesting and direct and indirect land-use change) to be allocated to the MSW refuse (Parliament 2004).

The production of drop-in chemicals from RDF is analyzed according to a previous work of the authors where a thermochemical biorefinery producing dimethyl ether (DME) and methyl acetate (MA) from lignocellulosic biomass was technically, economically and

environmentally assessed (Haro *et al* 2015a, 2013). For producing biofuels and chemicals from RDF in a thermochemical biorefinery, the same processing technologies can be used than from lignocellulosic biomass (e.g., pyrolysis and gasification). Following the original design of the thermochemical biorefinery, the RDF is pretreated and converted into syngas after indirect gasification at atmospheric pressure and 850 ºC. The produced syngas, a mixture of H_2, CO, CO_2, light hydrocarbons, tars and inorganic compounds (in order of importance), is cleaned. There are some technical limitations when processing RDF-derived syngas not considered in this study, (i.e., removal of tars, heavy metals and inorganic compounds) (Panepinto *et al* 2014, Prabhansu *et al* 2015). After the clean-up the syngas is conditioned (adapting the composition for catalytic synthesis, including H_2/CO adjustment, light hydrocarbon reforming and CO_2 removal to maximize the catalytic performance in the synthesis loop). The clean and conditioned syngas is converted into DME and MA by means of catalytic synthesis using same or equivalent units as in the chemical industry, i.e., slurry and fixed-bed chemical reactors and heterogeneous catalysts (alumina-supported Cu-ZnO and H-MOR zeolite, respectively). The maximization of the production is carried out by means of energy and material integration of the synthesis loop including recirculation of unconverted syngas. In this study (Figure S3), DME is used as a substitute for fossil diesel and as a drop-in chemical for plastics production (PP and PE). It is assumed for a base case scenario that half of the DME produced in the biorefinery will be used as a fuel and the other half as a drop-in chemical. MA is used as a drop-in chemical to produce PVC. The conversion efficiency from chemical to plastic (mass basis) and the energy and material balance of the biorefinery, which also produces biofuels and heat and/or electricity, are shown in Table S2. The share of LDPE and HDPE is assumed to be equal to the demand of LDPE and HDPE in Europe (see Table S9).

For the incorporation of Bio-CCS, the CO_2 capture unit already located in the syngas conditioning section is used. The capture unit (amines) operates at pre-combustion conditions (capture efficiency of 95%) generating a very pure CO_2 stream (more than 99% molar dry basis) ready for compression and subsequent transport and sequestration. The capture ratio is defined here as the carbon captured in Bio-CCS relative to the total carbon emitted by the biorefinery without CCS. The capture ratio in the biorefinery is in principle limited to 25%, corresponding to the amount of pure CO_2 that needs to be captured to adjust the CO_2 composition in the syngas for the DME and MA catalytic synthesis (Haro *et al* 2013). Larger capture rates would only be possible if the flue gases from the power island were also treated (post-combustion CO_2 capture).

The process unit for CO_2 capture with amines demands low-pressure steam (120ºC), with a consumption of 4.5 MJ/kg CO_2. Since the absorption is not completely selective to CO_2, the following recovery fraction are assumed for the stream: 95% CO_2 recovery, 1% H_2 slip, 2% CO slip, 2% CH_4 slip, 2% C_2 slip, 20% C_{3+} slip. Pumping and other power consumptions are neglected due to their minor impact and the excess electricity in the biorefinery (Aracil *et al* 2017). The compression of the CO_2 (for transport) is carried out using multi-stage compressor units to 150 bar (maximum compression ratio of 3.5 and isentropic efficiency of 78%) resulting in an electric consumption of 0.11 MWh/t of CO_2.

For the sensitivity analysis considering post-combustion CO_2 capture in the biorefinery, the change in the energy demand is subtracted from the electricity generation in the plant.

Table S2. Energy and mass balance of the BIO system for Spain

	MSW	MSW refuse	RDF (input to the biorefinery)	DME (output from the biorefinery)	MA (output from the biorefinery)	Electricity (output from the biorefinery)	Heat (output from the biorefinery)	Capture CO_2 (Bio-CCS)	Electricity from the grid	Heat from district heating	PE	PP	PVC	Waste PE[c]	Waste PP[c]	Waste PVC[c]
MW (LHV basis)			100	23.4	10.2	7.1	-	0.6	20.3	0	4.2	2.4	5.9			
kg/h	42,857	32,142	22,500	3,008	1,861			5,500			354	200	1.247	354	13	84
Biogenic fraction (kg/h)	32,571[a]	24,428	17,100	2,286	1,414			4,180			269	152	948	269	10	64
Fossil fraction (kg/h)	10,286[a]	7,714	5,400	722	447			1,320			85	48	299	85	3	20
Moisture (%)	44	25	15													
Carbon content (% mass)		40.3	39.5	52.2	48.6			27			85.7	85.7	38.7	85.7	85.7	38.7
Recyclable fraction (% mass basis)[b]		19%														
Short or Long-life plastic														Short	Long	Long
Incineration disposal (% mass basis)														17		
Emissions from incineration (g CO_2 eq. /MJ plastic)														26.7	23	60.5
Recycling (% mass basis)														33		
Landfilling (% mass basis)														50		
Emissions from landfilling (g CO_2 eq. /kg plastic)														0 (see section 3.3)		

[a] Calculated from Table S1.

[b] See Figure S2.

[c] Applying Eq. S3, 6.7% of long-life plastics and 100% of short-life plastics become waste every year.

Table S3. Energy and mass balances of the BIO system for Sweden

	MSW	MSW refuse	RDF (input to the biorefinery)	DME (biofuel from the biorefinery)	Electricity (output from the biorefinery)	Heat (output from the biorefinery)	Capture CO_2 (Bio-CCS)	Electricity from the grid	Heat from district heating	PE	PP	PVC	Waste PE[c]	Waste PP[c]	Waste PVC[c]
MW, (LHV basis)			100	9	5	10	0.6	18	61	4.2	2.4	5.9			
kg/h	42,857	32,142	22,500	1504			5,500			354	200	1.247	354	13	84
Biogenic fraction (kg/h)	28,286[a]	21,214	14,850	993			3,630			234	132	823	234	9	55
Fossil fraction (kg/h)	14,571[a]	10,928	7,650	512			1,870			120	68	424	120	4	29
Moisture (%)	25	25	15												
Carbon content (% mass)		47.2	46.3	26.1			27			85.7	85.7	38.7	85.7	85.7	38.7
Recyclable fraction (% mass basis)[b]		34%													
Short or Long-life plastic													Short	Long	Long
Incineration disposal (% mass basis)													59		
Emissions from incineration (g CO_2 eq. /MJ plastic)													26.7	23	60.5
Recycling (% mass basis)													38		
Landfilling (% mass basis)													3		
Emissions from landfilling (g CO_2 eq. /kg plastic)													0 (see section 3.3)		

[a] Calculated from Table S1.

[b] See Figure S2.

[c] Applying Eq. S3, 6.7% of long-life plastics and 100% of short-life plastics become waste every year.

