Thermochemical recycling of plastics for production of chemical intermediates at a Swedish chemical complex site

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Abstract:

This work investigates the implementation of a waste recycling process for sustainable production of chemicals and plastics with metal recovery at a Swedish chemical complex site. Plastics waste streams and forest residues undergo thermal gasification and the produced syngas is used for the synthesis of methanol and ethanol that serve as chemical intermediates at the site thus reducing the import of fossil-based feedstock. Additionally, two metal-rich waste streams are also considered: automotive shredder residues and electronic waste. These two streams are pre-treated by pyrolysis resulting in a solid residue suitable for metal recovery. The annual potential reduction of global GHG emissions of the proposed process was quantified using a life-cycle perspective. About 120 kt of ethylene per year and about 44 kt of syngas can be produced corresponding to about 15% and 26% of the site demand, respectively. The estimated contribution to global GHG emission reduction of the proposed process concepts lies in a range between 800 and 1300 kt $CO_{2\text{-eq}}$ per year.

1. Introduction

The largest Swedish chemical complex is located in Stenungsund on the West Coast of Sweden. It consists of six process sites producing a variety of different chemical products and is owned by five different major international chemical companies. The chemical complex currently features high material integration between the different production sites, where ethylene is the main chemical intermediate for polymers, alcohols, ethylene oxide, ethylene glycol and the base for large variety of further value-chains.

The companies have recently adopted a common vision, Sustainable Chemistry 2030, to increase the site energy efficiency and to reduce the fossil feedstock dependence by switching to renewable productions of chemicals. The integration of biogenic feedstock has been primarily considered not only by importing green drop-in chemicals from the market but also by integration of fully developed biorefinery concepts that process biomass into different chemical intermediates or products [1]. Recently, the option of processing waste streams in combination with biomass has also been advanced to increase feedstock flexibility, a key feature for producers of chemicals especially in countries lacking direct access to cheap fossil feedstock. The recently founded organization "West Swedish Chemical and Material Cluster" has also been created to promote collaborations between companies also outside the boundaries of the Stenungsund chemical complex. In the last years few projects were initiated in the field of circular economy and industrial symbiosis within the cluster.

In this paper we present the main results of PECREST, a collaboration between Borealis, Stena Recycling International, and Chalmers University of Technologies and financed by EIT Climate-KIC.

The objective of the present work was to identify relevant process concepts for plastics chemical recycling and metal recovery and to quantify their potential contribution to reduction of global GHG emissions. Preliminary mass and energy balances were established by flowsheet simulation and processes integration opportunities were investigated. The global GHG emission consequences were assessed by introducing expanded system boundaries and the contributions of the different process chains and changes in system material and energy flows to the GHG emission balance were estimated also considering different scenarios.

1.1. Overview of plastic chemical recycling

Plastic recycling can be categorized in three main types: (1) material recycling, (2) chemical recycling, (3) energy recovery. Material recycling, even though the purity of recycled products can limit the degree of substitution of virgin materials, allows the highest reduction of global GHG emissions for production of new products and should therefore be preferred. The target for Sweden since 2012 is to have at least 30% material recycling which is expected to increase to 50% sometime after 2020 according to EU directives [2]. At the opposite side of the recycling cascade is energy recovery for production of electricity and heat. It is currently the most common waste handling strategy in Europe, especially in the northern countries where heat recovery represent a bigger share of income due to past investment in district heating networks. There is a consensus that this strategy should be in the long-term future discontinued to favour larger share of material recycling and with increasing utilization of renewable energy resources.

Chemical recycling represents another way to avoid complete combustion of plastic and to recover at least part of the polymer or of its building blocks into production of new products. Depending on the substrate (e.g. polymer types) and on process type and conditions, the gaseous and liquid phases can be of different natures, but applications such as motor fuel or as chemical intermediates have been considered in the past. Although no significant differences in technology may appear between different applications, the difference between recovering plastic waste into motor fuels or chemical intermediates may be dramatic from a life-cycle perspective. Only recovering the chemical elements of plastics into new plastics can be regarded as close-loop recycling while plastic derived motor-fuel are indeed another way to fully release the plastic carbon in form of CO_2 to the atmosphere, and its impact on global GHG emission is therefore largely dependent on the future of the transportation sector. A petrochemical complex site is highly suitable for integration of plastic chemical recycle since multiple options are already in place for using different types of hydrocarbons and syngas for production of chemicals.

Thermochemical recycling of plastics for feedstock recovery has been largely investigated in the past and few demonstration plants were also built [3]. Among input waste streams, automotive shredder residues (ASR) and tyres, waste streams resulting from car demolition are also considered. As discussed later, ASR is a heterogeneous material rich in plastics but also in metal and may represent an interesting opportunity for an integrated feedstock and metal recycling [4]. The processes fall into two large categories: gasification and pyrolysis. The processes based on gasification generally decompose the substrate into syngas with downstream synthesis of chemicals or fuels. Pyrolysis processes can be tailored for a specific feedstock and/or product and can directly yield a desired product (in liquid or gaseous form) [5] while gasification processes rather are suitable for larger scale applications and mixed feedstocks, and need further downstream process steps.

A detailed life-cycle assessment of waste treatment technologies for the Greater London area [6] shows that the combination of plastic material recycling and waste-to-energy plants results the best option from a global warming impact if compared to landfill. However it was found that when material recycling products cannot fully substitute the virgin plastic, thermochemical recycling is a better option.

The issue about degree of substitution is also highlighted in [7] where a comparison is made between different life-cycle-analysis (LCA) studies on plastic recycling. When only looking at global warming potential, it is clear that material recycling results always favoured compared to other strategies.

Feedstock recycling appears however much better than energy recovery although results can be very different between different feedstock recycling processes.

A study by University of Naples of 2005 [8], discusses in detail LCA impact of different plastic waste recycling strategy. Particularly interesting is the comparison between mechanical recycling and two feedstock recycling options for polyolefins fractions: low temperature pyrolysis (BP polymer cracking) and hydrocracking (Veba Combi-Cracking). The global warming impact of the feedstock recycling processes appear quite similar and the estimated total GHG emission saving potential compared to combustion with energy recovery is substantial (about 5 kg CO_2-eq per kg recycled plastics).

LCA studies about recycling of ASR or WEEE are more abundant since the disposal of end-of-life vehicles and electronics impose greater challenges than mixed plastic waste for instance, but also greater economic opportunities appear for material recycling. In a study by University of Bologna of 2010 [9], a life-cycle assessment was conducted for different ASR treatment processes. In this study it appears that feedstock recycling can introduce similar environmental benefits as advanced material recycling with integrated incineration. Feedstock recycling from WEEE treatment has so far not been studied in detail from a system aspect point of view, life-cycle assessment being mostly conducted for advance material recycling concepts [10]

In fact it appears that studies on feedstock recycling from plastic waste, WEEE or ASR in the Swedish context has so far not been published. A core research contribution of the present work is to quantify greenhouse gas emissions with a system perspective. A key aspect of the proposed chemical recycling concept is the integration with a chemical complex site which allows to valorise the large amount of excess heat from the thermochemical recycling processes.

