

GHG Emissions by (Petro)Chemical Processes and Decarbonization Priorities—A Review

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Abstract: Global warming is becoming an increasing issue, and greenhouse gas (GHG) emissions represent the engine of such a phenomenon. This review aims to identify the origin of GHG emissions and focus in detail on the ones related to (petro)chemical industries. The industrial sector is the primary GHG emitter among all the other anthropogenic sources. The chemical industry is the first in charge of that (having accounted for about 6.5% of the global GHG emissions in 2018). Thought-provoking data such as yearly productivities and emission factors related to the predominant chemicals prompt the reader to acquire a sense of the critical activities responsible for carbon-intensive emissions, which should be the first to be decarbonized. Specifically, ammonia synthesis and steam cracking resulted in the most polluting processes of the chemical industry, being responsible for the release of about 440 and 228 Mt-CO_{2,eq}/y, respectively, in 2020. The same approach also applies to oil refining. Due to the massive amounts of oil barrels produced daily, oil refining is a key player in industrial GHG emissions (about 3% of the global emissions in 2018). Indeed, in 2020, refineries emitted nearly 1313 Mt-CO_{2,eq}/y.

Keywords: greenhouse gas emissions; climate change; carbon intensity; green policy; methodology; chemical industry; oil refining; commodities; energy

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1. Introduction

The awareness of the effects of greenhouse gas (GHG) emissions on climate change and the effort to reduce them from every human activity are increasing daily. In particular, the Paris agreement (2016), aiming to limit global warming to a maximum of 2 °C (preferably 1.5 °C) compared to pre-industrial levels, represents a true milestone on this path, being the first-ever universal and legally binding international treaty on climate change [1,2]. Nonetheless, GHG emissions still reach very alarming levels. Current estimations agree on global values having risen from 45 to 50 Gt-CO_{2,eq}/y in the last ten years [3,4] with a monotonically increasing trend (except for 2020, when a considerable decline occurred due to the SARS-CoV-2 pandemic [5]) due to the unrelenting demographic growth. According to the United Nations, the world population will reach 8 billion by the end of 2022 [6]. Such a tendency will inevitably lead to increased energy consumption and anthropogenic emissions.

Therefore, a proper long-term low GHG emissions development strategy is recommended, and, in this respect, it is crucial to assess how these emissions distribute in each different human activity. The paper quantifies the most responsible emitting sources and shows how to prioritize the decarbonizing policies. Indeed, efforts to reduce GHG emissions by focusing on relatively low polluting human activities would result in negligible benefits, even if very radical. Conversely, even mild environmental mitigation policies targeting remarkably polluting activities would significantly improve the global scale.

For clarity, it is essential to elucidate what “human activity” means. GHG emissions can be traced back to either the “sector” that produces them or the “end-user” they are made for. This review accounts for both categories by exploiting the data published by Climate Watch [3] and World Resources Institute (WRI) [7]. It is worth mentioning that most of the reviewed data refer to 2018, which is neither too distant (somewhat well representative of the current situation) nor too close (2018 did not suffer the impact of the economic shutdown originated by the SARS-CoV-2 pandemic). Table 1 lists the results of the analysis by sectors, with the most impactful one being *Electricity and Heat*, as it accounts for almost a third of the total. *Transportation; Manufacturing and Construction; Agriculture; Industrial Processes; Fugitive Emissions; Buildings; Waste; Other Fuel Combustion; and Land-Use Change and Forestry* follow in descending order (see also Table 1 for further details).

Table 1. World GHG emissions (2018) shared among production sectors (data from [3,7,8]).

Sector	GHG Emissions [Mt-CO _{2,eq} /y]	Mass Share [-]
<i>Electricity and Heat</i> ¹	15,875	32.2%
<i>Transportation</i>	8418	17.1%
<i>Manufacturing and Construction</i> ²	6223	12.6%
<i>Agriculture</i> ³	5803	11.8%
<i>Fugitive Emissions</i> ⁴	3354	6.8%
<i>Buildings</i> ⁵	3106	6.3%
<i>Industrial Processes</i>	2967	6.0%
<i>Waste</i> ⁶	1607	3.3%
<i>Land-Use Change and Forestry</i>	1388	2.8%
<i>Other Fuel Combustion</i> ⁷	627	1.3%
Total	49,368	100%

¹ Electricity and heat plants, other Energy Industries. ² Emissions due to direct fuel combustion in manufacturing and construction sites. ³ Including livestock and manure. ⁴ Intentional or unintentional releases of gases from human activities (mainly due to fossil fuels extraction, processing, and transmission). ⁵ Both residential and commercial. ⁶ Waste management activities (e.g., landfills and wastewater). ⁷ Emissions related to other unstated sectors, from stationary and mobile sources.