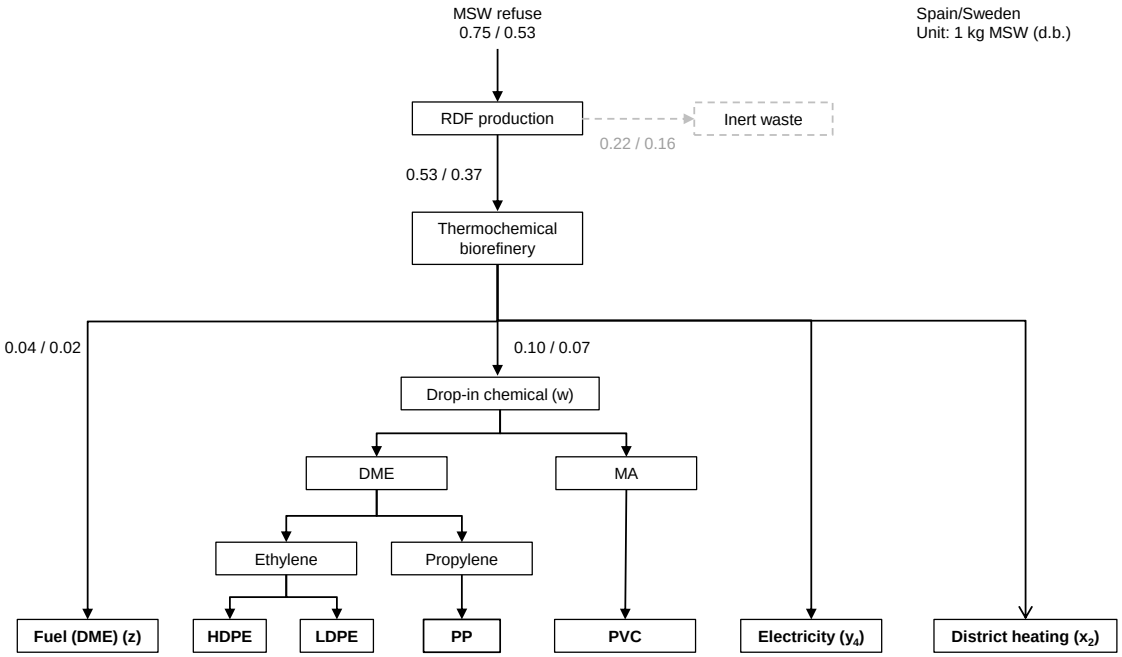


Figure S2. Description of the thermochemical biorefinery as a part of the BIO system. Final products are shown in bold. Values are in dry mass basis considering 1 kg of MSW as input for Spain and Sweden. The conversion efficiencies for renewable-derived plastics are in Table S2 and S3, and the shares of renewable-derived plastics, fuel, electricity and heat (district heating) in Table S4.

Table S4. Shares of renewable-derived plastics, drop-in chemicals, fuels, heat and electricity in the BAU and BIO systems (LHV basis), as defined in Figure 1 of the main text.

Share (LHV basis)	Spain	Sweden
w	24%	13%
x_1	0	54%
x_2	0	10%
x_3	0	44%
y_1	14%	0
y_2	39%	21%
y_3	40%	13%
y_4	13%	8%
z	23%	12%

The GHG impact of the BIO system (E_{BIO}) is calculated by adding up the emissions from the different processes involved (cradle-to-grave) in Eq. S2.

$$E_{BIO} = E_{TB} \cdot (y_4 + z + w + x_2) + EF_{electricity} \cdot y_3 + EF_{heat} \cdot x_3 \quad \text{(Eq. S2)}$$

The GHG balance of the biorefinery (E_{TB}) measures the average cradle-to-grave GHG emissions, in g of CO_2 eq. MJ^{-1} of total products, associated with the life cycle of the products from the thermochemical biorefinery. A methodology for the GHG balance in the production of biofuels was previously published based on an attributional LCA, and using the standard LCA characterization method, GWP(100), and characterization factors defined by IPCC AR5 (IPCC 2013). In this study, the production of plastics from renewable-derived drop-in chemicals entails some changes in the cradle-to-grave carbon flows (e) compared to the previous work:

- In the GHG emissions from the thermochemical biorefinery (e_p), the anthropogenic emissions in the transformation of the drop-in chemical into renewable-derived plastics are incorporated.
- The average biogenic carbon storage in renewable-derived plastic materials ($\bar{e}_{pool}$) is introduced in the equation as a negative term since it represents a GHG removal from the atmosphere (see section 5.1 for the modeling of average biogenic carbon storage in renewable-derived plastics).

Figure S3 shows the carbon balance in the production of renewable-derived plastics from MSW refuse. In the thermochemical biorefinery, around a third of the total carbon accumulated in MSW refuse is stored in the final products (fuels and renewable derived plastics), 17% is captured in the CCS process, the rest of the carbon (54%) is emitted to the atmosphere in flue gases. There are four fractions of biogenic carbon: biofuels, renewable derived plastics, CO_2 captured in the CCS process and CO_2 emitted to the atmosphere. The biogenic carbon stored in fuels is totally emitted to the atmosphere after it has been used (combustion). However, there is a variable biogenic carbon stored in the case of renewable-derived plastics since when they become waste, they can be recycled, incinerated or landfilled. If they are recycled, the carbon remains stored for at least one more life cycle. However, after a number of recycling cycles the plastic material will be eventually incinerated or landfilled. In the case of incineration with energy recovery, the carbon stored is totally

emitted to the atmosphere whereas in the case of the landfilling, the carbon is permanently stored since degradability of plastic waste is very low. Hence, there are three types of carbon storage: carbon stored through the Bio-CCS process, carbon stored in plastics still in use in the market (original and recycled plastics) and carbon stored in plastic waste landfilled. The fraction of total carbon stored after 100 years is higher in the case of Spain (8.0%), where landfilling is dominant, than in the case of Sweden (2.3%), where landfilling is negligible. The biogenic carbon stored by Bio-CCS incorporation would be about twice as the biogenic carbon stored in the renewable-derived plastics in the Spanish case whereas seven times in the Swedish one.

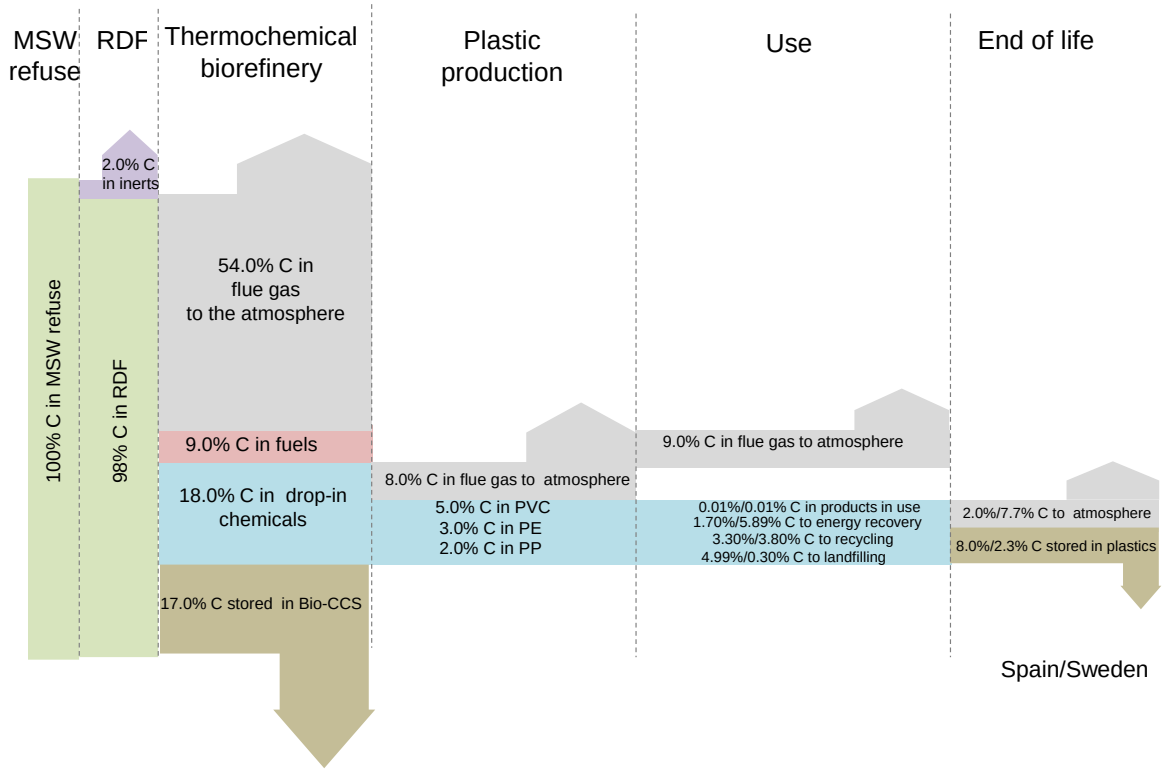


Figure S3. Carbon balance in the production of renewable-derived plastics from MSW refuse in Spain and Sweden.