1.2. Candidate input waste streams and products

1.2.1. Input waste streams characterisation

Following a rather conceptual character of the project, all plastic waste streams generated in Sweden that are currently disposed by combustion or landfilled are considered as a potential feedstock for thermochemical recycling. For this purpose a publication from 2012 [11] was used as main reference substantiated by other studies when possible. The estimated flow of plastic waste streams for the main sectors in Sweden that are shown to energy recovery (incl. cement industry) are shown in Table 1. These should be regarded as indicative values with large uncertainties.

Table 1. Summary of estimated plastic waste streams generated in Sweden, by sector and type (excluding electronics and vehicle demolition), which are sent to energy recovery (incl. cement industry). Estimates are based on aggregated data for 2010. (* only 25% of this value considered for chemical recycling)

	Household	Manufact. &Services	Construct.& Demolition	Medical application	Total Sweden	To chem.rec.
HDPE (kt/y)	30.6*	10.6*	2.2	1.6	44.8	14.0
LDPE (kt/y)	57.2*	15.0*	2.2	2.2	76.5	22.4
PP (kt/y)	64.1*	16.7*	4.3	2.5	87.5	27.0
PVC (kt/y)	4.6	10.6	25.8	1.6	42.5	42.5
PS (kt/y)	27.5	7.0	4.3	1.0	40.0	40.0
PET (kt/y)	15.4	5.3	-	0.8	21.4	21.4
PUR (kt/y)	0.5	6.2	4.3	0.9	11.9	11.9
ABS (kt/y)	0.5	4.2	-	0.6	5.3	5.3
PC (kt/y)	0.5	4.2	-	0.6	5.3	5.3
PMMA (kt/y)	0.5	4.2	-	0.6	5.3	5.3
PA (kt/y)	27.6	4.2	-	0.6	32.4	32.4
Total (kt/y)	229.0	88.0	43.0	13.0	373.0	227.5

As mentioned above, there are also heterogeneous waste streams such as ASR and WEEE which are rich in plastics and metals. ASR has also a discrete amount of wood and textiles. It was decided to retain the whole amount of these waste streams and consider the opportunity of an integrated feedstock and metal recycling plant that takes care of all ASR and WEEE generated in Sweden. Data about ASR and WEEE were provided by Stena Recycling International and refer in particular to those fractions of total ASR and WEEE that are currently sent to energy recovery.

Additionally, following the interest of the Stenungsund chemical companies to develop a feedstock recovery process with high flexibility of processed waste streams, we have included a given quantity of forest residues (with an ultimate analysis based on [12]). The amount of biomass was decided by fixing the total input chemical energy rate to 525 MW on higher heating value (HHV) basis. This corresponds to the value identified in a previous project [1] where only biomass was considered for production of methanol and olefins and therefore this assumption allows making some comparisons between process concepts processing different materials but having similar scale. Table 2 shows a summary of the input waste streams considered in this work.

Table 2. Summary of input waste streams considered for feedstock recycling at the Stenungsund chemical complex.

	Mixed plastic waste (Table 2)	*ASR*	*WEEE*	*Forest residues*	*Total*
Quantity (kt/y)	228	65	17	510	820
Chemical energy in HHV basis (GWh/y)	2173	238	125	1656	4 192
Averaged (8000 h/y) chemical energy rate in HHV basis (MW)	272	30	16	207	525

1.2.2. Candidate products for Stenungsund chemical complex

The chemical complex in Stenungsund is largely based on olefins production, currently performed by steam cracking of fossil feedstock such as naphtha and ethane. Ethylene is the main chemical intermediate for a large number of chemicals mainly via ethylene-oxide and OXO-aldehydes and also at the basis of plastic production. The olefin mix at the site is strongly dominated by ethylene and currently around 200 kt of ethylene are imported every year. Several recent projects have focused on the substitution of fossil ethylene with bio-based ethylene. So far two main routes have been considered: via dehydration of green-ethanol produced by fermentation of various sugar substrates, via methanol to olefins (MTO) process from methanol produced via synthesis from syngas obtained by biomass gasification [1].

The chemical complex has also a large import of natural gas. This has two main utilizations: as fuel in boilers for steam production and as feedstock for production of around 170 kt per year of syngas with a H_2 to CO ratio of 1 for OXO-synthesis. Both uses of natural gas can be addressed by the proposed thermochemical conversion processes within this study, either by replacing syngas or by heat recovery and integration for steam generation.

2. Methodology

2.1. Definition of process layouts

The two following process concepts were outlined:

- Mixed plastic waste and forest residue gasification, tar and CH_4 reforming, CO_2 separation, compression, methanol synthesis, methanol dehydration to DME, DME carbonylation into

methyl acetate, methyl acetate hydrogenation into ethanol and methanol, methanol recovery, ethanol dehydration into ethylene. The basic layout of the process is shown in Fig. 1.

- ASR and WEEE pyrolysis with integrated metal recycling, partial oxidation of pyrolysis gas into syngas, syngas cooling and compression. The basic layout of the process is shown in Fig. 2.
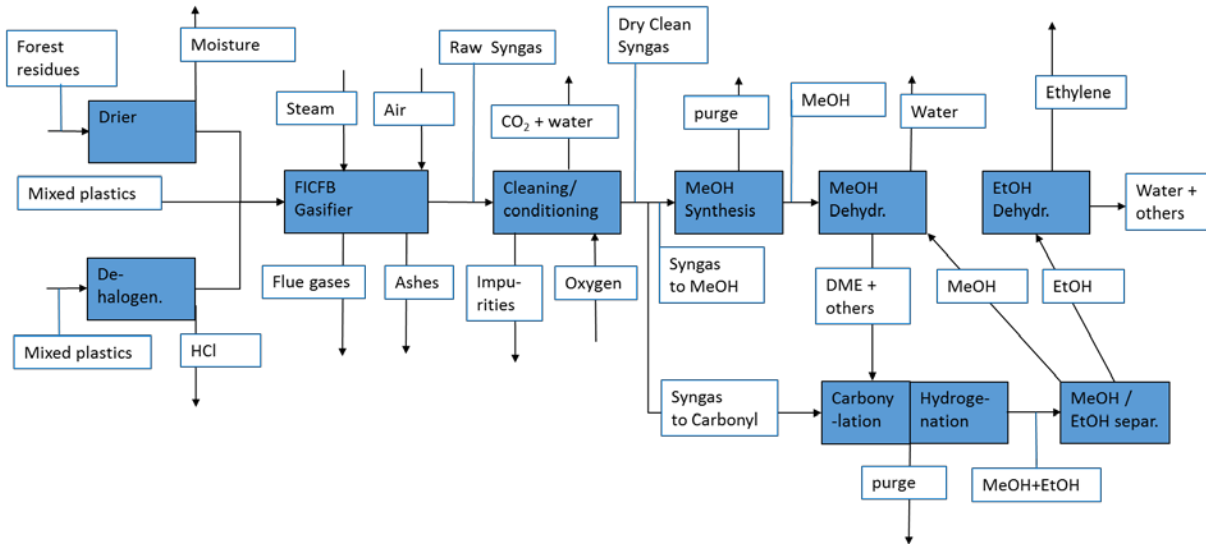