Electricity and Heat is at the top position as global electricity consumption, which recently topped 23 PWh (2019) [9], and most of its production bases on very carbon-intensive processes. A recent article quantified an average emission factor for electrical energy (which depends on the adopted fuel mix) of about 123 kg-CO₂/GJ [10]. Such an emission factor is way higher than the ones classically estimated for natural gas, oil, and coal (56, 73, and 95 kg-CO₂/GJ, respectively) [11]. That is because pretty low-efficiency processes mainly produce electricity (consider that the energy ratio of electricity output to fuel input typically ranges from 40 to 50%).

However, Table 1 still provides an incomplete picture of those activities responsible for such emissions. Instead of considering “upstream” sectors such as *Electricity and Heat* as distinct categories, it is particularly relevant to analyze how their emissions distribute among “downstream” activities or, in other terms, which is truly responsible for them. For the sake of detail, let us consider that the main requests for *Electricity and Heat* come from *Industry* and *Buildings*, each representing about 40% of the total demand. Regarding *Manufacturing and Construction*, the leading consumer is *Industry* again, accounting for almost 98% of the whole sector [7]. As a result, *Industry* stands as the top emitter among the considered end-users, as reported in Table 2.

Table 2. World GHG emissions (2018) shared among end-users (data from [3,7]).

End-User	GHG Emissions [Mt-CO _{2,eq} /y]	Mass Share [-]
<i>Industry</i>	15,163	30.7%
<i>Buildings</i>	9325	18.9%
<i>Transportation</i>	8617	17.5%
<i>Agriculture</i>	6489	13.1%
<i>Unallocated Fuel Combustion</i> ¹	3425	6.9%
<i>Fugitive Emissions</i>	3354	6.8%
<i>Waste</i>	1607	3.3%
<i>Land-Use Change and Forestry</i>	1388	2.8%
Total	49,368	100%

¹ Includes Own use in electricity, CHP, and heat plants; Nuclear Industry; Biomass combustion; Pumped Storage; Other.

A comparison between Table 1 and Table 2 reveals the remarkable influence of “upstream” activities on “downstream” ones. It is evident how considering emissions associated with productive processes only, makes *Industry* a relatively minor emitter (6% of the total GHG emissions). Conversely, considering the indirect emissions (such as those related to electricity and fuel consumption) makes *Industry* the major emitter (almost 31%).

2. Industry

As aforementioned, *Industry* is the primary source of GHG emissions, accounting for almost a third of the total value worldwide. Therefore, it is relatively straightforward that any effective decarbonization strategy should primarily point at this sector.

Table 1 provides valuable information regarding both environmental and economic data. Worldwide, lawmakers have used these data to enact suitable “carbon taxes”, which charge GHG emissions and/or fuels that release them [12]. Carbon taxes promote two synergistic consequences: (i) increase public revenues and (ii) encourage CO₂ reduction. The cost escalation induced by carbon taxes incentivizes companies to manufacture their products in ways that would result in fewer emissions. Ultimately, higher production costs lead to higher end-prices of carbon-intensive goods and services, which eventually induce households to sober use.

The assessment of the carbon intensity of each industrial sub-sector has to account for both the direct process emissions (e.g., the CO_x and NO_x from the synthesis routes) and the indirect ones (e.g., from utilities such as electricity, fuel gas, fuel oil, etc.).

An accurate analysis of the diverse industrial sub-sectors is recommended to help address environmental mitigation policies where they are needed the most. Such an approach may prove helpful in identifying the real “players” among the industrial activities in terms of anthropogenic emissions (see Figure 1).