For the electricity balance, the EF (Table S5) depends on the selected country and, therefore, the average values from the grid mix are used (Jacopo Giuntoli *et al* 2015). For the heat balance, a conservative value is taken from the Swedish heat mix based on heat production from waste and biomass combined heat and power plants, as well as from

industrial excess heating (Chalmers University of Technology 2014). There is no heat demand in the Spanish case.

Table S5. Relevant data for emissions in the BAU and BIO systems (biogenic-CO_2 emissions are excluded).

Emissions (g CO_2 eq.·kg^{-1} MSW)		
BAU system	Spain	Sweden
$E_{incineration}$	331	543
$E_{landfill}$	454	0
Emission factors (g CO_2 eq.·MJ^{-1})		
BAU system		
EF_{fuel}(Directive 2015/1513)	90.3	
$EF_{PE/PP}$ (Plastics Europe, 2014)	38	
EF_{PVC} (ECVM and Plastics Europe, 2005)	94	
BIO system		
$EF_{electricity}$ (EUR 27215 EN, 2015)	110.7	17.5
EF_{heat} (Systems Perpectives on Biorefineries, 2014)	-	-68

3.1 Modeling of biogenic carbon in renewable-derived plastics

For the modeling of biogenic carbon in renewable-derived plastics, products still in use in the market (P) and plastics becoming waste (W) are distinguished. Short-life plastic products ($P_{short\text{-}life\ plastics}$) are considered to become waste in less than a year. However, most of long-life plastics usually remain in the market for more than one year. Therefore, Eq. S3 defines the fraction of the long-life plastic products becoming waste ($W_{long\text{-}life\ plastics}$) in one year. Long-life plastic products still in use ($P_{long\text{-}life\ plastics}$) are calculated as 1-$W_{long\text{-}life\ plastics}$.

$$W_{long-life\ plastics} = \frac{W - P_{short-life\ plastics}}{P_{long-life\ plastics}} \quad \text{(S3)}$$

The horizon for this study is 100 years as recommended by the Intergovernmental Panel on Climate Change (IPCC) (IPCC 2014). In the year 0, $e_{material}$ represents the input of new plastic products in the market in terms of g CO_2 eq.·MJ^{-1} of plastics (C input) whereas $e_{landfill}$ and e_{energy} have a zero value. From year 1 to 100, $e_{landfill}$ and e_{energy} increase since more and more plastic waste is landfilled or energy recovered and, therefore, $e_{material}$ decreases. Eq. S4-S9 show the calculations:

- Year 0:

$$e_{material} = C\ input \cdot \alpha \quad \text{(S4)}$$

where α is the biogenic fraction of the MSW refuse (%)

- Successive years for short-life plastic materials:

$$e_{material\ (year\ i)} = e_{material\ (year\ i-1)} \cdot W_{short-life\ plastics} \cdot r_{recycling} \quad \text{(S5)}$$

The parameter $e_{landfill\ (year\ i)}$ is calculated as $e_{material\ (year\ i)}$ replacing $r_{recycling}$ by $r_{landfilling}$.

$$e_{energy\ (year\ i)} = e_{material\ (year\ i-1)} \cdot \frac{(1-\alpha)}{\alpha} \cdot W_{short-life\ plastics} \cdot r_{energy\ recovery} \quad \text{(S6)}$$

- Successive years for long-life plastic materials:

$$e_{material\ (year\ i)} = e_{material\ (year\ i-1)} \cdot (1 + W_{long-life\ plastics} \cdot (r_{recycling} - 1)) \quad \text{(S7)}$$

The other two equations ($e_{landfill}$ and e_{energy}) differ from those of short-life plastic materials changing $W_{short\text{-}life\ plastics}$ by $W_{long\text{-}life\ plastics}$. Finally, the parameter e_{pool} is calculated (Eq. S8).

$$e_{pool\ (year\ i)} = (e_{material} + e_{landfill} + e_{energy})_{year\ i} \quad \text{(S8)}$$

Eq. S9 is used to calculate the average biogenic carbon storage in renewable-derived plastics for the differential GHG impact.

$$\overline{e_{pool}} = \frac{\sum e_{pool\ (from\ year\ 0\ to\ 100)}}{100} \quad \text{(S9)}$$

In Figure S4, the evolution of each parameter from a single carbon input in the year 0 (i.e., not a sustained production) is shown. The carbon input is higher in the case of Spain due to the higher biogenic fraction in the Spanish MSW refuse. The impact of the $e_{material}$ in the carbon pool is higher than the impact of $e_{landfill}$ for the first 15 years in Spain whereas in the case of Sweden, $e_{material}$ is dominant for 60 years. The high Swedish incineration ratio makes e_{pool} positive from year 20 whereas this is permanently negative in the case of Spain.

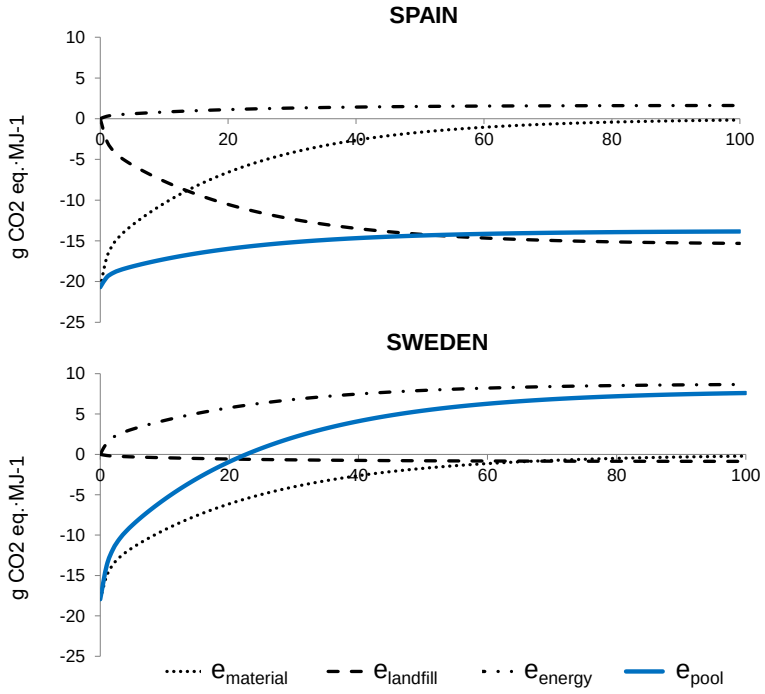


Figure S4. Evolution of the biogenic carbon pool for a single 1 MJ of renewable-derived plastic produced in year 0 (e_{pool}), as a function of the carbon flow (e_{energy}) and pools ($e_{landfill}$ and $e_{material}$) for 100 years in g of CO_2 eq.·MJ^{-1} of renewable-derived plastics. For the representation, specific data for Spanish and Swedish waste management schemes are used (Figure S2).

