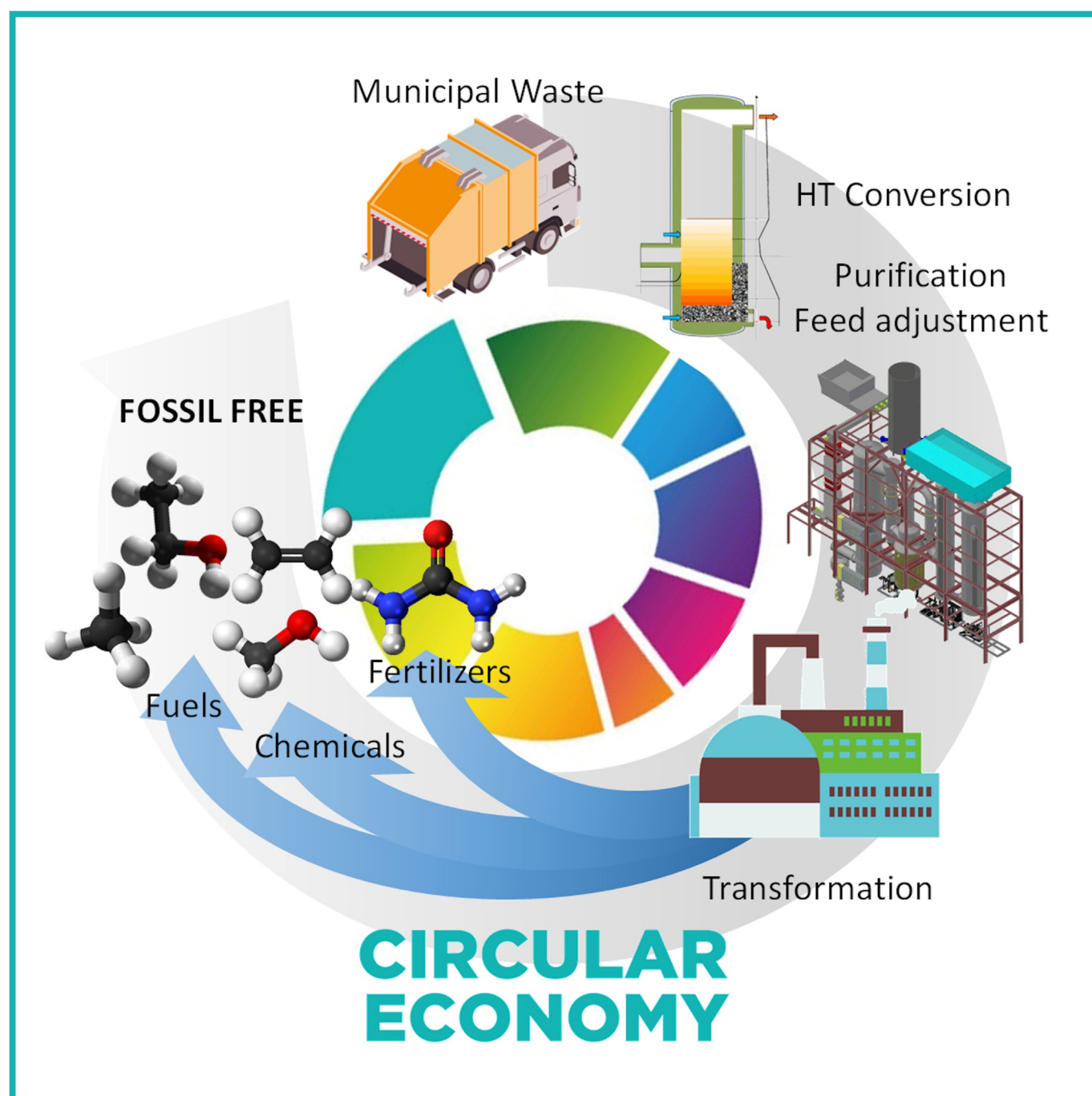


■ Recycling

 Waste to Chemicals for a Circular Economy

Gaetano Iaquaniello,^[b, c] Gabriele Centi,^{*, [a]} Annarita Salladini,^[b] Emma Palo,^[c] and Siglinda Perathoner^[d]



Abstract: The implementation of a circular economy is a fundamental step to create a greater and more sustainable future for a better use of resources and energy. Wastes and in particular municipal solid waste represent an untapped source of carbon (and hydrogen) to produce a large range of chemicals from methane to alcohols (as methanol or ethanol) or urea. The waste to chemical process and related economics are assessed in this concept article to show the validity of such solution both from an economic point of view and from an environmental perspective considering the sensible reduction in greenhouse gas emissions with respect to conventional production from fossil fuels.