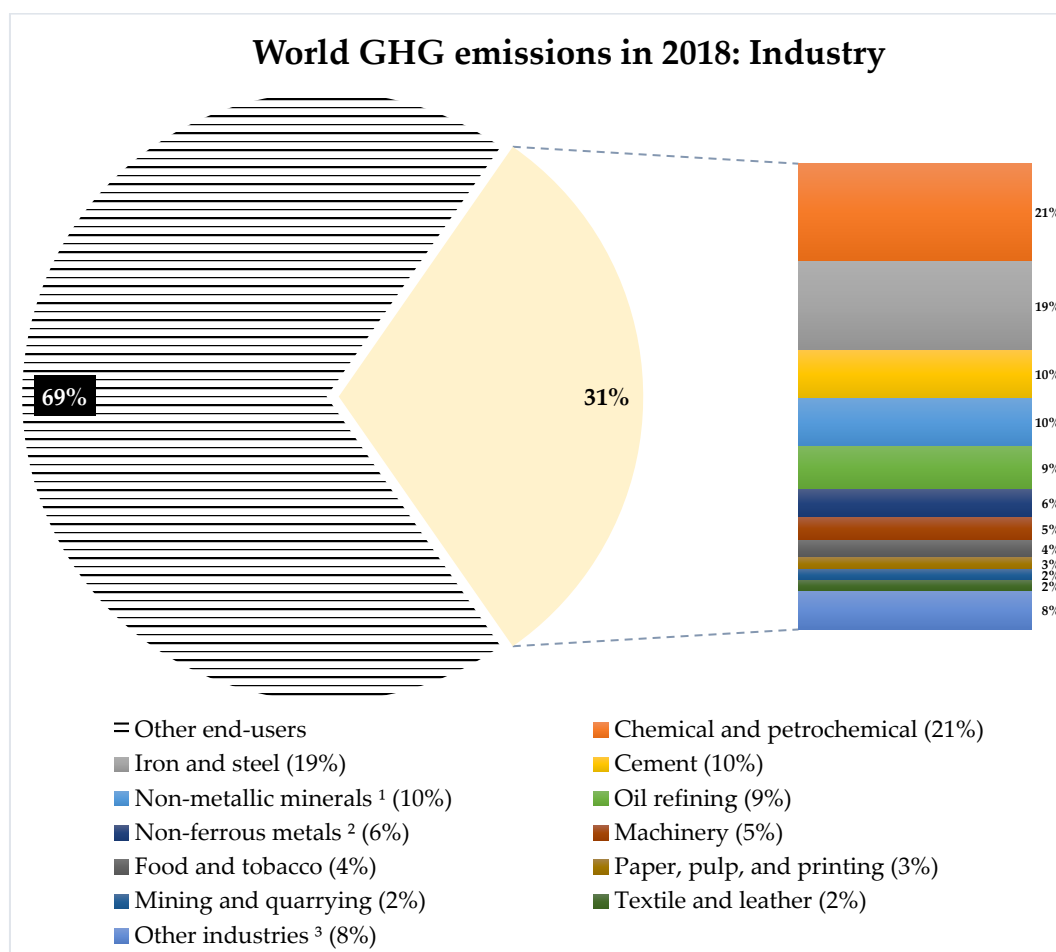


Figure 1. Focus on the share of global GHG emissions of the industry sector (2018). ¹ E.g., lime, glass, and ceramics. ² E.g., aluminum and magnesium. ³ Includes Transport equipment, Wood industry and products, Electronics. Data from [3,7,8,13,14].

Figure 1 highlights the sub-sectors of *Industry*. As can be seen, some of them are much more polluting than others. They mainly are *Chemical and petrochemical*; *Iron and steel*; *Cement*; *Non-metallic minerals*; *Oil refining*; *Non-ferrous metals*; *Machinery*; *Food and tobacco*; *Paper, pulp, and printing*; *Mining and quarrying*; *Textile and leather*; *Transport equipment*; *Wood industry and products*; *Electronics*, here listed in descending order of GHG emissions. It is worth noting that the first five sub-sectors alone amount to about 70% of the total *Industry* emissions. Finally, it is worth noting that all these five sub-sectors fall under the expertise of chemical engineers.

3. Chemicals and Petrochemicals (Plus Oil Refining)

The *Chemical and petrochemical industry* is the top emitter (21%) among all the industrial sub-sectors. This sub-sector includes the production of fertilizers, pesticides, pharmaceuticals, plastics, resins, refrigerants, paints, solvents, soaps, perfumes, and synthetic fibers, as well as chemicals derived from oil refining: ethylene above all, and the so-called petrochemicals, such as polyethylene, polystyrene, and polyvinyl chloride. If one adds the emissions due to *Oil refining* (which, after all, is the precursor of almost every petrochemical process), the whole category accounts for about 30% of the *Industry* emissions. In other words, the emissions related to the sum of oil refining and chemical plants represent more than 9% (30% of the 31%) of the global GHG emissions.

Similar to *Industry*, it is rather interesting to investigate the most impacting products that make *Chemical and petrochemical industry* so polluting. In this respect, two parameters

are crucial to identifying these “dirty” products: their annual production volumes and the corresponding gate-to-gate GHG emission factors.

Chemical products may be divided into two main groups by production volumes: commodity and fine chemicals. Commodity chemicals are compounds produced on a vast scale (mostly in dedicated continuous plants) and sold at relatively low prices. Fine chemicals are synthesized in limited volumes (usually in multipurpose batch plants) and sold at higher prices. In our investigation, the compounds of interest are commodity chemicals. This category is associated with significantly high production volumes and is responsible for direct and indirect GHG emissions. In addition, it is involved in several downstream processes (e.g., the ones needed to synthesize the majority of fine chemicals). In this respect, Figure 2 lists the analyzed commodity chemicals and reports their production volumes in 2020.