4. Attributional carbon cycle assessment: GHG balance and GHG impact

4.1. GHG balance in the production of biofuels and renewable-derived drop-in chemicals (BIO system)

In the GHG balance, the considered cradle-to-grave carbon flows (e) are:

- GHG emissions from pretreatment and RDF production (e_{pt}).
- GHG emissions from transport of the RDF to the thermochemical biorefinery (e_t) (Table S6).

Table S6. Emission factors for feedstock transport and final products distribution. Data include empty return trip for a maximum distance of 250 km by truck (Giuntoli *et al* 2015).

	$g \cdot t^{-1} \cdot km^{-1}$
CO_2 emissions	59.4097
CH_4 emissions	0.0034
N_2O emissions	0.0015

- GHG emissions from the thermochemical biorefinery (e_p), which include all process units processing RDF into biofuels (gasification, gas cleaning, synthesis, power island and product upgrading) (Haro *et al* 2015b). There are three contributors: the upstream emissions associated to consumables used in the process, the combustion emissions from the fossil fraction (Jones *et al* 2013) and the fossil emissions from the chemical-to-plastic process.
- GHG emissions from carbon capture and storage ($e_{Bio\text{-}CCS}$). It is a negative contributor since only the biogenic carbon fraction is considered (Directive 28/2009). In this parameter, the electricity consumed in the compression and injection of CO_2 captured is also considered. GHG emissions associated to the transport by pipelines are considered negligible (leakages).
- GHG emissions from final products distribution (e_d). In case of producing more than one product (biofuels and/or renewable-derived drop-in chemicals), this parameter should be allocated according to wet low heating value of the biofuels as RED establishes. Electricity does not have associated emissions from its distribution.
- GHG emissions from the use of the final products (e_u). Biofuels combustion emits GHG other than CO_2, so we consider these gases have to be accounted for since they are emitted in a discernible amount, e.g. CH_4; or have a high GWP, as in the case of N_2O (265) (IPCC 2013). Besides, the fossil fraction in the biofuels should be included. In case of producing more than one biofuel, this parameter should be allocated. Electricity does not have associated emissions from its use.
- Average biogenic carbon storage in renewable-derived plastics (e_{pool}). This is introduced in the equation as a negative term since it represents a GHG removal from the atmosphere (see point 5.1 for calculation of e_{pool}).

Equation (S10) shows the calculation of the global GHG balance for the advanced waste-to-energy plant (E_{TB}) considering DME is used to produce both biofuels ($f_{biofuel}$) and renewable-derived drop-in chemicals ($f_{biochem}$).

$$E_{TB}=e_{pt}+e_p+e_t+\left(x_{DME}\cdot f_{biofuel}\ (e_d+e_u)+x_{DME}\cdot f_{chem}\left(e_d+e_u+e_{no_comb}\right)\right)+x_{MA}(e_d+e_u)+x_{elect}(e_d+e_u)+x_{heat}(e_d+e_u) \quad \text{(S10)}$$

where f_i is the fraction of product i produced from DME (in %) being $f_{biofuel}=f_{chem}= 0.5$ and x_i is the fraction of product i in the biorefinery (%),

4.2. <u>GHG balance in the landfill (BAU system)</u>

Table S7. Emission factors used in the calculation of the GHG balance in landfilling (BAU system) (see Aracil *et al* 2017 for additional details on landfill modeling).

Default values			
Biogas composition	CH_4	50%	
	CO_2	50%	
CH_4 oxidized in cover soils of modern, managed landfills.		10%	
Degradable organic carbon (DOC)	DOC=0.4·A+0.2·B+0.15·C+0.43·D+0.24·E		A = paper (%) B = garden and park waste (%) C = food waste (%) D = wood and straw waste (%) E = textiles (%)
Fraction of C anaerobically	50%		

decomposed in the landfill		
Destruction efficiencies for CH_4 in the electricity production	99%	
Country-specific data		
MSW generation per capita	435 (2014)	kg/cap/year (Eurostat)
Ratio of MSW landfilled	76%	
Ratio of biogas recovered	70%	
Results		
C stored	70,000	g C·t refuse^{-1}·year^{-1}
Average CH_4 emissions	20,654	g CH_4·t refuse^{-1}·year^{-1}

*Values are calculated or taken as default values in weight fraction and wet basis.

4.3. GHG balance in the incineration plant

Table S8. Emission factors used in the calculation of the GHG balance in incineration plant (BAU system) (see Aracil *et al* 2017 for additional details on incineration).

Default values			
Non-CO_2 emissions	CH_4	0.25	g CO_2 eq.·MJ^{-1}
	CO_2	0.444	
Conversion factor	CO_2	99%	
	Non-CO_2 GHG	1%	
Energy efficiency	25% (electricity) 65% (heat)		

Table S9. Demand of selected plastics in Europe, expressed as share of total plastic demand (Plastics Europe 2015).

Plastic	**HDPE**	**LDPE**	**PP**	**PVC**
European demand ratio (%)	12.1	17.2	19.2	10.3

4.4. Differential GHG impact

The differential GHG impact in the case of using MSW refuse as feedstock (Eq. S11) determines whether climate change mitigation would be higher when this fraction of the MSW goes to landfilling and incineration or to the thermochemical biorefinery. The differential GHG impact is expressed in terms of g CO_2 eq.·MJ^{-1} of output for 100 years.

Differential GHG balance = E_{BIO} - E_{BAU} (Eq. S11)

The functions represented are the same in all the systems considered. To compensate for the deficit in energy functions (i.e., heat and electricity) in the BIO system and the substitution of transportation fuels and plastics in the BAU system, we use background processes (emission factors). For the calculation of the differential GHG impact, the BAU system is unchanged for 100 years (static model). Table S5 and Table S9 present the emission factors and the shares of renewable-derived plastics, drop-in chemicals, fuels, heat and electricity in the BAU and BIO systems, respectively.

In Equation S13, E_{BAU} is calculated considering that both waste management systems (landfilling and incineration) are fed by an equivalent amount of MSW to the advanced waste-to-energy plant; then, the emissions are allocated according to the rate ($r_{incineration}$) (see Fig. S2).

The GHG impact is calculated in terms of grams of CO_2 equivalent per ton of MSW refuse and then converted using the system energy efficiency (Equation (S14)) to the same functional unit in both BAU and BIO systems, i.e., 1 MJ of final product mix from the advanced waste-to-energy plant. The differential GHG impact (Equation (S15)) compares the GHG emissions reduction potential for the replacement of the BAU system with the BIO system (Gaudreault and Miner 2015).

$$E_{BIO} = E_{TB} \cdot (y_4 + z_2 + w_2 + x_2) + EF_{electricity} \cdot y_3 + EF_{heat} \cdot x_3 \quad \text{(S12)}$$

$$E_{BAU} = EF_{fuel} \cdot z_1 + EF_{chem} \cdot w_1 + (\sum_i E_i \cdot r_i) \cdot (y_1 + y_2 + x_1) \quad \text{(S13)}$$

$$E_i = \frac{\text{g } CO_2 \text{ eq}}{\text{t MSW refuse}} \cdot \frac{\text{t MSW refuse/year}}{(\text{MJoutput/year}) \cdot \left(\frac{\eta_i}{\eta \text{ biorefinery}}\right)} \quad \text{(S14)}$$

where i is landfill and incineration.

$$\text{Differential GHG impact} = E_{BIO} - E_{BAU} \quad \text{(S15)}$$

5. Modeling of time-dependent GHG emissions

AGTP is used to calculate the DCI, a measurement of the climate benefit in the production of renewable-derived plastics from MSW refuse to compare the results of regions with different waste management systems. The units of DCI are K·kg MSW^{-1}. The DCI is based on the AGTP metric as the surface temperature response to the replacement of BAU with BIO (Eq. S6). The values of AGTP for BIO and BAU systems are calculated from the annual emissions of each WMGHG as explained elsewhere (Aracil *et al* 2017, Giuntoli *et al* 2015, IPCC 2013).