Fig. 1: overview of the ethylene production process from gasification of mixed plastics and forest residues
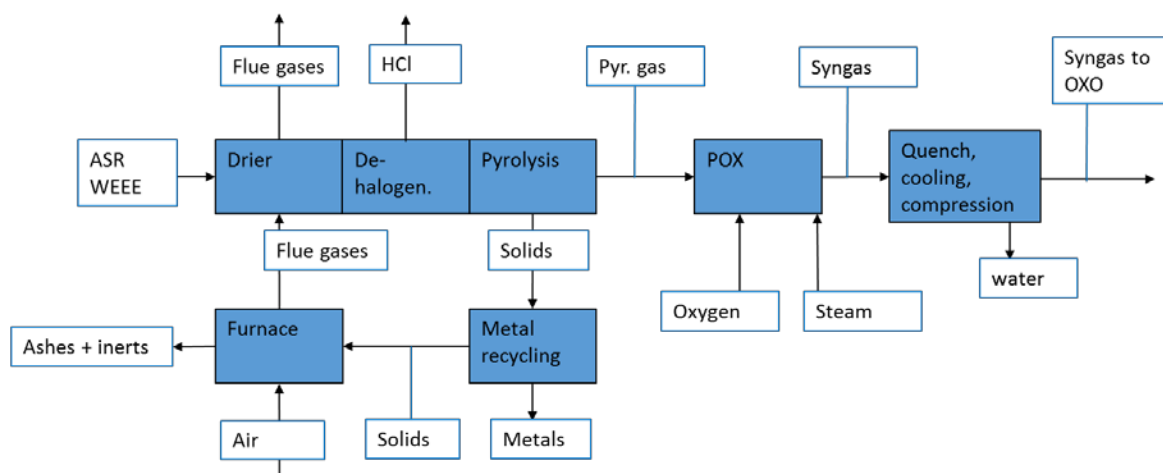

Fig. 2: overview of process for production of syngas for OXO-synthesis applications

The amount of the input plastic waste stream considered is large and we therefore focused our attention primarily on gasification technology opening up for a large spectrum of biorefinery concepts and integration opportunities as shown in previous studies [13, 14].

For the two plastic and metal-rich waste streams, ASR and WEEE, pyrolysis was assumed allowing for metal recovery. A semi-quantitative modelling approach based on literature data on similar materials was used for establishing mass and energy balances. From pyrolysis a complex mixture of hydrocarbons in gaseous phase and a solid metal-rich residues are obtained. The pyrolysis gas is then sent to partial oxidation to convert all the hydrocarbons into syngas.

Based on the H_2:CO ratio of the syngas produced from gasification of mixed plastic waste and biomass, and of the syngas obtained from ASR and WEEE pyrolysis two different downstream process layouts were identified suitable for integration to the chemical cluster site. The syngas from

gasification has a H_2:CO ratio around 2 which is convenient for methanol synthesis. To close the material loop from plastic material to building blocks for production of virgin plastics, the methanol was further converted to ethylene. Since ethanol is also a candidate product, we have considered the route via methyl acetate to produce ethanol proposed by University of Seville and similar to the Enerkem technology [15], which is then dehydrated into ethylene. The syngas stream obtained from the pyrolysis process, of smaller amount, has a H_2:CO ratio around 1 which is suitable for OXO-synthesis applications.

2.2. Modelling

2.2.1. Gasification of mixed plastics and forest residues

The modelling of the indirect gasification step is mainly based on data from biomass and plastics gasification as well as mixtures of the two fractions [12]. Using experimental data with similar feedstock composition to the one in the present study, a previously developed model [16] was adopted to fit the published data prior to being used with the feedstock material of the present study. This allows estimating syngas yield and composition as well as steam demand and flue gases for indirect gasification [12].

The reforming of tars, methane and light hydrocarbons (C_2H_4) prior to downstream synthesis is assumed to be done using a two-step autothermal reformer. As the chlorine content in the plastic waste streams (mainly from PVC) is too high to allow for syngas production with downstream synthesis (corrosion and poisoning issues), the waste stream containing the highest fractions of PVC was considered for a pretreatment step for dehydrochlorination. Low-temperature pyrolysis at 300°C as proposed by Bockhorn et. al. [17] is used to pretreat the waste stream from building and construction prior to gasification, resulting in a HCl rich stream that potentially could be a valuable by-product. The further use of HCl was not considered within this study.

2.2.2. Syngas to ethylene

The syngas from gasification having a H_2:CO ratio of about 2 can be directly used for methanol synthesis without adjustment in a water-gas-shift reactor. The modelling of the methanol synthesis section was based on previous work [13] while the modelling of the methanol dehydration, DME carbonylation, and methyl-acetate hydrogenation was mainly based on [18]. The final step from ethanol to ethylene was not modelled but the results from [19] were used and scaled according to the ethanol mass flow rate.

2.2.3. Pyrolysis of ASR and WEEE and product gas partial oxidation

The pyrolysis of ASR and WEEE were considered separately although the results are shown here as if the two waste streams were processed together. In practice it is probably convenient to have two separate processes since metal recycling is mostly relevant for ASR and since pyrolysis of WEEE may generate complex chemical compounds that deserve particular care. Such aspects are however beyond the scope of the present work. As shown in Fig. 2, the waste streams are first dried to remove moisture by direct contact with low temperature flue gases from the furnace. Similar to gasification of plastics rich in PVC, a dehydrochlorination step is assumed for chlorine separation. The waste stream is further heated up to 500°C. This temperature was chosen to prevent aluminium melting in order to allow for high recovery of this metal and also because this appears the temperature considered in the literature for similar technologies [20].

The pyrolysis of ASR was modelled as yield reactor and mainly adopting the data published in [20] and adjusting the gas and solid yields to close the element balance of the organic fraction according to the ultimate analysis of ASR. Similarly, the pyrolysis of WEEE was modelled as yield reactor considering the overall yield to gas and solids reported in [21] for similar waste stream. The composition of the gas was instead assumed equal to the composition reported in [22] and by adjusting the CO_2 yield to close the element balance.

The product gas at 500°C is sent to a partial oxidation step where it is reformed in presence of oxygen and steam mainly into a mixture of H_2, CO, CO_2, water, with some traces of other hydrocarbons. This partial oxidation step is modelled as a Gibbs reactor and the flow of oxygen is adjusted to obtain a temperature at the outlet of about 1300°C. The steam injection is adjusted to prevent carbon deposition.

The syngas obtained is too hot for heat exchanging and therefore is mixed with some syngas recycled from a downstream process point to reach a temperature of 900°C after which is cooled by heat exchanging, compressed to 25 bar and sent to OXO synthesis.