Introduction

Oil is the current largely dominating carbon source for chemical production, but a series of issues currently pose the need to urgently find alternative raw materials:^[1–3] i) reduction of the greenhouse gas emissions to mitigate climate change and meet emission targets, ii) geopolitical issues (security and diversification of resources), iii) support to the rural development and use of the local resources, and last, but not least, iv) need to find alternative C-sources, which are less dependent on the current large fluctuations and uncertainty in future costs of fossil raw materials. These aspects are interconnected with the ongoing energy transition and the related impact on the substitution of fossil-based energy resources, with the consequent change in terms of the energy–chemistry nexus.^[4] These factors push the shift from fossil-raw materials to the use of locally available C-sources. Biomass, however, does not allow alone to account for this transition, and there is the need to use less costly C-sources. In addition, the reduction of the environmental impact related to biomass growing and harvesting is another crucial element, particularly for dedicated crops.

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Municipal Solid Waste as a C-source

Municipal solid waste (MSW) or fractions of MSW having a sensible calorific value, the so-called refuse derived fuels (RdF) or organic fraction of MSW, have the potential to support the growing demand of chemicals commodities and at the same time mitigate concerns regarding climate change and energy scarcity associated to the use of fossil fuels. The carbon content of solid MSW fraction varies from about 38 to 51 % (average about 47 % wt on dry bases), depending on countries and their style of life.^[5a] The total organic fraction ranges between 30 and 50 % wt. of the MSW. The MSW production in the Organization for Economic Cooperation and Development countries was about 673 and 278 Mt (total and Europe, respectively) in year 2016.^[5b] MSW amount is going to double in the next years because of the increasing gross domestic product and population, with the generation rate expected to increase to 2.2 billion tons per year by 2025 worldwide.^[6] Just limiting to Europe as an example, the MSW production is enough to overcome the actual olefin production by cracker in Europe (about 23 Mt capacity ethylene per year in 2016).

The use of MSW as C-source could thus be a significant component, covering at least one third of the demand of alternative sources of carbons to reach the target of a 30 % decrease of fossil fuel use by year 2030, or even higher targets.^[7]

The Role of Waste Utilization for Circular Economy

The use of MSW waste as C-source is an important element to push forward a circular economy. Circular economy is a concept promoted at both policy-makers and business community, especially in EU and in general worldwide.^[8] Differently from recycling practice, circular economy emphasizes, among other aspects, waste utilization as a way to close the cycle and minimize the use of resources. The recent (year 2018) EU action plan for the Circular Economy has remarked to set in the revised legislative proposals on waste “an ambitious and credible long-term path for waste management and recycling”, including for MSW, because they represent a major potential resource, and still “only a limited share (43 %) of the municipal waste generated in the Union is recycled”, as indicated in the first sentence of the memorandum to European Parliament for the Directive on waste (COM2015 595 final). Thus, the waste-to-chemicals solution, as alternative to landfill or incinerated (accounting 31 and 26 % of the municipal waste generated in the Union, according to the cited document) represents an important element for the circular economy strategy.

In a circular economy, in addition to using and reducing waste, it is also necessary to incentivize making products that do not become waste in the first place. For MSW, it is certainly advisable to minimize their production, but between 2005 and 2016, the MSW decreased by only about 7 % (average on EU28, Eurostat source) remaining around 500 kg per capita. MSW will be thus a still major waste even in the next decades, and the more rational solution for their handling will be their valorization focused at reducing the need of new raw materials

(fossil fuels) to provide the services (fuels, chemicals, fertilizers) need anyway for our style of life. In a sustainability vision, the circular economy objective is thus a reduction of the use of resources at equal level of quality of life (and thus related services needed), rather than just to minimize waste. In this sense, waste-to-chemicals will be an important element to reach this scope.

Waste Biorefinery

The concept of waste bio-refinery has been proposed,^[9] but mainly for using waste bio-products from agro-food industry. On the contrary, MSW and derived products represents a largely available and widespread carbon source, which valorization, particularly within the framework of biorefinery, opens valuable opportunities.^[10]

RdF, the organic component of MSW (comprising both organic matter and other C-based non-recyclable fraction, including, for example, plastic, paper and textiles) has typically a calorific value (LHV-lower heating value) ranging from 14,000 to 18,000, even 20,000 kJ per kg. Although RdF comprises of both bio-based fractions and others derived from fossil fuels, such as plastic, being considered a recyclable waste, the products obtained from it are considered from the legislation perspective bio-equivalent. For example, methanol produced by MSW is qualified by the EU's Renewable Energy Directive as a bio-fuel, with even double recognition, that is, a supplier needs only half of the quantity of such bio-fuel in place of 1st generation ethanol to meet their obligations.