The emissions to the atmosphere of each individual Well-Mixed GHG (WMGHG) from the amount of MSW refuse managed in a year are called pulse emissions. These pulse emissions are considered constant over time for biofuel production and incineration but in the case of the landfill, emissions must be modeled. The CH_4 emission profile is expressed as actual annual emissions using IPCC Waste Model (Figure S5) (IPCC 2013).

Then, the remaining GHG in the atmosphere is calculated by multiplying the pulse emissions of previous years by the atmospheric decay of the gas at time t (R) (Eq. S16-18). Table S10 shows the values for the parameters. The sum of the pulse emissions in the year i and the remaining GHG in the atmosphere from the year 1 to (i-1) is the cumulative GHG (GHGt) (Eq. S20).

$$R_{CO2}(t) = a_0 + \sum_{i=1}^{3} a_i \cdot e^{-t/\tau_i} \quad \text{(Eq.S16)}$$

$$R_{CH4}(t) = e^{-t/\tau_{CH4}} \quad \text{(Eq.S17)}$$

$$R_{N2O}(t) = e^{-t/\tau_{N2O}} \quad \text{(Eq.S18)}$$

Table S10. Parameters used for the calculation of R in Eq. S16 to S18

a_0	a_1	a_2	a_3	τ_1	τ_2	τ_3	τ_{CH4}	τ_{N2O}
0.2173	0.224	0.2824	0.2763	394.4	36.54	4.304	12.4	121

$$rGHG(t) = \sum_{1}^{t} E(t-1) \cdot R(t) \quad \text{(Eq.S19)}$$

$$GHG_t = E(t) + rGHG(t) \quad \text{(Eq.S20)}$$

The CO_2 concentration is calculated from cumulative CO_2 and used to calculate the Radiative Forcing (RF) according to equation S22 and Table S11, whereas cumulative CH_4 and N_2O are directly used in the formulas (Equation S23-S24). Table S12 shows the values for the parameters. RF is divided by the kilograms of MSW refuse per year in such way that the functional unit is 1 kg of MSW refuse. The cumulative Radiative Forcing or Absolute Global Warming Potential (AGWP) is calculated by integrating the RF over a defined time horizon. Absolute Global surface Temperature change Potential (AGTP) is the global mean surface temperature change at a given future time horizon (Equation S25-26). Table S13 show the values for the parameters. In our case, the time horizon is set to 100 years where GHG emissions start in the year 0. According to IPPC, the uncertainty range for RF and AGWP is ±24% and ±26% respectively. Final AGWP and AGTP are obtained by adding those ranges and integrating the same system.

$$[CO_2] = \frac{(CO_2)t \cdot 10E3}{\text{atmosphere mass}} \cdot \frac{\text{dry air molecular mass}}{CO_2 \text{molecular mass}} \quad \text{(Eq. S21)}$$

Table S11. Parameters used in the calculation of $[CO_2]$ in Eq. S21.

Atmosphere mass (kg)	5.14E+18
Dry air molecular mass (g/mol)	28.97
CO_2 molecular mass (g/mol)	44.01

$$RF_{CO2} = 5.35 \cdot \ln\left(1 + \frac{[CO_2]}{C_0}\right) \quad \text{(Eq. S22)}$$

$$RF_{CH4} = (1 + f_1 + f_2) \cdot A_{CH4} \cdot CH_{4T} \qquad \text{(Eq.S23)}$$

$$RF_{N2O} = \left(1 - 0.36 \cdot (1 + f_1 + f_2) \cdot \frac{RE_{CH4}}{RE_{N2O}}\right) \cdot A_{N2O} \cdot N_2O_T \qquad \text{(Eq.S24)}$$

where

C_0: CO_2 concentration in the atmosphere (ppm_v)

f_1 and f_2: correction factor due to effects on ozone and stratospheric H_2O respectively

A_i: radiative forcing per unit mass ($W/m^2 \cdot kg$)

RE_i: radiative efficiency of gas I on volume basis ($W/m^2 \cdot ppb$)

Table S12. Parameters used for the calculation of RF in Eq. S22 to S24.

Parameter	Value	Unit
A CH_4	1.28E-13	$W/(m^2 \cdot ppb)$
RE CH_4	3.63E-4	$W/(m^2 \cdot kg)$
A N_2O	3.85E-13	$W/(m^2 \cdot ppb)$
RE N_2O	3.00E-3	$W/(m^2 \cdot kg)$
f1	0.5	-
f2	0.15	-

$$AGTP(t) = \int_0^t RF(t') \cdot \delta T(t-t') dt' \quad \text{(Eq. S25)}$$

$$\delta T = \sum_{i=1}^{2} \frac{ci}{di} \cdot \exp\left(-\frac{t}{di}\right) \quad \text{(Eq. S26)}$$

Table S13. Parameters used for the calculation of AGTP in Eq. S26.

Parameter	1st term	2nd term	Unit
c_i	0.631	0.429	$K/(W \cdot m^2)$
d_i	8.4	409.5	years

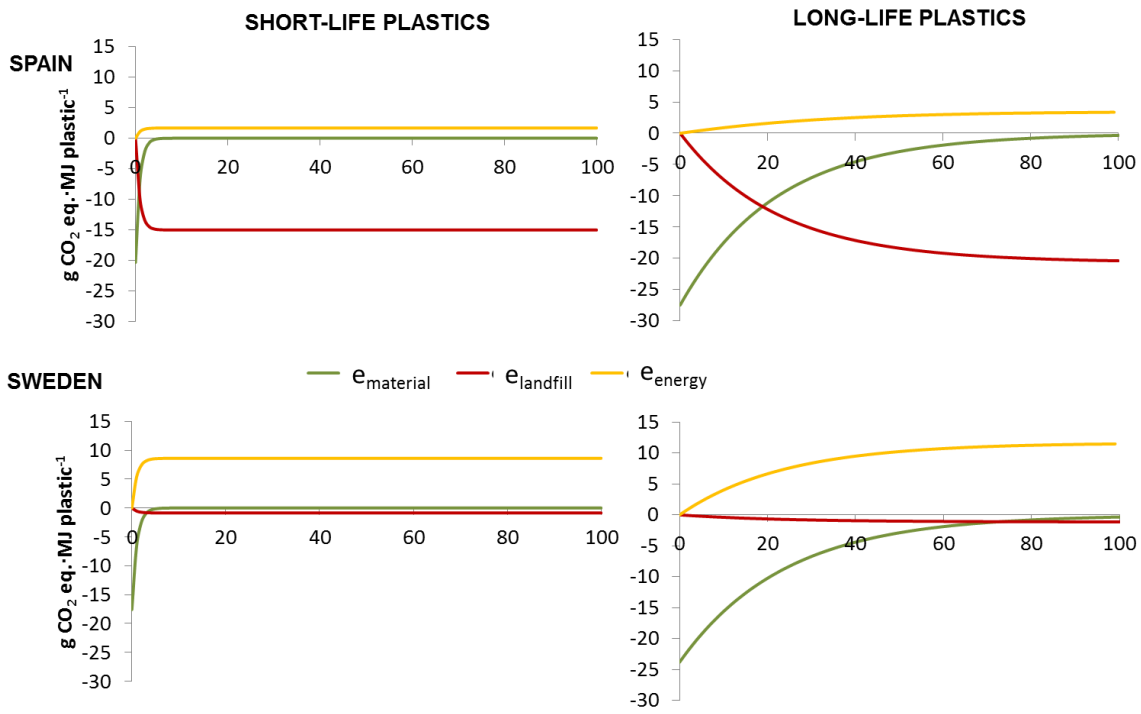


Fig. S5. Evolution of the carbon flow (e_{energy}) and carbon pools ($e_{landfill}$ and $e_{material}$) over time in Spain and Sweden distinguishing between short-life (LDPE and HDPE) and long-life plastics (PP and PVC) in terms of g CO_2 eq.·MJ of plastic^{-1}. The evolution in the plastics waste management system is considered.