2.3. Process integration

Inevitably, during thermochemical conversion, part of the chemical energy of the raw material is converted into heat, such as via combustion. Rational heat management is therefore a key to high efficiency. For this purpose an energy targeting method based on Pinch Analysis was adopted. As a result of flowsheet simulation, all the heat loads and temperatures of thermal streams are obtained and the maximum heat recovery can be estimated through an algebraic procedure as explained in [23] by imposing a minimum temperature difference between hot and cold streams. In this work a global minimum temperature difference of 10°C was assumed.

As the processes under consideration have a large net heat excess, heat recovery for steam generation, replacing steam production in natural gas boilers was the major aim of the energy targeting procedure. The maximum steam production was therefore established by solving a linear programming problem where the heat transfer feasibility is imposed as set of linear inequality constraints as explained in [24]. The temperature profiles of steam productions were obtained by imposing the target pressure and temperatures and considering a common feedwater temperature of 90°C.

2.4. Efficiency definition

Two indicators are used to keep track of the efficiency of the process:

- Energy Conversion η, the ratio between the chemical energy rate of an outlet product stream and the chemical energy rate of the input waste stream, on HHV basis.
- Carbon Conversion χ, the ratio between the carbon in the main outlet product stream and the carbon in the inlet waste stream.

2.4. Estimation of impact on global GHG emissions

The production of chemical intermediates from the identified waste streams has a direct impact on the GHG emissions at the Stenungsund chemical complex site, for instance by substitution of part of the natural gas used for syngas production or gas that is used in natural gas boilers. On the other hand, the production of ethylene from plastic waste streams and the reduction of the import of fossil ethylene do not create any significant change of site emissions but reduces the emissions somewhere else, primarily at the site where the imported fossil ethylene is produced.

To rigorously take account such global effects, it is necessary to extend the boundaries of the system to include all the flows of commodities and industrial activities that are affected by changes connected to the implementation of waste-to-chemical processes, according to a life-cycle perspective. We introduce for this purpose *Fig.3* and *Fig. 4*. Although at the end a cumulative value of change in global GHG emissions is estimated, it is convenient to describe the various contributions associated with the two process concepts separately: for the process from mixed plastic waste and forest residues to ethylene (*Fig.3*) and for the process from ASR and WEEE to syngas with integrated metal recycling (*Fig.4*).

In these figures, the reference industrial activities or energy conversion technologies are shown in yellow boxes, the proposed waste-to-chemical plants are shown with green boxes, the commodities produced and consumed and that are assumed to be constant are shown with white circles, the fossil resource with blue circles, and biomass (forest residues or wood chips) with a green circle.
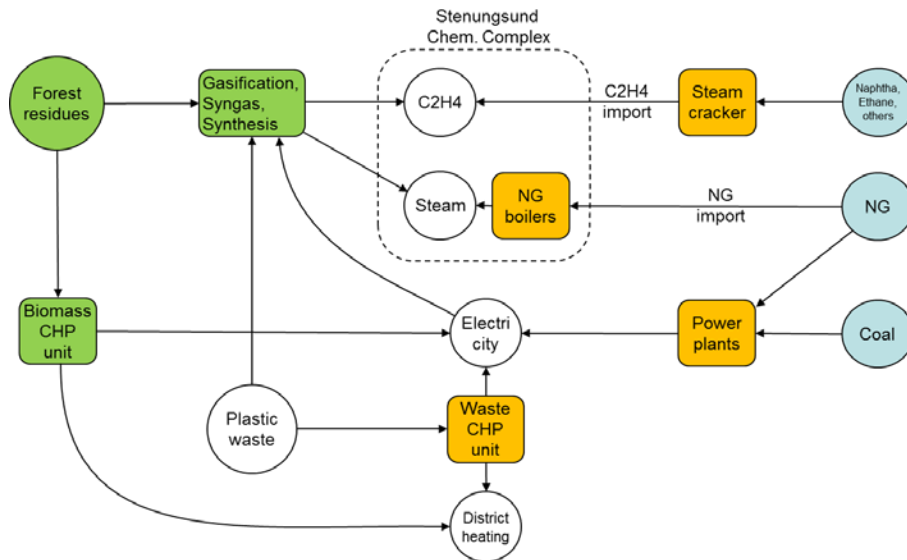
Fig. 3. *Overview of extended system that is used to estimate the GHG emission consequences of producing ethylene (C_2H_4) from mixed plastic waste and forest residues.*
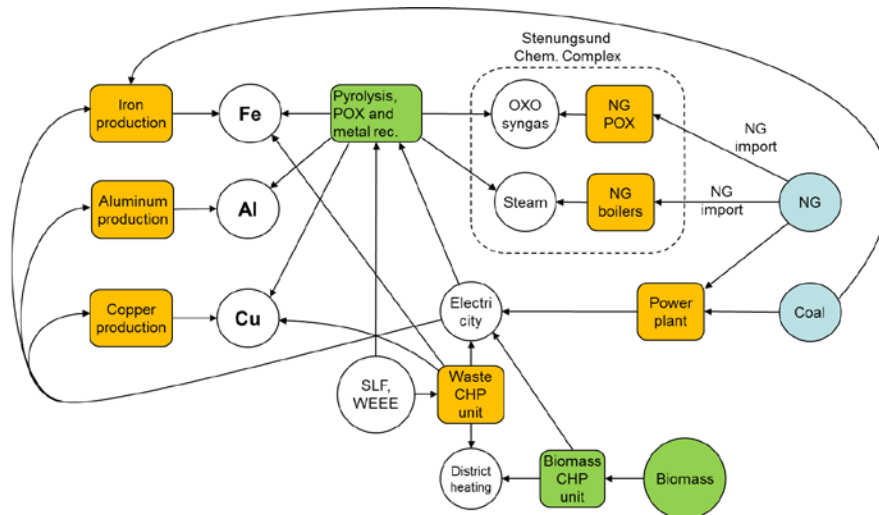

Fig. 4. *Overview of extended system that is used to estimate the GHG emission consequences of producing OXO-syngas from ASR and WEEE.*

It should be observed that in these figures only the parts of the extended systems that are affected by significant changes are shown and some of technologies involved in production and utilization of the commodities that remain unaffected by the implementation of the proposed processes are left out. Note, in particular, that plastic waste and, to some extent, ASR and WEEE partly consist of polyethylene. When waste polyethylene is recycled into production of ethylene that ends up in polyethylene again, a loop of carbon is created and such stream of carbon does not leave the system in form of CO_2 anymore. This cycle has been neglected in our calculations since polyethylene is only a small part of the considered waste stream, and since the actual carbon conversion is much lower than 1.

Similarly, we have neglected the GHG emissions associated with the transportation of all the various commodities to the Stenungsund site.

Table 3 provides an overview of assumptions made for estimating the various contributions to the change in global GHG emissions, which are further described in the following sections. To take into

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account possible differences in performances of various industrial activities and energy conversion technologies, two scenarios were formulated: scenario "HIGH" where high emissions factors are considered, and scenario "LOW" where low emission factors are considered.