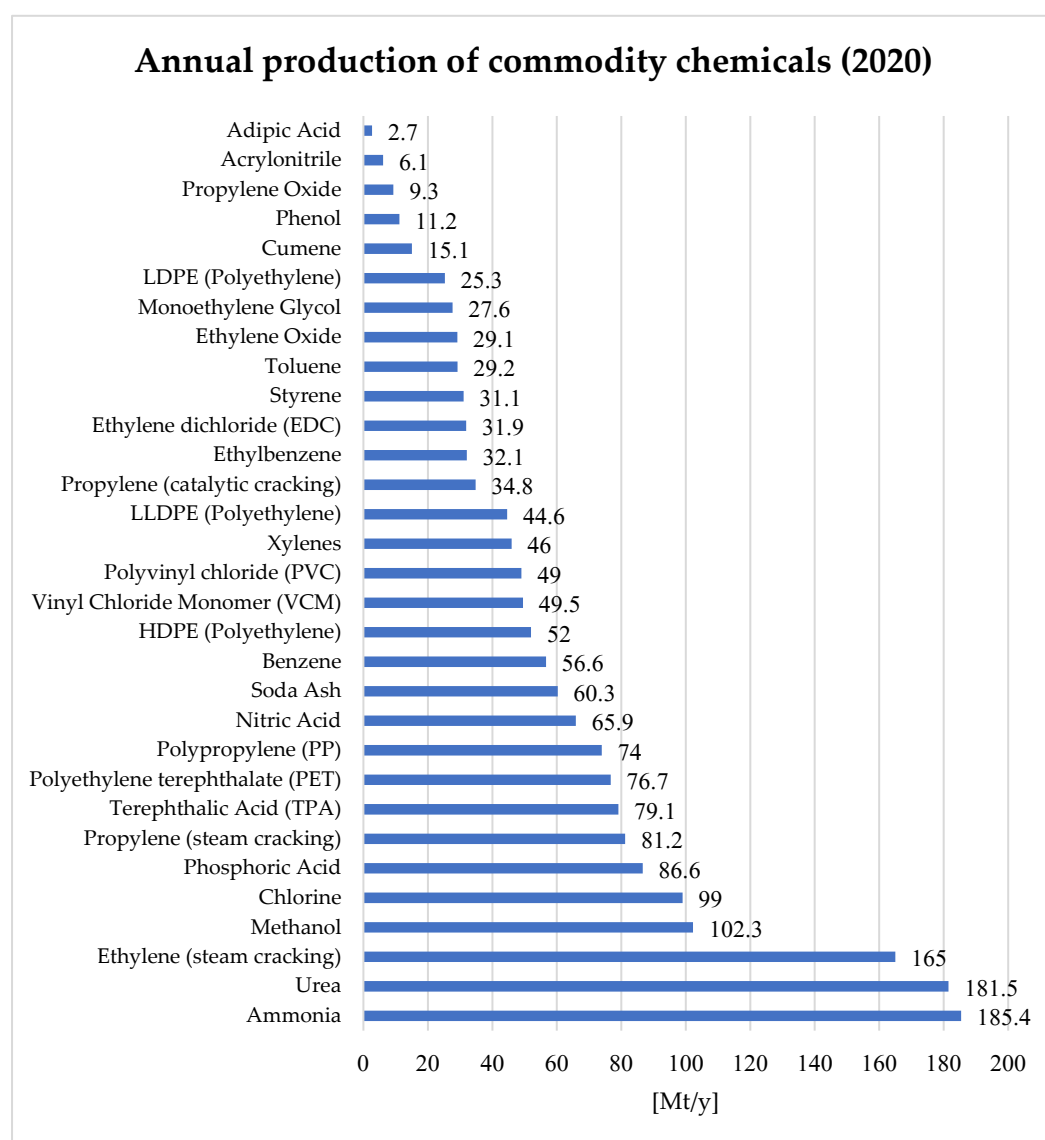
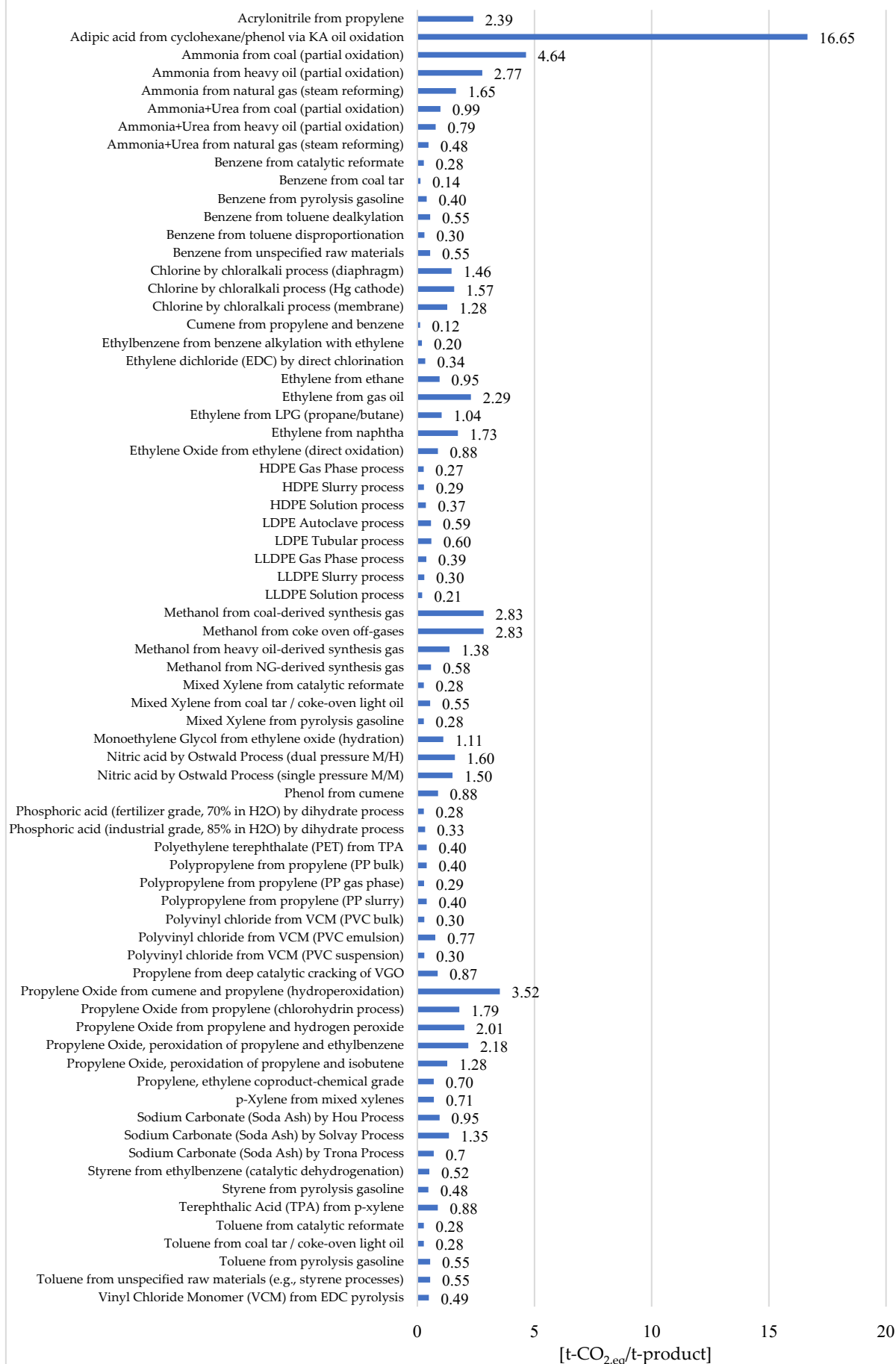