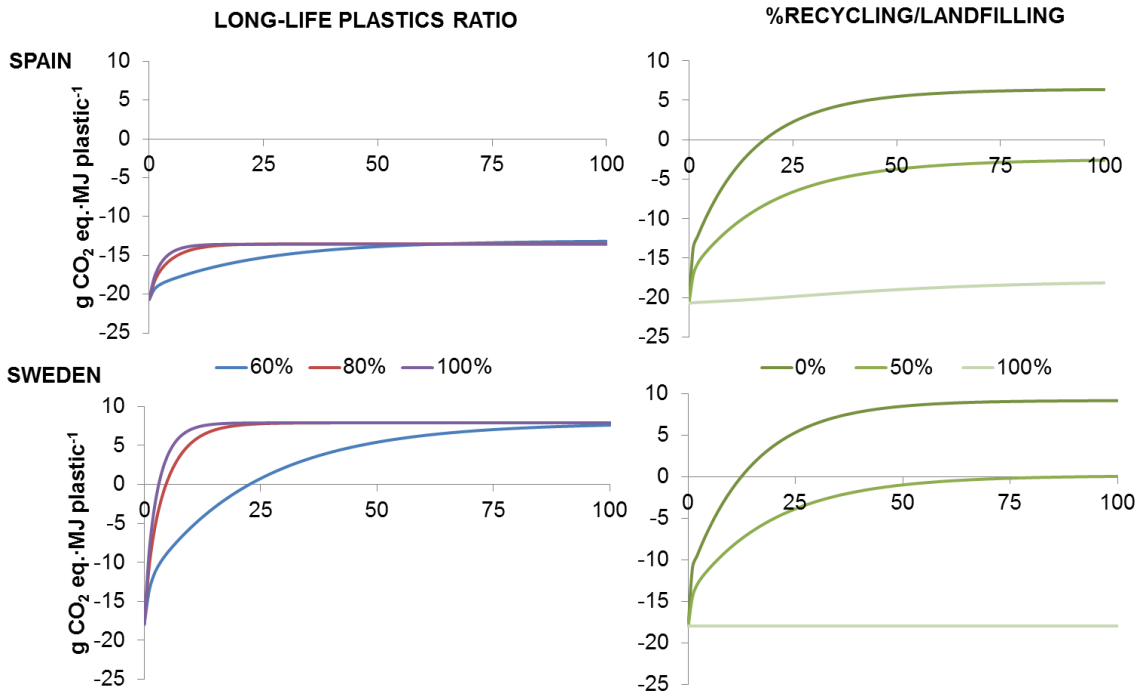


Fig. S6. Sensitivity analysis of the e_{pool} to the ratio of long-life plastics (PP and PVC) demanded in the market (left) and to the recycling/landfilling ratio in the plastics waste management system (right) in Spain and Sweden in terms of g CO_2 eq.·MJ of plastic^{-1}. The evolution in the plastics waste management system is considered.

6. Summary of assumptions for the study

Table S14 Definition and common-specifics assumptions for both systems and scenarios considered in this study.

	Definition	Common assumptions	Specific assumptions for time-dependent scenario
Both systems	- Both systems are designed to treat the same amount of MSW refuse, while producing the same amount and type of products (energy products and plastics)	- The functional unit is 1 MJ of final products from the thermochemical biorefinery, according to European standard (International Reference Life Cycle Data System (ILCD) Handbook 2010).	- Landfilled plastic waste form a permanent carbon pool
			- Plastics waste recycled form a temporary carbon pool. The permanence depends on the lifetime of the plastic material and the number of recycling cycles achieved
		- Only Well Mixed GHG (WMGHG) including CO_2, CH_4 and N_2O are considered.	- In the case of energy recovery, there is only one carbon flow to the atmosphere.
			- LDPE and HDPE are used in the production of short-time products whose

	Definition	Common assumptions	Specific assumptions for time-dependent scenario
			lifetime is under 1 year, i.e., plastic bottles. - PP and PVC present a longer durability and resistance and they are considered to be used mostly in the production of long-life products (over 1 year). - The absorption of CO_2 in the original biomass waste in the MSW refuse cancels out between the two systems and we do not attempt to account for it. - To calculate the equivalent storage of carbon in 1 MJ of plastic produced in one year (e_{pool}), three parameters are defined: the biogenic carbon captured in products still in use and in recycled products ($e_{material}$); the biogenic carbon captured in plastic waste landfilled ($e_{landfill}$); and the anthropogenic emissions (carbon flow) from incineration (e_{energy}). - The system assumes a progressive banning of landfilling in Europe, a decarbonization of the electricity sector and an increase in the emissions from fossil transportation fuels (due to more emissions in the use of non-conventional crude oil in European refineries). - For Spain, the targets set in the national plan are used to define the evolution of the MSW management system for the first 5 years of the period analyzed. - From the year 2025 to 2120, the management is split into (mass basis): 1% of landfilling, 65% of recycling and 34% of energy recovery. - For Sweden an objective of 1% of landfilling, 65% of recycling and 34% of energy recovery are assumed in the year 2120 (mass basis). - The electricity mix is assumed as follow: Sweden would keep constant emissions while Spain would gradually reduce its emissions until both countries reach the same level in 2120. - GHG emissions from district heating in Sweden would also remain constant. (there is no district heating in Spain)
Specific for BIO system	- MSW refuse was used to produce renewable-derived plastics following a drop-in		- Emissions trajectories of biogenic CO_2, instead, are considered in detail for all the systems.

	Definition	Common assumptions	Specific assumptions for time-dependent scenario
	approach, fuels, electricity and district heating. - A thermochemical biorefinery was employed whose configuration is independent of the region assessed.	- For MSW refuse composition see Aracil 2017 - For balance of electricity and heat, district heating and production from conventional waste management see JRC 2015 - The deficit of electricity production from the regional grid and the deficit of heat from the heat mix were balanced in accordance with each region - Landfilled plastic waste form a permanent carbon pool - Plastics waste recycled form a temporary carbon pool. The permanence depends on the lifetime of the plastic material and the number of recycling cycles achieved	- The dynamic storage of biogenic carbon is incorporated considering the evolution of the waste management scheme as has been done for the BAU system. - The biogenic carbon stored in renewable-derived plastics (e_{pool}) and from Bio-CCS ($e_{Bio\text{-}CCS}$) are modeled as negative contributions.
Specific for BAU sytem	- Conventional MSW refuse management scheme was considered. This means that MSW refuse is landfilled or incinerated to produce district heating and/or electricity which can be exported to the grid. - It also includes the production of transportation fuels and plastics from fossil fuels.		

7. Additional results

7.1. GHG balance of the advanced waste-to-energy (WtE) plant

Fig. S7 shows the individual contribution of each parameter to the global GHG balance (E_{TB}) based on the methodology used in our previous work (Aracil et al. 2017). The GHG balances achieve values of 1 g CO_2 eq.·MJ^{-1} for Spain and 39 g CO_2 eq.·MJ^{-1} for Sweden. The difference comes from the higher biogenic fraction in Spanish MSW refuse, reducing the GHG emissions in the life cycle. The parameter e_{pt} is not in the figure since the electricity and heat needed for the RDF production is considered to come from the advanced waste-to-energy plant. The emissions from the processing (e_p) are the main contributor to the GHG balance for both countries. $\bar{e}_{pool}$ is the equivalent carbon storage considering the 100 years. It is negative in the case of Spain (-7 g CO_2 eq.·MJ^{-1}) compared with the positive value in the case of Sweden (1 g CO_2 eq.·MJ^{-1}) due to a higher landfilling ratio. The ratio of carbon captured in the Bio-CCS process and carbon captured in renewable-derived plastics changes considerably in the GHG balance regarding the carbon balance since an average of 100 years is calculated.