Table 3. Summary of assumptions of GHG emission factors and efficiencies of relevant processes

	Reference	Unit	HIGH scenario	LOW scenario
Iron production	[25]	t CO_2 / t Fe	2.1	1.4
Aluminium production	[25]	t CO_2 / t Al	22.5	13.0
Copper production	[25]	t CO_2 / t Cu	3.3	1.9
Ethylene production (cradle-to-gate)	[26, 27]	t CO_2 / t C_2H_4	1.44	1.15
OXO-syngas production via NG POX at Stenungsund site	[14]	t CO_2 / t syngas	0.42	0.42
NG production (cradle-to-gate)	[28]	kg CO_2 / MWh NG	42	42
NG combustion	[28]	kg CO_2 / MWh NG	206	206
NG boiler efficiency at the Stenungsund site (LHV basis)		-	80%	85%
Marginal electricity production Reference technology (built-in) Electrical efficiency (LHV basis) Emission factor	[28]	- kg CO_2 / MWh el.	Coal Cond. 45% 913	NGCC 64% 388
Waste-to-energy CHP units electrical efficiency (HHV basis) total efficiency (HHV basis)		- -	10% 95%	30% 95%
Biomass CHP units electrical efficiency (HHV basis) total efficiency (HHV basis)		- -	30% 95%	30% 95%

2.4.1. Gasification of mixed plastics for production of ethylene

Mixed plastics shown in Table 2 is used to produce ethylene. As discussed in the introduction and shown in *Fig.1*, plastics is chemical recycled instead of being sent to energy recovery. The carbon in the mixed plastics is not released anymore into the atmosphere by combustion in combined heat and power (CHP) units but, depending on the overall carbon conversion, the major fraction ends up in ethylene.

The end-uses of the ethylene produced at the Stenungsund site, independently of whether it is produced via steam cracking or from waste, remain unchanged, thus no change in emission were accounted for in the downstream value chain. Accordingly, the GHG reduction contribution of producing ethylene instead of burning mixed plastics was calculated considering that the molar flow of avoided carbon dioxide is equal to the molar flow of carbon from plastics that ends up in ethylene.

2.4.2. Gasification of forest residues

The carbon in forest residues comes from carbon dioxide sequestration during the tree growth. When forest residues are utilised for production of ethylene, part of the carbon ends up in ethylene, the rest being lost in form of carbon dioxide along the process. Similarly to mixed plastics, the net contribution to GHG emission reduction is calculated considering that the molar flow of avoided carbon dioxide is equal to the molar flow of carbon from biomass that ends up in ethylene.

2.4.3. Pyrolysis of ASR and WEEE

The fraction of total ASR and WEEE produced in Sweden considered in this work, is the part that currently is sent to energy recovery. ASR and WEEE are used for production of syngas for OXO-synthesis. In analogy to plastic waste gasification, the GHG reduction contribution of producing

syngas instead of burning ASR and WEEE was calculated considering that the molar flow of avoided carbon dioxide is equal to the molar flow of carbon from ASR and WEEE ending up in the syngas.

2.4.4. Metal recycling

The relevant fractions for recycling of iron (Fe), aluminium (Al), and copper (Cu) are present in ASR, being recovered after pyrolysis. The amounts entering the pyrolysis process, the assumed present recovery in incineration plants, as well as the assumed recovery in the proposed pyrolysis process are given in Table 4. Precise data about today's degree of metal recovery from ash from combustion processes in Sweden are not available but an overview of state of the art metal recovery can be found for instance in [29]. Data about possible recovery targets after ASR pyrolysis are also unavailable, and the values assumed here were estimated in discussion with experts from Stena Recycling and should be regarded as indicative. In principle, larger metal can be recovered by placing metal recovery equipment after the pyrolysis section but prior the char combustion thus avoiding part of the intrinsic metal losses of incineration plants.

To estimate the contribution of metal recycling to global GHG emission reduction, these quantities of metals were multiplied by the specific emission factors of metal production according to Table 3.

Table 4. Assumptions on metal recycling.

	Amount treated in pyrolysis (t/y)	Current degree of recovery from combustion ashes	Assumed recovery from pyrolysis	Incremental amount of recycled metals (t/y)
Iron	7 440	30 %	70%	2 980
Aluminium	2 000	0 %	70%	1 400
Copper	1 720	10 %	90%	1 375

2.4.7. Reduction of import of fossil feedstock for chemicals production

The proposed waste-to-chemical plants contribute to the reduction of import of fossil feedstock at the Stenungsund site. By reducing the import of ethylene, the GHG emissions of ethylene production in marginal steam cracker units are avoided. Due to large variety of steam cracker technologies and feedstock it was decided to use a general value of GHG emission factor reported in the literature for ethylene for the LOW [27] and HIGH [26] scenarios, respectively.

The production of syngas for OXO synthesis applications contributes to the reduction of natural gas currently feeding a partial oxidation plant [14]. Due to partial oxidation of natural gas, some of the carbon in the feedstock leave the plant in oxidised form. This flow of carbon dioxide is avoided when introducing the proposed pyrolysis plant. The value of 0.42 tonne CO_2 per tonne syngas as given in Table 5 is based on data from [14].

2.4.5. Reduction of natural gas import by steam production by excess heat recovery from waste-to-chemical plants

The export of steam produced by recovering the excess heat from the waste-to-chemical processes contributes to a reduction of natural gas combustion in steam boilers at the site. The steam export targets were calculated following the above mentioned energy targeting method. The natural gas consumption was calculated by dividing the steam heat load by the boiler efficiency. The GHG emissions of natural gas combustion were then calculated by multiplying the natural gas consumption by the specific emissions of natural gas combustion (well-to-gate emissions included).

2.4.6. Effects on marginal heat and electricity production technologies

One of the major consequences of shifting from a recycling strategy mostly based on energy recovery to a scenario where plastics is recycled into new chemicals or materials is the reduction in heat and electricity generation in waste-to-energy plants. This is particularly true for Sweden, since the large

district heating networks often rely on waste-to-energy plant as base load technology together with industrial excess heat.

The effects on marginal heat production technologies are therefore largely dependent on the regional energy systems. In this work we assumed that the reference built-margin heating production technology in Sweden are biomass CHP units. To take into account possible revamping of existing waste-to-energy plants and possible technological advancements different assumptions were made for the electricity and thermal efficiency in the HIGH and LOW scenarios as shown in Table 5.

By assuming biomass CHP units for replacing the heat production from waste-to-energy plants, more electricity could be produced by CHP units (HIGH scenario). Imposing a global electricity generation balance, this surplus of electricity contributes in turn to decrease the production in marginal electricity production technologies. Ultimately, the contribution to global GHG emission of the change in marginal electricity production was calculated by multiplying the change in electricity production by emission factors for built-margin power plants as discussed in [28]. For the HIGH scenario we have assumed coal-condensing power plants and for the LOW scenarios natural gas combined cycle.