The major advantage with respect to other biomasses is that their use avoids the additional costs and environmental impact, related to biomass growing, collection and harvesting. In fact, MSW needs to be anyway collected and disposed. As commented later, waste-to-chemicals offers a more sustainable route for MSW disposal. In terms of cost, this translate to a negative cost feedstock, which thus become competitive (or at least comparable) with natural gas or other hydrocarbons to make chemical commodities, something that other bio-renewable resources are unable to do due to their higher cost per energy unit.

Today, half is disposed either through landfilling or thermochemical treatment processes aiming to produce electricity, the so-called waste-to-energy.^[11] Chemical composition of RdF is typically the following (% wt): 29–38 C, 4–5 H, 14–18 O, 19–22 H₂O, 17–30 ashes, or in terms of components (% wt.): 1–4 wood, 10–34 paper, 26–36 plastic, 7–8 textile, 10–14 organic fraction and 10–27 inert fraction.

MSW incineration/thermovalorization is still the main solution adopted on a worldwide basis as alternative to landfilling.^[11]

Waste to Chemicals

Still very limited attention is given in literature and scientific research to this waste to chemical possibility,^[12] although some industrial initiatives are present (for example, by Enerkem and Fulcrum BioEnergy).^[13] We reported the waste-to-chemical ap-

proach in relation to the production of urea and methanol from RdF.^[14] In this concept paper, we will address the waste-to-chemical from a more general perspective, which includes techno-economic feasibility and impact considerations in terms of benefits for the environment. It is also remarked the role in moving to a distributed, low carbon and sustainable chemical production. Key chemical and technological aspects are outlined with the aim to push research and development and socio-political interest on this option that we feel represent a relevant, underestimated possibility for the future sustainable chemical production.

While the waste-to-chemical concept is not limited to RdF derived from MSW, and includes the possible use of other waste with enough calorific value (from agricultural or industrial production), we feel that MSW is the most relevant case, being a general worldwide issue, for which still the high environmental impacting landfill technology (still often uncontrolled) is used. In addition, even when waste-to-energy technology is used, the overall process efficiency is limited (even below 40%), particularly in area where co-generation technologies cannot be used. There is also often strong social opposition to waste-to-energy, often called with the old indication of incineration. Furthermore, as common to other power plant technologies, the highly fluctuating request of electrical energy, may often pose severe limits on the electrical grid capacity to accept the produced electrical energy, with the consequence that waste-to-energy plants may often not be able to work at the full capacity, with relevant impact on the process economics. The production of chemicals, or products used for the liquid fuel market, may instead overcome these limitations, because these products can be easily stored and distributed.

We limit discussion here, in terms of process analysis, to waste gasification as the first step, to produce syngas, which may be further processed to produce the target chemicals. The alternative (fast) pyrolysis solution^[11b] produces a liquid fuel (together with gas components) characterized by a large range of products, and quite low quality. Beside to the need of severe upgrading treatments, the pyrolysis liquid product can be essentially used only as fuel. On the contrary, different products can be obtained from syngas in waste-to-chemical process. Their use ranges from chemicals to fuels. This large flexibility is a key aspect of the technology, because allows a much better tailoring to different demands.

There are some possibilities also in terms of gasification technology. We consider that the one presented here we consider is the preferable for typical sizes as discussed below. However, other cases exist, in which alternatives could be better. An example is the use of the technology for MSW treatment in small islands. There are various practical examples in which the produced MSW actually needs to be transported by ship to distant areas, with large impact on costs. In this case, it may be worthy to have a gasification technology, such as that in nearly supercritical water,^[15,16] which is more compact than the high temperature gasification discussed below. A target product of syngas upgrading could be methane, in this case, because it can be distributed in the island for local heating uses. Typically, these islands are not reached by the natural gas

grid and thus local substituted natural gas could be an added value.

In general, waste-to-chemical technology may be considered composed by established technologies, which do not need to be further discussed. Although the general process Scheme discussed in more detail below is composed from apparently known technologies (gasification, syngas purification and composition adjustment, syngas catalytic conversion to the target chemicals), the integration of these steps and their optimization in relation to the use of MSW determines a series of peculiarities and in some cases still need of developments, the most relevant of which are discussed below. In addition, we feel that this technology may play a strategic role for the future low carbon and sustainable chemical production, although still largely underestimated.

Few studies exist about the techno-economic and the environmental benefits of waste-to-chemical technology. This paper could thus stimulate both the research to solve the remaining issues and the investors to proceed in application of the technology. For this reason, we feel that a concept paper as the present one could be a stimulus to accelerate the developments for a large-scale implementation of waste-to-chemical technology.

Syngas Options and Opportunities

Syngas is a crucial intermediate resource for production of hydrogen, ammonia, methanol, ethanol and synthetic hydrocarbons (Figure 1). The fields of use of these products range from fuels to chemicals and fertilizers.