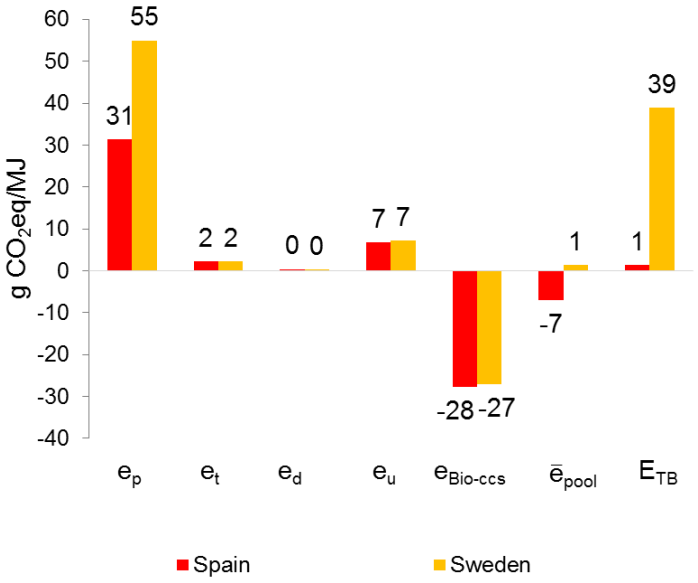


Fig S7. GHG balance of the cradle-to-grave emissions associated with the life cycle of the thermochemical biorefinery using MSW refuse as feedstock. Units: g CO_2 eq. per of 1 MJ of products (sustained production).

7.2. Differential GHG impact (BIO-BAU)

The differential GHG impact does not consider neither the evolution of MSW management in Europe, nor the dynamic storage of biogenic carbon in renewable-derived plastics (i.e., only the average biogenic storage is considered assuming current waste management, $\bar{e}_{pool}$). Thus, it cannot give an accurate comparison of the two GGR technologies (renewable-derived plastics and Bio-CCS). However, it serves to understand the behavior of the BAU and BIO system and the relative impact of the main parameters on the study. Prior to directly compare the production of renewable-derived plastics and the Bio-CCS incorporation, the emissions in the BAU and BIO system are presented (Figure S8). The emissions associated with the BIO system (E_{BIO}) are higher in Spain than in Sweden (68 and 15 g CO_2 eq.·MJ^{-1}, respectively). Therefore, the balance of electricity and heat has a larger impact than the higher biogenic fraction of MSW refuse in Spain. Sweden has a very low-carbon electricity grid and heat mix. Conversely, the comparison of the emission associated with the BAU system (E_{BAU}) (134 and 183 g CO_2 eq.·MJ^{-1} for Spain and Sweden, respectively) reveals the impact of the larger biogenic fraction in Spain and high landfilling rate. There is little impact of renewable-derived plastics (-7 and +1 g CO_2 eq.·MJ^{-1} for Spain and Sweden, respectively –orange dotted area in Figure 8–). The $\bar{e}_{pool}$ is positive for Sweden due to the low biogenic fraction in MSW refuse and the high incineration rate. The impact of renewable-derived plastics production is less significant than for Bio-CCS (-27 and -28 g CO_2 eq.·MJ^{-1} for Spain and Sweden, respectively –blue dotted area in Figure S8–). Therefore, Bio-CCS would seem to be a more appropriate GGR technology using a static assessment. Anyway, the differential GHG impact is negative in all cases, i.e., there is a climate benefit considering a static assessment.

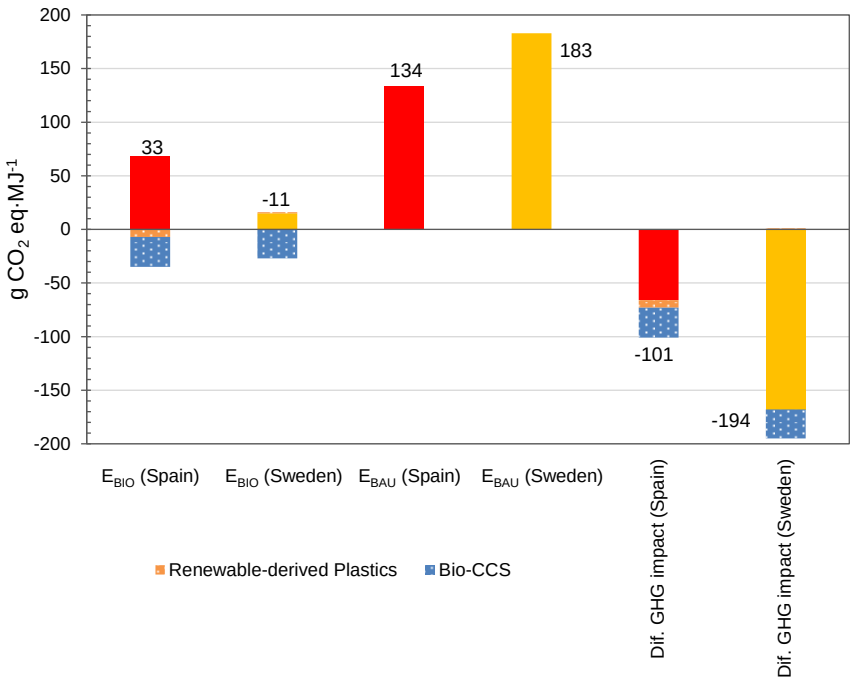


Fig S8. Differential GHG impact based on the emissions from the BIO and BAU systems. The impact of renewable-derived plastics and Bio-CCS is disaggregated. The numbers refer to net values including both renewable-derived plastics and Bio-CCS.

7.3. Sensitivity analysis of the differential GHG impact

Figure S9 shows the impact of the biogenic carbon storage on plastics ($\bar{e}_{pool}$) and the Bio-CCS process ($e_{Bio\text{-}CCS}$) on the global GHG balance of the advanced waste-to-energy plant (E_{TB}), which depends on the biogenic fraction of MSW refuse. In the sensitivity analysis, the biogenic carbon in MSW refuse varies from 25 to 100%, although only variations from 50 to 80% have been reported in the literature (IEA 2012). The higher the biogenic fraction, the lower the GHG balance (E_{TB}). As an extreme case, if biowaste were used to produce plastic materials, the biogenic fraction would be 100%, which is also shown in the figure.

Sweden only achieves a negative $\bar{e}_{pool}$ if the biogenic fraction is over 75%, since landfilling is negligible, and the potential of carbon storage only lies in the plastics still in use and recycled plastics. For both countries, $e_{Bio\text{-}CCS}$ represents a higher carbon pool than $\bar{e}_{pool}$. The difference between Spain and Sweden lies in the emissions associated with the electricity consumption during the compression and injection of the carbon in the Bio-CCS process.