3. Results

3.1. Mass and energy balances

3.1.1. Gasification of mixed plastics waste and forest residues for production of ethylene

The mass balances across the main process steps for production of ethylene from mixed plastics and forest residues are shown in Fig. 5. Overall, the yearly production of ethylene is estimated to about 124 kt which is about 60% of the current import of ethylene at the site and about 15% of the total ethylene used at the site. For this purpose all the ethanol produced by hydrogenation of methyl-acetate is dehydrated and all the methanol is recycled back to DME synthesis.
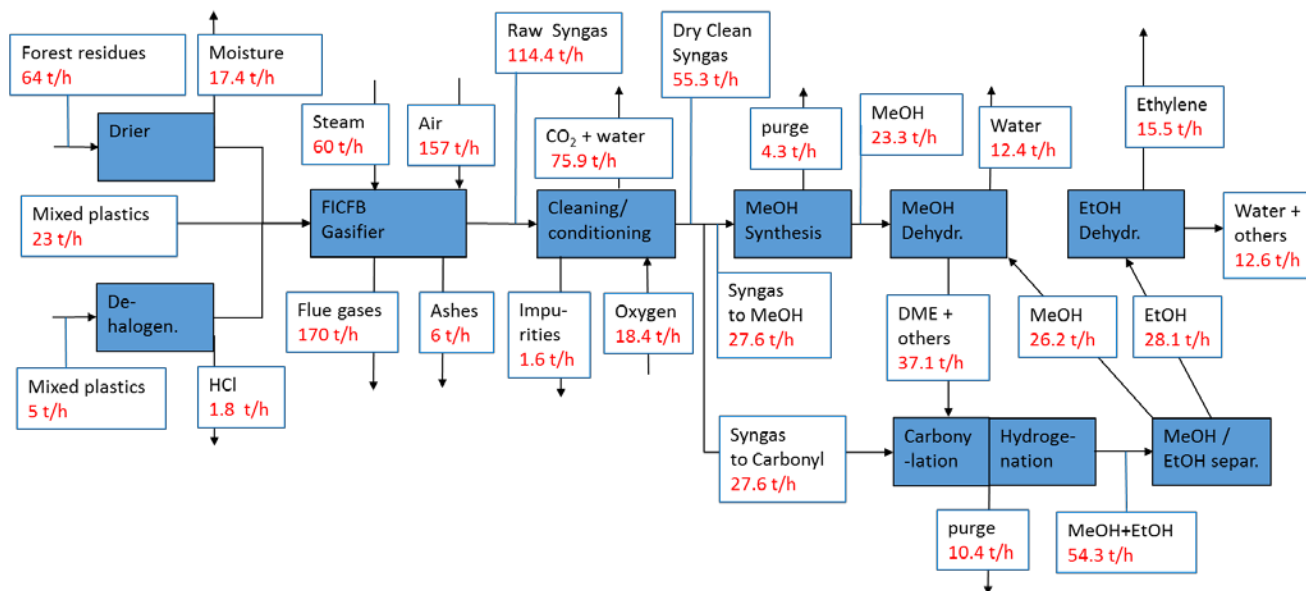

Fig. 5. Mass balances around main process steps for production of ethylene from mixed plastics and forest residues.

The total yearly flow of carbon entering the process with plastics waste and the forest residues is about 160 kt and 150 kt respectively, while the carbon leaving the process in form of ethylene is about 106 kt per year. This corresponds to a total carbon conversion χ of about 34%. The main energy flows and efficiencies are shown in Table 5. Generally the conversion efficiency is rather high. Considering feedstock to methanol energy conversion (23.3 t/h of methanol from half the dry clean

syngas or half the feedstock energy content) a value of 59% (HHV basis) is obtained, exceeding values reported in literature for biomass based methanol production [30]. This can be explained by a higher gas yield from plastic or plastic-biomass gasification (as for example reported in [12]) and the optimistic assumption of complete tar and light hydrocarbon reforming to syngas without losses, overestimating the yield of clean syngas. The overall energy conversion from waste to ethanol is 47% and is in line but somewhat greater than the value reported in [18] and maybe due to high methanol yield and optimistic assumptions on the hydro-carbonylation reaction especially the large syngas recirculation which may be very costly in practice. The overall conversion to ethylene is 46%.

Table 5. Summary of values of the chemical energy rate of the main material flows and energy conversion along the process for ethylene production.

Stream description	Mass flow rate (t/h)	HHV (MJ/kg)	Chem. energy rate (MW)	η
Forest residues	63.7	11.7	207	-
Total mixed plastics	28.5	34.4	272	-
Raw gas after gasifier	114.4	12.3	392	82%
Dry clean syngas after conditioning	55.3	23.8	365	76%
EtOH from MeAC	28.1	28.8	225	47%
Ethylene	15.5	50.9	219	46%

3.1.2. Pyrolysis of ASR and WEEE for production of OXO-syngas

The mass balances across the main process steps for production of syngas from ASR and WEEE are shown in Fig.6. Overall, the yearly production of syngas is estimated of about 44 kt which is about 26% of the current amount of syngas used for OXO synthesis purposes at the Stenungsund site. The total yearly flow of carbon in ASR and WEEE is about 30 kt per year, while the carbon leaving the process in form of syngas is about 17 kt per year. This corresponds to a total carbon conversion χ of about 57%.

Due to the high temperature partial oxidation step and gas quenching, the syngas stream leaving the process is almost completely clean of heavy hydrocarbons. The resulting H_2:CO ratio is close to unity (0.93) and other compounds that should be removed prior OXO-synthesis are also quite low in concentration. This syngas could be blended with the syngas produced from natural gas partial oxidation which composition can be adjusted to accommodate the small deviations of the H_2:CO ratio of the syngas from the pyrolysis process. In addition, a cleaning section already exists at the site which can be used to remove the impurities before OXO synthesis.
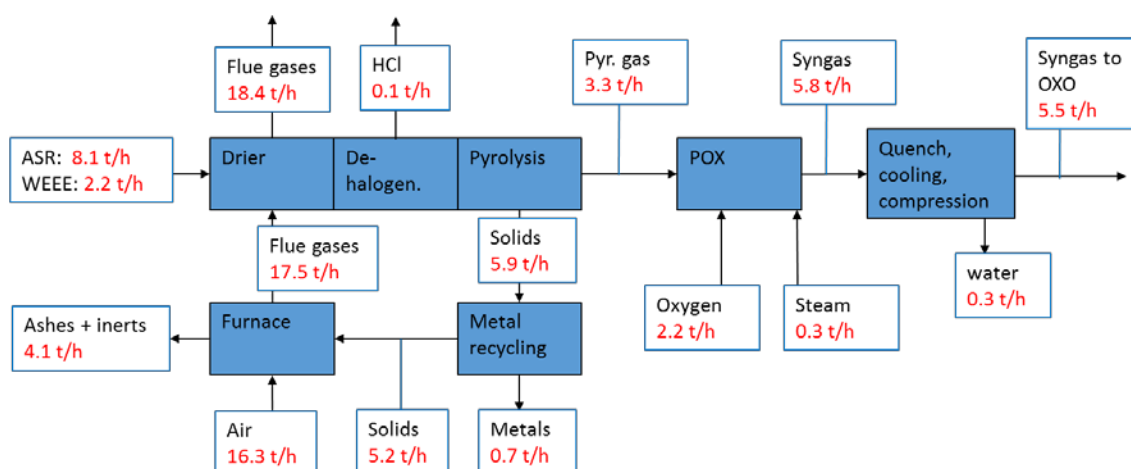

Fig. 6. Mass balances around main process steps for syngas production from ASR and WEEE.