Figure 2. Annual production of commodity chemicals (2020). Note that 4165.1 Mt/y of oil (including crude oil, shale oil, oil sands, condensates, and natural gas liquids) were processed in the same year [13]. Data from [15–45].

The second fundamental indicator to be evaluated is the gate-to-gate GHG emission factor. This parameter (borrowed from the Life Cycle Assessment (LCA) jargon [46,47] and typically expressed in mass of carbon dioxide equivalent per a specific “functional unit”) quantifies the carbon footprint associated with a production plant (from the entrance “gate” to the exit “gate”). Similar indicators are the cradle-to-gate and cradle-to-grave GHG emission factors, wherein “cradle” accounts for the extraction of raw materials. At the same time, “grave” considers the waste disposal of the products. However, since this manuscript focuses on the *Industry* sector, the cradle-to-grave approach, besides being more complicated, may prove improperly loose. Since we are interested in chemical process emissions, only gate-to-gate information counts. As far as calculations are concerned, the broader scope of cradle-to-grave might lead to subtle errors, especially related to double counting. In fact, since many chemicals, once synthesized, become the reagents for further downstream processes and products, it is advisable to analyze every single production step individually. For instance, when computing the amount of GHG emissions related to ethylene and polyethylene syntheses, it is better not to use “cradle-to-” data as by doing so, one would compute twice the emissions from the ethylene process, as ethylene is also the cradle of polyethylene. Conversely, if one considers the emissions of the sole production steps for each species (i.e., “gate-to-gate”), there are no risks of either over- or under-estimation errors since each compound is handled as an isolated compartment. Accordingly, Figure 3 lists the gate-to-gate GHG emission factors of the leading commodity processes (alongside the main processes typically performed in oil refineries).

Concerning Figure 3, firstly, the emission factors cover very different ranges, where the lower is the better, as they quantify the carbon intensity of the process. Secondly, the emission factors were selected from several sources, with a few of them as old as 15 years. Nevertheless, such values should not be considered outdated as they result from material and energy balances, which are universally valid. Deviations may arise concerning time-dependent variables such as (i) the change in the fuel mix of electricity generation or (ii) remarkable modifications in the design of the process units involved. These would lead to updated material and energy balances (e.g., new arrangements of the CO₂ streams within the battery limits of the production plant).