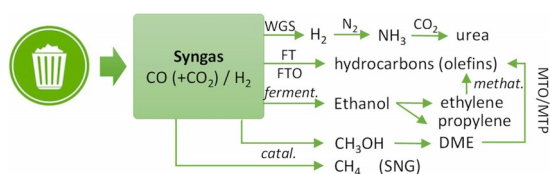


Figure 1. Versatility of syngas intermediate for chemical and fuels production. WGS: water gas shift; FT: Fischer-Tropsch process; FTO: Fischer-Tropsch to Olefins; ferment.: gas fermentation; methat.: metathesis process; catal.: catalytic process; DME: dimethyl ether; SNG: substituted natural gas.

A more specific block diagram for waste-to-urea process is reported in Figure 2. From the syngas, H_2 is first produced, which is then reacted with N_2 (deriving from the air separation unit used to produce the oxygen used in the HT conversion of

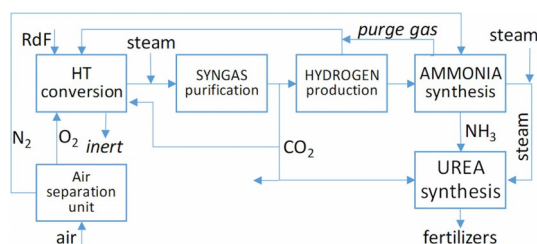


Figure 2. Block diagram for waste-to-urea process.

RdF) to form ammonia (NH_3), followed by conventional reaction with CO_2 to produce urea.

Here the main challenge is the process intensification, to realize an efficient technology on the medium-scale suitable for MSW (RdF) use, as commented below. Reduction in the process steps, as well as microreactors use,^[17] are the two related keywords. The most effective possibility is the development of a technology for the direct syngas to urea conversion. There are very limited studies in this direction. Akay^[18] indicated the possibility to use catalytic multi-reaction-zone reactors with nonthermal plasma and simultaneous reactive separation for direct fertilizer production. An extension of current electrocatalysts for direct ammonia synthesis^[19] could allow producing directly urea.

Urea is one of the largest volume chemicals, with current production over 190 Mt per year, about 80 % of which used as fertilizer. It is also a market in still continuous expansion, at a rate estimated between 2–4 %. In the actual process of urea production, starting typically from methane to produce the H_2 necessary for ammonia synthesis, the most critical process step (from an energy intensive point of view) is the ammonia synthesis integrated with H_2 production. The total actual natural gas consumption in best-available-technology new ammonia plants is estimated to be between 27.4 and 31.5 GJ/t, corresponding to CO_2 emissions ranging from 1505 to 1729 kg/t.^[20]

Using the waste-to-urea technology, a saving of about 0.113 tons CH_4 and about 0.78 tons CO_2 per ton urea produced could be achieved.^[14a] In the case of introducing new advanced technologies for direct syngas to urea conversion, a reduction in the capital expenditure and energy intensity higher than 20 % could be expected, although difficult to be estimated, being still at a too early stage. However, already with the actual technologies, but to be improved to realize an efficient process and energy integration even at a medium-size plant discussed below, the waste-to-urea process represents an opportunity from both economic and environmental protection perspectives^[14a] for a distributed fertilizer production.

Methanol production is another valuable target for waste-to-chemical.^[14b,21] Methanol is a large volume product which found use as both chemical and fuel in several applications. The current world demand is raising at a rate over 3–4 %, due to new applications from fuel area and for the production of olefins. Currently, it is produced for over 80 % from natural gas, but its synthesis from coal, via syngas formation, is increasing. The advantage of the production from waste is that the (bio)-methanol produced has the premium of being considered as a biofuel counted twice to meet biofuel targets.^[21]

The process scheme from RdF was earlier discussed.^[14] In addition to good economics, with a return of investment of up to about 30 %, the waste-to-methanol process allows halving the greenhouse gas emissions with respect to methanol production from natural gas and shows lower greenhouse gas emissions with respect to other bio-methanol productions.^[14] Worth to note, the process may be coupled with the use of renewable electrical energy (for example, surplus during night) to produce O_2/H_2 from water electrolysis and increase process productivity.