The values of the chemical energy rate of the main material flows are shown in Table 6. By performing separate simulation, we obtained that the energy conversion from ASR to syngas is about 51%, while the conversion from WEEE to syngas is about 79%. A straight linear composition of two processes results in an overall conversion from ASR and WEEE to syngas of 60%. Both carbon and energy conversion of this process are larger than the corresponding values of the ethylene production process (χ 34%, η 46%). This is apparent since ethylene production from syngas is associated with additional losses.

Table 6. Summary of values of the chemical energy rate of the main material flows and energy conversion along the process for syngas production from ASR and WEEE.

Stream description	Mass flow rate (t/h)	HHV (MJ/kg)	Chem. energy rate (MW)	η
ASR	8.12	13.15	29.7	-
WEEE	2.07	27.09	15.6	-
Raw gas after pyrolysis	3.3	33.98	30.3	67%
Syngas after POX, cooling, to OXO	5.5	17.81	27.4	60%

3.1.3. Heat recovery

The recovered excess heat for steam generation for both processes according to the energy targeting method is shown in Fig. 7. The theoretical amount of excess heat from the waste-to-ethylene process is about 200 MW as shown by the abscissa of the low-temperature end of the process grand composite curve. In fact, not all the 200 MW of excess heat but only 104 MW at sufficient temperature level can be recovered for steam production, as shown with the dashed line in Fig. 7 (left). For the pyrolysis process (Fig. 7 right), the combustion of the solid residue, mainly char, and cooling of the combustion effluents and syngas from partial oxidation is sufficiently large to satisfy the pyrolysis heat demand. This leaves about 10 MW of excess heat which can almost entirely recovered in form of steam.
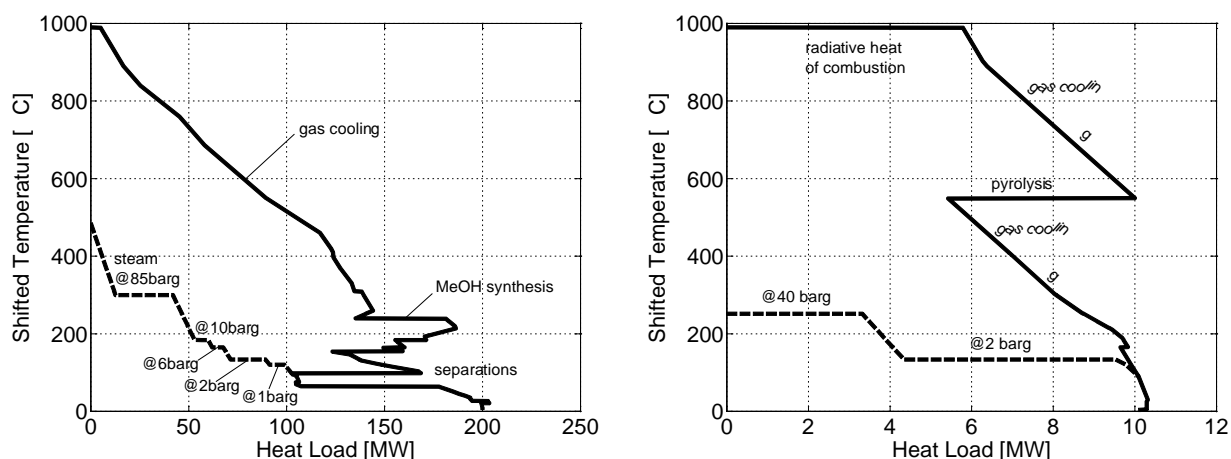

Fig. 7. Grand composite curve of the process from waste to ethylene (left)/ ASR and WEEE to syngas (right) (solid line) and steam production targets at relevant pressure levels for the Stenungsund site (dashed line).

The processes electricity consumption is mainly due to oxygen generation and compression. The electricity demand for the waste-to-ethylene plant is about 35 MW, the pyrolysis processes requires 1.3 MW electricity for syngas compression prior OXO synthesis. The production of oxygen for partial oxidation of the pyrolysis product is counterbalanced by the decrease in oxygen consumption for the natural gas partial oxidation and therefore does not contribute to any net increase in electricity use.

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Table 7 provides a summary of relevant input and output streams of the proposed waste-to-chemical processes. Among the products we have included HCl which could be integrated into PVC production at the site, although quality constraints might hinder the use of the gas from dehydrochlorination.

Table 7. Summary of main input and output streams of the proposed waste-to-chemical processes

Stream description	Mass flow rate (t/h)	Amount per year (kt/y)	Percentage of site demand	Associated energy rate (MW)
Input				
Mixed plastics	28.4	228	-	271.7
Forest residues	63.7	510	-	207.0
ASR	8.1	65	-	29.7
WEEE	2.1	17	-	15.6
Electricity (incl. ASU)	-	-	-	36.4
Output				
Ethylene	15.5	124	~ 15%	219.4
Syngas to OXO	5.5	44	~ 26%	27.4
Steam @ 85 barg, 485°C	75.0	600	100%	62
Steam @ 40 barg, saturated	7	56	substitute POX	4
Steam @ 10 barg, saturated	12.4	99	69%	8.3
Steam @ 6 barg, saturated	9.8	78	100%	6.5
Steam @ 2 barg, saturated	31.4	251	100%	25
Steam @ 1 barg, saturated	12.3	98	100%	8
Iron	0.372	2.976	-	-
Copper	0.172	1.376	-	-
Aluminium	0.175	1.400	-	-
HCl	1.9	15.2	n.a.	-

3.2. Impact on global GHG emissions

Figure 8 shows the estimated potential reduction of the global GHG emission by implementing the proposed waste-to-chemical processes and the various contributions according to the description in the methodology section. The values are reported in more detail in Table 8.
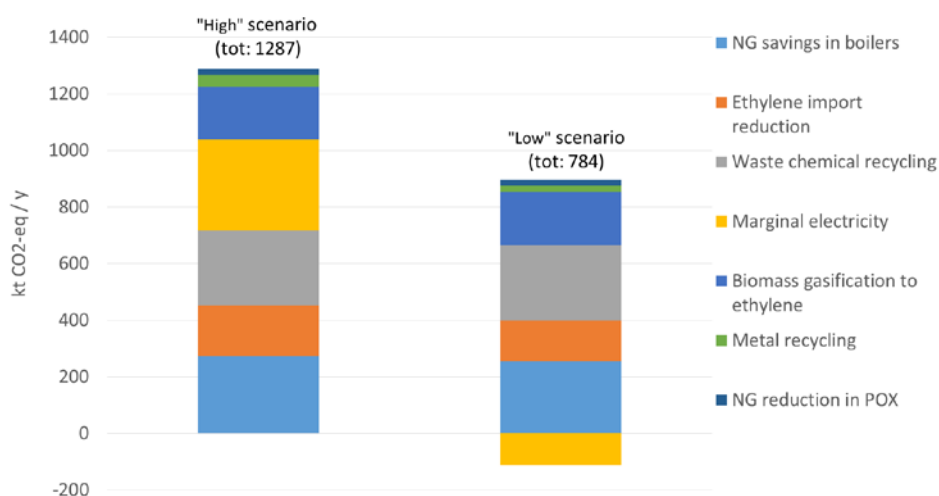