a. Average gate-to-gate GHG emissions in chemical sector



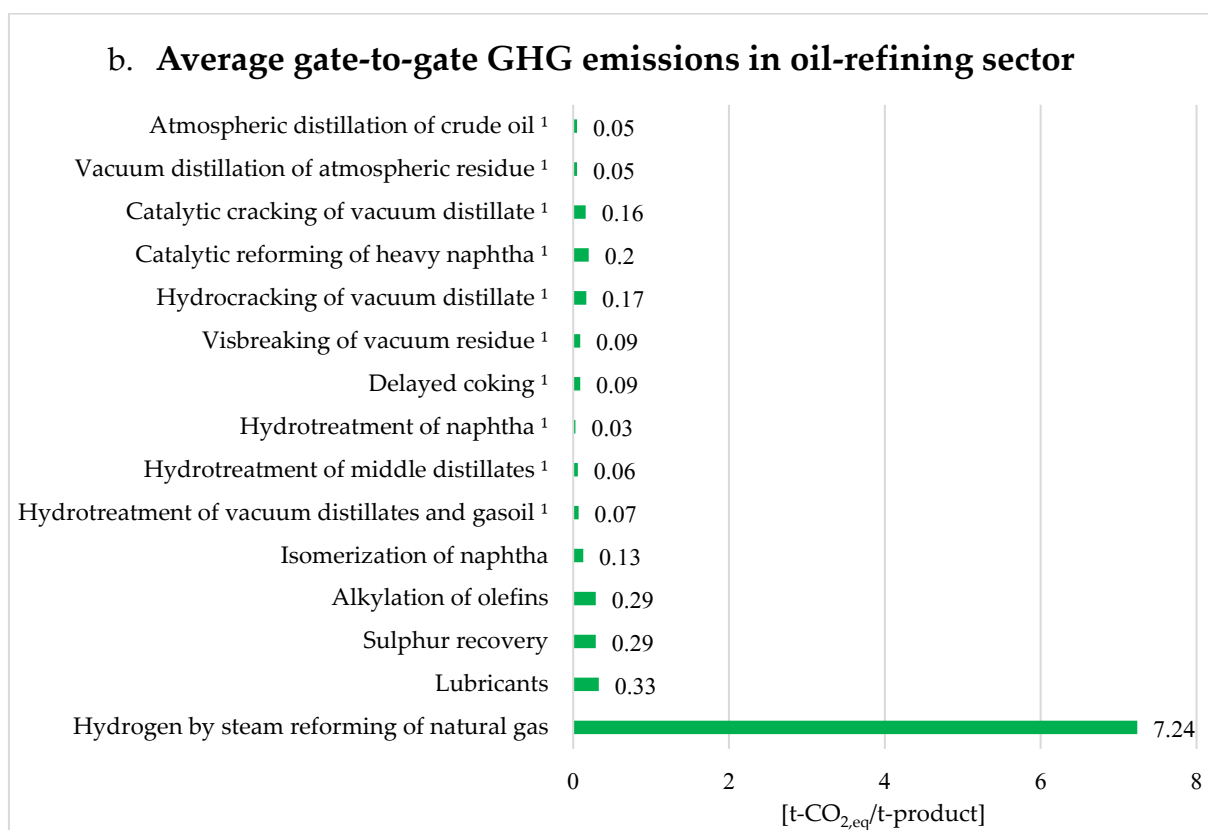


Figure 3. Average gate-to-gate greenhouse gas emission factors related to the main processes and products of the (petro)chemical (Panel (a), in blue) and oil refining (Panel (b), in green) industries. ¹ Expressed per metric ton of feedstock (instead of per metric ton of product). Data from [48–54].

Regarding this last point, it is also worth mentioning that the aforementioned 15-year span still falls within the average life of existing chemical plants, whose commissioning and main technological assets date back to those years. Thirdly, the reported values also account for the contribution of indirect emissions (e.g., the ones due to power and fuel consumption). For instance, chlorine production is carried out by a chemically carbon-free reaction with sodium chloride and water as reactants. Therefore, no emissions are expected if limited to its synthesis. However, chlorine production may produce GHG emissions due to the electricity consumed by the electrolyzer. Indeed, the current fuel mix of electricity generation is very carbon-intensive, and the overall emission factor is significant. Moreover, it is worth considering that these emission factors are expressed per metric ton of product. This means that the lighter the product, the higher the emission factor. For instance, if one considers two compounds produced in the same reaction with the same stoichiometric coefficients, more feedstock is required to collect a metric ton of the lightest one. This explains why the same process (e.g., steam reforming of natural gas) exhibits different emission factors for the products being considered. When referred to the production of 1 kg of hydrogen, the emission factor is 7.24 kg-CO_{2,eq}/kg-H₂ (see Figure 3). Conversely, when referred to the production of 1 kg of ammonia, the emission factor is 1.65 kg-CO_{2,eq}/kg-NH₃ (as 1 kg of ammonia contains 0.18 kg of hydrogen that is produced in the steam reformer and contributes to CO₂ emissions, whilst the remaining 0.72 kg is nitrogen and has nothing to do with the carbon intensity of the reaction).