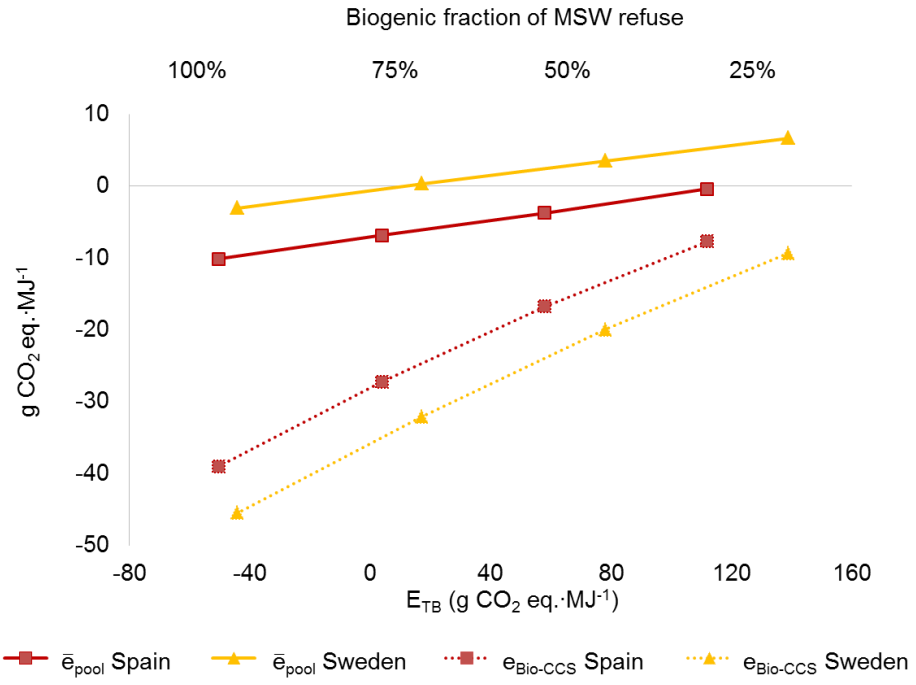


Figure S9. Sensitivity analysis of the global GHG balance (E_{TB}) and average biogenic carbon storage ($\bar{e}_{pool}$) to the biogenic fraction of the feedstock in Spain and Sweden. The difference in Bio-CCS process between Spain and Sweden is due to the emissions associated with the electricity consumption during the compression and injection of the carbon. $e_{Bio\text{-}CCS}$ in Sweden is better than in Spain since Sweden has a lower-carbon energy mix.

References

Aracil, C., Haro, P., Giuntoli, J., & Ollero, P. (2017). Proving the climate benefit in the production of biofuels from municipal solid waste refuse in europe. Journal of Cleaner Production, 142, 2887-2900.

Arena, U., Di Gregorio, F., De Troia, G., & Saponaro, A. (2015). A techno-economic evaluation of a small-scale fluidized bed gasifier for solid recovered fuel. Fuel Processing Technology, 131, 69-77.

Chalmers University of Technology. (2014). Systems Perspectives on Biorefineries (Goteborg, Sweden) Online: https://www.chalmers.se/en/areas-of-advance/energy/Documents/Systems Perspectives on/Systems_Perspectives_on_Biorefineries_2014_v3.1b.pdf

COM 2016 Proposal for a DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on the promotion of the use of energy from renewable sources (recast). Online: http://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1485356116722&uri=CELEX:52016PC0767

EPA 2014 Framework for assessing biogenic CO2 emissions from stationary sources. Washington, DC: Environmental Protection Agency. Online: http://www.epa.gov/climatechange/downloads/Framework-for-Assessing-Biogenic-CO2-Emissions.pdf.

Fischer C, Gentil E, Ryberg M and Reichel A. (2013). Managing municipal solid waste — a review of achievements in 32 European countries. EEA Report No 2/2013

Gaudreault, C., & Miner, R. (2015). Temporal aspects in evaluating the greenhouse gas mitigation benefits of using residues from forest products manufacturing facilities for energy production. Journal of Industrial Ecology, 19(6), 994-1007.

Giuntoli, J., Caserini, S., Marelli, L., Baxter, D., & Agostini, A. (2015). Domestic heating from forest logging residues: Environmental risks and benefits. Journal of Cleaner Production, 99, 206-216.

Haro, P., Aracil, C., Vidal-Barrero, F., & Ollero, P. (2015a). Balance and saving of GHG emissions in thermochemical biorefineries. Applied Energy, 147, 444-455.

Haro, P., Aracil, C., Vidal-Barrero, F., & Ollero, P. (2015b). Rewarding of extra-avoided GHG emissions in thermochemical biorefineries incorporating bio-CCS. Applied Energy, 157, 255-266.

Haro, P., Ollero, P., Villanueva Perales, A. L., & Gómez-Barea, A. (2013). Thermochemical biorefinery based on dimethyl ether as intermediate: Technoeconomic assessment. Applied Energy, 102, 950-961.

Haro, P., Villanueva Perales, A. L., Arjona, R., & Ollero, P. (2014). Thermochemical biorefineries with multiproduction using a platform chemical. Biofuels, Bioproducts and Biorefining, 8(2), 155-170.

IPCC. (2014). Climate Change 2014: Mitigation of Climate Change Online: http://www.ipcc.ch/report/ar5/wg3/

IPCC. (2013). IPCC Fifth Assessment Report (AR5) IPCC s. 10-12

Jacopo Giuntoli, Alessandro Agostini, Robert Edwards L M 2015 European Commission EUR 27215 EN – Joint Research Centre – Institute for Energy and Transport Title: Solid and gaseous bioenergy pathways: input values and GHG emissions Office of the European Union.

Jones, F. C., Blomqvist, E. W., Bisaillon, M., Lindberg, D. K., & Hupa, M. (2013). Determination of fossil carbon content in swedish waste fuel by four different methods. Waste Management and Research, 31(10), 1052-1061.

Network E C 2010 Organic resources and biological treatment (Spanish Report).

Onel, O., Niziolek, A. M., Hasan, M. M. F., & Floudas, C. A. (2014). Municipal solid waste to liquid transportation fuels - part I: Mathematical modeling of a municipal solid waste gasifier. Computers and Chemical Engineering, 71, 636-647.

Panepinto, D., Tedesco, V., Brizio, E., & Genon, G. (2015). Environmental performances and energy efficiency for MSW gasification treatment. Waste and Biomass Valorization, 6(1), 123-135.

Parliament E 2004 Directive 2003/71/EC Euratom 2001 20–30

Patel, C., Lettieri, P., & Germanà, A. (2012). Techno-economic performance analysis and environmental impact assessment of small to medium scale SRF combustion plants for energy production in the UK. Process Safety and Environmental Protection, 90(3), 255-262.

Penman, J., Gytarsky, M. I. C. H. A. E. L., Hiraishi, T. A. K. A., Irving, W., & Krug, T. (2006). IPCC guidelines for national greenhouse gas inventories. Directrices para los inventarios nacionales GEI.

Plastics Europe. (2015). Plastics Europe: Plastics-The Facts 2015. An Analysis of European latest plastics production, demand and waste data Online: http://www.plasticseurope.org/Document/plastics---the-facts-2015.aspx.

Prabhansu, Karmakar, M. K., Chandra, P., & Chatterjee, P. K. (2015). A review on the fuel gas cleaning technologies in gasification process. Journal of Environmental Chemical Engineering, 3(2), 689-702. #

Report F. (2012). Energy recovery from renewable content of waste : incentives and methodology for analysing biogenic content of mixed waste Topic 1 – Policy Support

Vandecasteele, C, Billen, P, Verbinnen, B, Caneghem J. (2016). How to choose between recycling, incineration and landfill in a LCA presepective. (Waste Eng Conference)

Yassin, L., Lettieri, P., Simons, S., Castillo-Castillo, A., Leach, M., Ryu, C., ... & Sharifi, V. N. (2009, August). From incineration to advanced fluid-bed gasification of waste. In Proceedings of the Institution of Civil Engineers-Waste and Resource Management (Vol. 162, No. 3, pp. 169-177). Thomas Telford Ltd.