Another interesting process option is the production of low-density polypropylene. A block diagram is presented in Figure 3, where syngas is routed to a gas fermentation^[22] step to produce ethanol. The ethanol can be dehydrated to ethyl-

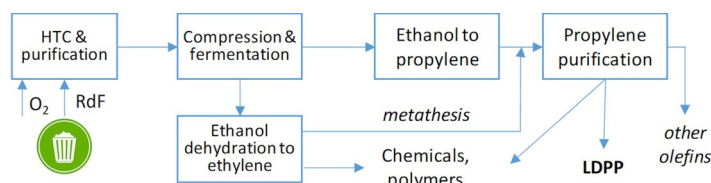


Figure 3. Block diagram to make low density polypropylene (LDPP) from waste (RdF).

ene efficiently by using acid catalysts,^[23] and then ethylene can be used as building block for other chemicals or polyethylene. However, the actual demand and price value is especially for low-density polypropylene. While ethylene metathesis to propylene and butenes is well established commercially, a valuable option in this case is the direct catalytic conversion of ethanol to propylene, which has been reported to be possible in high yield over a composite In₂O₃/zeolite beta catalyst.^[24] This reaction has not been extensively studied, or applied commercially, but the low production cost associated to ethanol deriving from a waste, can open new perspectives. Propylene can be then fed to a conventional low-density polypropylene unit. From a ton of RdF (or equivalent waste), about 0.26 tons of low density polypropylene could be produced.

Only for low-density polypropylene, the demand today is higher than 20 Mt per year, and it is expected to reach 30 Mt per annum in 2030. The possibility to produce low density polypropylene from alternative sources than fossil fuels is currently a challenging possibility, taking into account also that currently the perspectives in using shale gas has been significantly revised. The production of low-density polypropylene from waste has the advantage of using an unused carbon source and widespread available, with thus a further step towards to a distributed production and a circular economy. Also in this case, the step of low density polypropylene production should be optimized for medium-scale production.

Process Layout

Looking at the existing literature, waste-to-chemical is not yet considered as a way to convert waste to produce chemicals, but to produce energy (electrical energy with eventual heat co-generation, the waste-to-energy technology), fuels (by pyrolysis, anaerobic digestion) or eventually as substrate for some enzymes or to recover some components for recycling. The only specific waste-to-chemical process has been suggested by Antonetti^[14a] and Iaquaniello^[14b] by using high temperature gasification or conversion with pure oxygen. This is the key step to convert RdF into a syngas having a composition that enables to a further transformation into several chemicals.

Production and Purification of the Syngas

Figure 4a reports a scheme of high temperature conversion, in which a temperature control is done along the vertical axis with two oxygen injections in the so-called heating area (800–1000 °C) and in the melting area (1000–1600 °C).

Such high temperature conversion may be considered as a sort of fixed bed, where the waste is fed from the side. The partial conversion of the waste in the bed leads to the formation of a syngas, which moves to the upper part of the reactor, the stabilization chamber, where the temperature is maintained higher than 1000 °C in order to complete the cracking of the long chain organic molecules as the tars and the destruction of other noxious molecules such as dioxins and furans.

The typical composition of the syngas produced is in this range (% vol): H₂ 36–40, CO 37–43, CO₂ 8–16, H₂O 6–8, N₂ 1–5, O₂ < 2, CH₄ < 5, Argon < 2. Typical impurities (mg/Nm³) are the following: H₂S 100–1500, COS 10–150, other S compounds < 10, HCl < 5, HF < 1, HCN < 10, Hg < 0.2, Ti + Cd < 0.2, heavy metals < 1, particulate matter < 3.

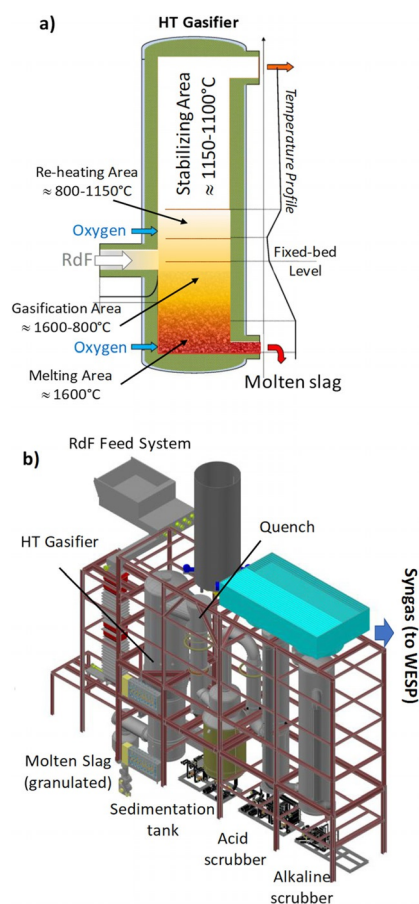


Figure 4. (a) HT converter for waste-to-chemical plant with indications of different reaction zones and of the temperature profile. (b) Unit of HT gasification and related purification section. Reproduced with permission from Ref. [10] Copyright Elsevier, 2017.

Such a syngas has a CO/H₂ ratio around 1,2 which indicates a shortage of hydrogen for manufacturing methanol or urea, or conversely an excess of CO + CO₂. Of course, the syngas contains a fraction of the impurities contained typically in the waste, mainly S compounds, HCl and HCN, which need to be removed from the gas stream before the downstream processes.