After having collected the two main parameters of interest (i.e., yearly productivity of the main chemicals and their emission factors) for all the examined chemicals, the carbon footprint of each compound can be evaluated by multiplying its annual production(s) by the emission factor(s) of its process route(s). For instance, in the case of ammonia, Figure 3 lists three main production routes for its synthesis (i) partial oxidation of coal, (ii) partial oxidation of oil, and (iii) steam reforming of natural gas. Each of these processes

features an emission factor weighing 22%, 6%, and 72% of the global ammonia production, respectively [10,55]. This approach to quantifying GHG emissions is simplified as its grounds on average emission factors to account for whole classes of production plants. However, production plants, although based on the same process, may differ in terms of direct and indirect emissions. For instance, deviations may occur due to the operation of the plant, its size, age, location, and underlying technology. Moreover, the present analysis discarded minor synthesis routes due to their negligible contribution to the global scale (e.g., ammonia from water electrolysis). However, we deem that the assessment procedure proposed in this paper, although based on some approximations, is relatively reliable in quantifying the GHG emissions of the (petro)chemical industries.

Figure 4 shows that oil refining is the greatest emitter among the chemical processes; Indeed, oil refining accounts for about 3% of the annual global anthropogenic GHG emissions. This is not due to the relatively high carbon intensity of refinery processes (which present quite low emission factors, as reported in Figure 3) but to the massive quantities that undergo such treatments. In fact, according to BP, more than 88 million bbl/d of crude oil were extracted and refined in 2020 (in 2019, just before the COVID-19 pandemic, that value was almost 95 million bbl/d) [13].

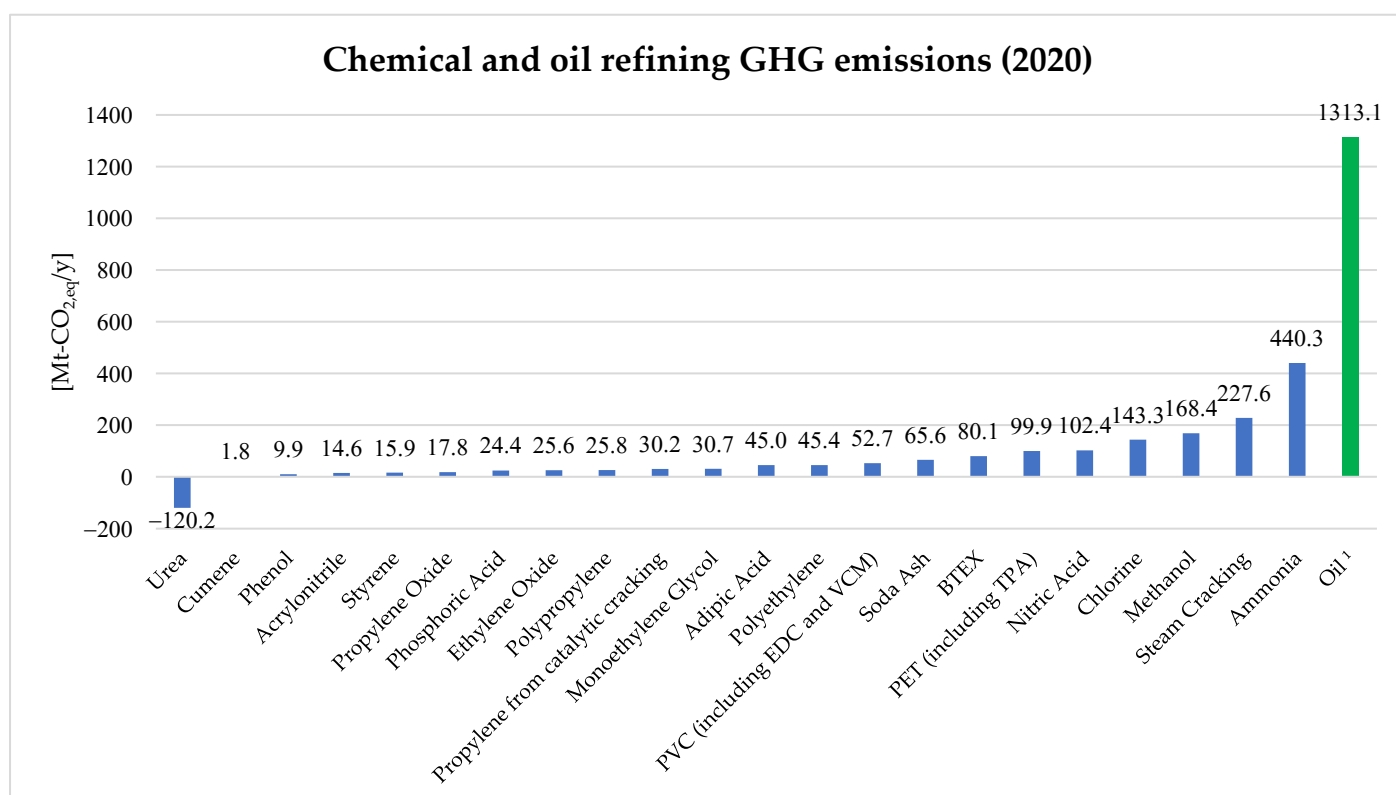


Figure 4. Annual global greenhouse gas emissions related to the main products of the chemical (in blue) and oil refining (in green) industry (2020). ¹ “Oil” includes crude oil, shale oil, oil sands, condensates, and natural gas liquids. Based on the same references of Figure 2 and Figure 3 with the addition of [10,28,48,49,52,53,55–67].