Fig 8: Potential reduction of GHG emission of the proposed waste-to-chemical processes for the two scenarios formulated on the basis of different assumptions

Table 8. Overview of contributions to the GHG emission reduction potential for the two scenarios formulated on the basis of different assumptions

Description of contribution	"High" scenario (kt CO_2-eq / y)	"Low" scenario (kt CO_2-eq / y)
Waste-to-chemical of which …	266	266
plastics gasification to ethylene	201	201
ASR + WEEE pyrolysis to syngas	65	65
Forest residues gasification to ethylene	188	188
Metal recycling	40	24
Reduction of ethylene import	179	142
Reduction of NG partial oxidation	21	21
Reduction of NG combustion to boilers of which …	272	256
due to steam export from ethylene process	258	243
due to steam export from syngas process	14	13
Change in marginal electricity production of which…	321	- 113
related to avoided plastic energy recovery	490	0
related to avoided ASR and WEEE energy recovery	97	0
related to import of electricity to process	- 267	- 113
Total estimated reduction of global GHG emissions of which..	1287	784
related to plastics and biomass to ethylene process	1060	665
related to ASR and WEEE to syngas process	227	119

The "high" and "low" scenarios were formulated based on different assumptions on marginal technologies for the production of various commodities. This results in a large span of estimated GHG emission reduction potential which goes from about 1300 kt CO_2 equivalent per year in the "high" emission scenario to about 800 kt CO_2 equivalent per year in the "low" emission scenario. This is about the same order of magnitude of the current on-site GHG emissions of the Stenungsund chemical complex (about 900 kt CO_2-eq per year).

By looking at the different contributions, it is worth comparing the impact of plastics gasification with biomass gasification. If compared in specific energy terms, the gasification of plastics for production of ethylene contributes to about the same reduction of global GHG emissions as ethylene production via biomass gasification. Behind this result, lies an important assumption. Plastic waste is assumed constant and its chemical recycling is considered as alternative to combustion for energy recovery. Conversely, gasification of forest residue does not compete with an alternative utilization.

Also, when comparing on energy basis, pyrolysis of ASR and WEEE contributes to a larger reduction of GHG emission (65 kt CO_2-eq per 45 MW) than gasification of plastics (201 kt CO_2-eq per 272 MW) which is due to larger losses in the process chain. This is somewhat compensated by two main other consequences: the emission reduction associated with avoided marginal ethylene production is much larger compared to the reduction in emission associated with syngas production via natural gas partial oxidation; much more steam can be produced by recovering excess heat from the waste-to-ethylene plant than from the pyrolysis plant, leading to higher reductions in GHG emission by avoided natural gas combustion in boilers. Another important aspect of distinction between the waste-to-ethylene plant and the pyrolysis plant is the large amount of electricity needed in the first case. This contributes to significant emissions in marginal electricity producer.

Overall, if compared on energy basis, pyrolysis of ASR and WEEE appears to contribute to larger emission reductions than the plastics and biomass to ethylene process. This is mainly due to the assumption of chemical recycling of plastics, ASR and WEEE replace energy recovery and that

avoided production of electricity and heat in marginal CHP plants is compensated by biomass based CHP plants. In the "high" emission scenario we assume that this even contributes to higher electricity production for the same heating basis which reduces the production of electricity in coal condensing plants. Since in the ethylene process almost half of the input in energy basis is biomass, the process utilizing ASR and WEEE is favoured in this comparison since the impact in marginal heat and electricity production technology is proportionally higher. Also, the increase of metal recovery compared to current ASR and WEEE recycling technology has a minor but still positive impact which favoured this process when comparison is done in energy basis.

4. Conclusions

In the present work, process concepts for chemical recycling of waste streams for production of chemical intermediates at a Swedish chemical complex site were identified and their GHG emission reduction potentials quantified by keeping the energy recovery alternative as reference of comparison. The total Swedish waste stream of plastics, automotive shredder residues (ASR) and electronic waste (WEEE) currently sent to energy recovery were considered and metal recovery was also considered for the relevant streams. Forest residues were also used as an input following a vision of feedstock flexibility and carbon-neutral production of chemicals.

The layout of the envisioned waste-to-chemical plant includes a process for production of ethylene via gasification of plastics and forest residues and a process for production of syngas for OXO-synthesis applications via pyrolysis of ASR and WEEE. Mass and energy balances were established by process flowsheet simulations and process integration opportunities were identified by applying an energy targeting methodology. Based on rather optimistic assumptions it was found that about 120 kt of ethylene per year and about 44 kt of syngas can be produced which are respectively about 15% and 26% of the site demand of ethylene and syngas to OXO synthesis respectively.

Considering that forest residues were also included among the input (about 40% in energy terms), these results are on one hand a sign that the contribution of chemical recycling to production of chemical and plastics may be moderate. On the other hand, among the input waste stream we have selected mixed plastic waste and very heterogeneous waste (ASR, WEEE) which may be very difficult to recycle using a material/mechanical strategy. Thus, these results are also quite encouraging and should motivate a further investigation of the economic feasibility of proposed concepts.

Overall, the estimated contribution to global GHG emission reduction lies in a range between 800 and 1300 kt CO_2-eq per year depending on the different scenarios of marginal technologies for production of ethylene, electricity and heat. This is about the same order of magnitude of the current on-site GHG emissions at the Stenungsund chemical complex site. This result is based on assumption that chemical recycling is alternative to energy recovery which in Sweden is done in CHP units connected to district heating networks. By diverting waste to chemical production, we assumed that biomass CHP units compensate for electricity and heat production and that this can even create a surplus of electricity in short term which in turns reduces the production of electricity in coal power plants. This results highlights that the climate consequences of the proposed recycling strategy are largely dependent, at least in Sweden, on the future development of the biomass prices and utilization.

The results also show that an important reduction of GHG emissions can be obtained by recovering the large amounts of excess heat available from the thermochemical processes for production of steam which can be exported to the various chemical plants by appropriately placing the proposed processes close to or in the middle of the chemical complex site. This steam is about 70% of the steam currently produced at the site in natural gas boilers. The reduction of natural gas consumptions in steam boiler contributes to about 20 to 30% of the total GHG emission reduction potential which highlights the suitability of the Stenungsund site for large-scale implementation of biorefineries and waste-to-chemical plants.

Acknowledgments

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