The syngas production may change due to feedstock composition changes and irregularities in the reactor bed behavior. Different feedstocks cause variation in the syngas quality/quantity. Some examples of impact of feed composition on the syngas output are presented in Table 1.

Table 1. Dependence of syngas characteristics from the feed composition to the high temperature conversion unit.				
Feed [kg/h]	9000	9000	7000	7000
	Composition [% wt.]			
Wood	3	3	35	1
Paper	29	34	24	10
Plastic	31	36	5	68
Textile	7	8	7	6
Organic fraction	12	10	14	7
Inert fraction	18	9	15	8
LHV waste [MJ/kg]	14.05	16.04	11.21	20.97
Syngas [Nm ³ /h]	10,837	12,444	7605	11,708
H ₂ [%vol]	41.0	41.8	39.3	42.1
CO [%vol]	41.4	42.4	40.1	44.4
CO ₂ [%vol]	4.7	4.7	4.7	4.7
H ₂ O [%vol]	12.9	11.1	15.8	8.8
LHV syngas [MJ/Nm ³]	9.58	9.79	9.23	10.08

The magnitude of the changes depends on the feedstock supply strategy, but a proper premixing of different wastes allows minimizing such a change, which in any case, is in the order of magnitude of a few percentage of points per hour.

The non-uniformity of the reactor bed behavior introduces variations in the syngas flow. In regular operations, a fluctuation of a few percent per minute is considered normal. Additionally, a partial clogging of the bed (as bridge formation), with subsequent temporary decreasing of the syngas production, might occur. At a later stage, the bridge collapses, generating a peak of syngas and a short period of overproduction. Applying a suitable dimensioned gasometer and, where it will be possible, operating with multiple parallel units, peaks and fluctuations can be reduced or even eliminated.

After the waste conversion step to syngas, a subsequent purification of the raw gas is required, as shown in Figure 5 and Figure 4b. The high temperature and the appropriate temperature profile are the key parameters to achieve the proper performance of the high temperature conversion step. In particular, hydrogen content increases and tar remarkable decreases at temperature higher than 1000 °C, methane and other hydrocarbons tend to decompose at temperatures higher than 600 °C. By proper selection of the operative conditions, the amount of char becomes negligible. The gas leaving the converter at around 1100–1150 °C is quenched with water to ambi-

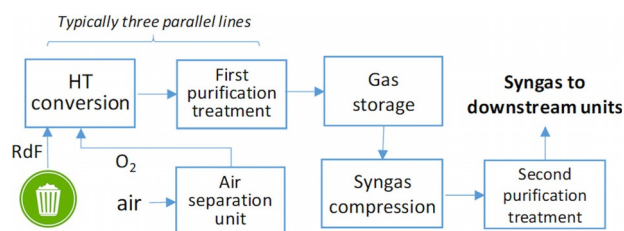


Figure 5. Block diagram of the waste conversion and purification.

ent temperature and enters two adsorption towers in series, the first with water and the second with an alkaline solution in order to remove particulate, metals and HCl. A wet electrostatic precipitator (WESP) will act as a final polisher. The raw gas coming from different lines is routed to an atmospheric tank. From the storage, the gas is compressed and moved into the second purification treatment where demetallization and dechlorination steps are carried out before the H₂S/COS removal and conversion to solid sulphur. The purified syngas is now ready to downstream processing according to final chemical product.

A Distributed Approach in Making Chemicals

Once a clean purified syngas is produced, we need to identify what kind of chemicals we may produce, choice that will depend on the amount of syngas available. For an average RdF, LHV equal to 14,000 kJ/kg, the syngas production is approximately 1200 Nm³ per ton. To explore better this concept let us look at Figure 6, which depicts the overall material bal-

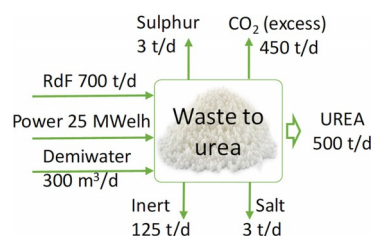


Figure 6. Overall material balance for a 500 metric tons per day waste-to-urea plant. Adapted from Ref. [14].

ance for a 500 metric tons per day (MTPD) waste to urea plant. For such a plant, 700 tons per day of RdF will be required. Considering an average of 320 working days per year, this translates into 225,000 tons per annum. By considering an average of 475 kg MSW annual production per habitant and that about 40% is the RdF fraction, a population of about 1.1 million persons would be necessary to produce the required fuel, if RdF is collected within a maximum distance of about 100 km to limit transport costs and impact. This would require a population density of about 35 persons/km². This is a population density met over most of European areas, for example. It is quite evident that a distributed approach can be adapted in Europe for the waste-to-chemical production.

Economic Assessment

All the process schemes presented here could be considered reliable and technologically feasible today, even if some further developments are necessary in terms of process intensification and step reduction, as commented before. There is also a need to tailor the catalysts for the different options for syngas conversion, because the syngas composition, both in terms of $\text{CO} + \text{CO}_2$ ratio to H_2 and in terms of impurities, is different from that of current commercial syngas catalysts. A pre-requirement for these developments is the demonstration of the techno-economic feasibility, one of the objectives for this Concept paper.

The key aspect for the possibility for exploitation is the economic feasibility. Economic parameters used to estimate the cost of production are summarized in Table 2. Capital expenditures have been calculated as a percentage of the delivered equipment costs, following usual cost estimation procedures for initial feasibility. The typical accuracy of this procedure is around 30%, which could be considered acceptable for preliminary estimations.

Table 2. Key economic elements and parameters used to estimate the costs of production in waste to chemical processes.

Parameter	Costs
RdF price	80 € per ton
Electricity price	50 € per MWh
Slag disposal	20 € per ton
Maintenance costs	25 % of the capital expenditure (CAPEX)
Methanol capacity	105,000 ton per year, capital expenditure 350 m€
Hydrogen capacity	30,000 Nm^3/h (900 t/y), CAPEX 110 m€
Methane capacity	36,000 t/y, CAPEX 150 m€
Low density polypropylene capacity	100,000 t/y, CAPEX 590 m€
CO_2 avoided	15 € per ton
Capacity factor	8000 h/y
Depreciation factor	0.0875 based on 20 years and 6 % interest rate
Labour and other costs	2 % of CAPEX

Table 3 provides the costs of production compared with the actual market price of the same chemical produced starting from fossil fuels. These results and the estimated profit per ton of chemicals indicate an estimated return of investment higher than 15%, which indicate an interesting profitability and value

Table 3. Cost of production of various chemicals via the waste-to-chemical concept.

Chemical	Cost of production [€]	Average product value [€]
Urea [€/t]	135	225
Methanol [€/t]	150	325
Low density polypropylene [€/t]	550	1000
H_2 [€/Nm ³]	0.07	0.12
CH_4 [€/Nm ³]	0.16	0.25

for further process development and exploitation. Although costs of production have been calculated considering an average situation, which may change from country to country, and even from the specific location within one country, the values presented in Table 3 remark that it is worthy to explore in a more detail the waste-to-chemical technology.

Environmental Benefits

In the analysis of the environmental benefits for waste-to-chemical technology, the following aspects have to be considered: the new process will substitute the equivalent currently based on fossil raw materials, which show highly fluctuating prices, difficult to predict on a long term, and which extraction/distribution has also its relevant environmental impact, although often not considered;

MSW should be treated anyway, with the current approach still largely based on landfill (for over 50% on the average) with the related impact in terms of greenhouse gas (CO_2 , CH_4 , N_2O), odors and other VOCs (volatile organic chemicals) emissions as well as highly polluted wastewater; the actual main alternative to landfill for MSW is waste-to-energy technology, for which cogeneration is not always used (with thus limited energy efficiency), and with increasing issues related to the limited capacity of the electrical grid to accept the produced electrical energy, due to the increasing competing production based on renewable energy sources; the distributed production of chemicals at a regional level will bring benefits in terms of local use of the resources and integration with territory needs, as well as job preservation.

The discussed aspects are part of the general concepts of i) waste biorefinery, based on the integrated use of different waste local resources (from MSW to agro-food wastes) to produce different fuels/chemicals for the local needs, and ii) circular economy. The benefits of the waste-to-chemical approach are thus going beyond the simple substitution of fossil fuels with an alternative C-source and the reduction of the environmental impact, which can be estimated for this substitution.

For the waste-to-urea process, the comparison of the inputs-outputs with that of the conventional process, should consider that RdF alternative conversion by waste-to-energy technology will produce greenhouse gas emissions, and will eliminate part of the need of use of fossil fuels to produce the equivalent amount of energy. The net impact in producing urea from RdF (with respect to the actual process from natural gas) should thus consider the amount of methane necessary to produce urea in the conventional process minus the amount of methane needed to produce the same amount of electrical energy obtained in RdF waste-to-energy process. To estimate the impact on CO_2 emissions, the differences in CO_2 emissions for waste-to-urea versus the conventional process should be included. In this way, may be estimated that the production of urea from RdF will save about 0.13 tons CH_4 per ton urea produced and about 0.78 tons CO_2 per ton urea (Figure 7).^[14a] In the conventional urea process from natural gas, about 0.382 tons CH_4 per ton urea produced are required, and thus there is an increase in energy efficiency (in terms of natural gas saving)

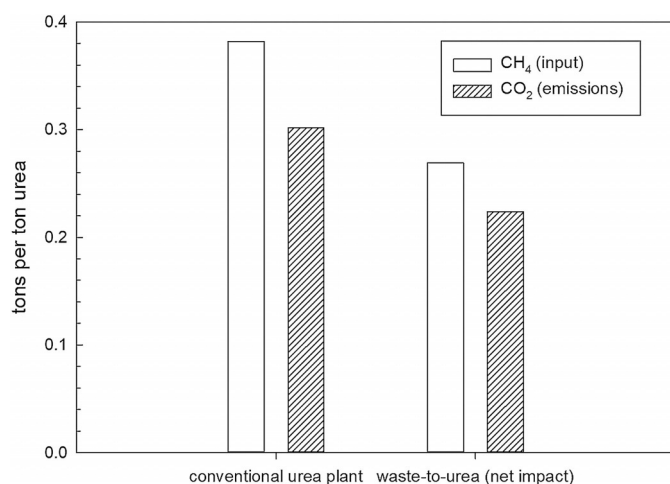


Figure 7. Comparison of methane input and CO₂ emissions between the conventional urea process and the waste-to-urea technology. For the latter, the net impact is considered, for example, the methane input and CO₂ emissions associated to produce the same amount of electrical energy obtained in RdF waste-to-energy process.

of about 30%, with an analogous saving in greenhouse gas emissions.

For the waste-to-methanol process, CO₂ emissions should be compared to the actual routes for bio-methanol production which range from 0.56 kg CO₂ equivalents per kg methanol from forest residues to 0.64 kg CO₂ equivalents per kg methanol for short rotation coppice,^[14] with respect to methanol from natural gas (0.84 kg CO₂ equivalents per kg methanol). The reduction in greenhouse gas emission ranges around 30%. For a new waste-to-methanol plant, it should be considered the balance between carbon (as CO₂ equivalents per kg) entering as RdF and the CO₂ emitted, by considering also in this case the alternative of waste-to-energy. In this way, the estimated CO₂ emissions are about 0.44 kg CO₂ equivalents per kg methanol, with thus a reduction of about 45–50%.^[14]

Even with a conservative approach, we may thus indicate that also for waste-to-methanol case, the environmental benefit is a reduction of over 30% in greenhouse gas emissions. The energy efficiency, calculated from the LHV of methanol with respect to the LHV of inlet RdF, is close to 70%, although slightly reduces when the energy input necessary for producing the O₂ required for high-temperature converter is considered. However, it is an energy efficiency typically higher than the average for waste-to-energy plants.

In general terms, all the different waste-to-chemical solutions show an environmental benefit in terms of greenhouse gas emissions higher than 20% with respect to the current processes using fossil raw materials and the alternative use of MSW for energy generation. Together with the improved economics (Table 3) it is possible to conclude that waste-to-chemical is a valuable solution for a more sustainable use of MSW.

Conclusion

Waste-to-chemical technology, based on the valorization of the C-component of the municipal solid waste, represents an un-

tapped opportunity to promote a distributed and low-carbon production of chemicals, which will significantly contribute to the reduction of the dependence from fossil resources. We have shown in this concept paper that this technology, which can be flexibly adapted to produce different type of chemicals, is techno-economic feasible, and allows a reduction of over 20–30% in energy intensity and greenhouse gas emissions.

Although some aspects in terms of process intensification and reduction of process steps could bring further benefits, and catalysts tuned for the specific cases and syngas composition should be developed, the main knowledge and technologies to exploit this solution exist. A short-term exploitation is thus possible, and we hope that this concept paper will stimulate this possibility, which is an important element to promote a circular economy.

The crucial element of the technology is to produce a syngas (CO₂-rich) with purity characteristics suitable for downstream catalytic transformation to the aimed products. This poses constraints in terms of the gasification units, which have been shortly discussed. We indicated high-temperature gasification using O₂ as oxidant as a solution, but the development of improved purification technologies together with more poison-resistant catalysts for downstream processing could allow milder operations. There is also the need to optimize the downstream processing for efficient operations also on relatively small-scale processes. New process and reactor intensification solutions are thus needed. An optimization of the single components and of the integrated process is thus necessary, but this paper remarks how both techno-economic and environmental motivations to develop this technology to a commercial level exist already.

From an educational perspective, we hope that this paper has demonstrated that it is feasible to consider alternative C-sources to fossil fuels and that exist largely available waste such as MSW that could play a relevant role in moving out from the predominant role of fossil-derived chemicals. MSW represents a C-resource already available in a distributed manner, which could offer the starting element on a short-term to move out from fossil fuel dependence. In medium-longer terms, other solutions could be possible, but it is necessary to have already some solution available in the shorter-term to catalyze the transition.

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Conflict of interest

The authors declare no conflict of interest.

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