On the other hand, ammonia is the most pollutant chemical as it reaches a total amount of GHG emissions, almost a third of the oil refining ones. In this case, the significant production volumes of ammonia (over 185 Mt/y in 2020, as of Figure 2) contribute to such an outcome. At the same time, there is also a significant problem in terms of carbon intensity for its synthesis. As easily understandable from Figure 3, the gate-to-gate GHG emission factors of ammonia strongly depend on the fossil feedstock provided to the reactors: the richer in carbon the fossil fuel, the dirtier the whole process. Specifically, let us consider the most critical player, China, and another notable one, India. They produce

ammonia mainly through coal- and oil-based processes [55,68]. Such evidence makes ammonia stand as the leading chemical in this ranking.

Next, on the third step of the podium, we have steam cracking which is the primary process to produce ethylene and propylene. These olefins are the precursors of many chemicals, primarily the ones related to the plastics sector.

Among all the other compounds, it is worth mentioning the very tail end of the ranking in Figure 4, urea, which presents a beneficial effect (i.e., negative contribution) as CO₂ is consumed for its synthesis. Indeed, one mole of urea is made by combining two moles of ammonia and one mole of carbon dioxide (with the release of one mole of water); this explains why such a chemical presents a negative balance. However, each urea molecule guarantees a “temporary storage” of CO₂. Mainly utilized as a nitrogen-release fertilizer, when applied to soil, urea hydrolyzes in the presence of the urease enzyme to ammonia and carbon dioxide [69]. Afterward, ammonia is bacteriologically converted to nitrate (and, as such, absorbed by crops), and carbon dioxide is reemitted in the atmosphere.

Finally, the lack of other notable commodity chemicals in this investigation can be explained as they present minor values of at least one of the two analyzed parameters (i.e., annual productivity and the emission factor(s)). For instance, the absence of sulfuric acid in Figure 4 can be explained by its relatively clean synthesis, having gate-to-gate GHG emission factors below 10^{−2} t-CO_{2,eq}/t-H₂SO₄ [48]. Consequently, despite 256 Mt/y of sulfuric acid production in 2020 [70], its carbon intensity is negligible compared to other less widespread processes.

It is worth mentioning that the ranking shown in Figure 4 is consistent with data published in 2010 [53], which are still the most recent ones [70]. This accordance mainly relies on the qualitative trend of the annual productions ranking, which has been the same for years. Reasonably, the examined top processes (i.e., oil, ammonia, olefins, methanol, etc.) are expected to retain their position in the near future, as it happened in the last decades. It is worth noting that the present days coincide with the so-called energy transition age (the Paris Agreement dates back to 2016). As far as forthcoming works/reports on GHG emissions are concerned, this article may represent a pre- early-transition benchmark assessment for discussing and implementing future trends and policies.

4. Conclusions

This review focused on anthropogenic greenhouse gas emissions by adopting a general global approach. By considering the so-called indirect emissions (i.e., the ones generated from electricity and fuel consumption), *Industry* is the first GHG emitter (totaling 31% of GHG global emissions). *Industry* and *Buildings* are the primary users of both heat and electric power. Within *Industry*, chemical industries and oil refining are the main CO₂ emitters with 9.5% of GHG worldwide emissions.

Moreover, the paper reports a list of the most carbon-intensive syntheses with details on the main chemicals and processes. The productivities of such chemicals and the gate-to-gate emission factors of the processes were analyzed, compared, and discussed. Oil refining, ammonia synthesis, and hydrocarbon steam cracking are the most polluting processes responsible for releasing 1313, 440, and 228 Mt-CO_{2,eq}/y, respectively, in 2020. The primary rationale behind this work was to provide a reference list and suggest a methodology that can be updated periodically. Such a methodology may be referred to when having to deal with decarbonization policies in the chemical industry. Notably, ranking chemicals by order of GHG emissions allows the stakeholders to adopt environmental mitigation policies through suitable priorities.

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Nomenclature

BTEX	benzene, toluene, ethylbenzene, and xylenes
CHP	combined heat and power
CO _{2,eq}	carbon dioxide equivalent
EDC	ethylene dichloride
GHG	greenhouse gas (es)
HDPE	high-density polyethylene
KA	ketone-alcohol
LCA	life cycle assessment
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
LPG	liquefied petroleum gas
M/H	dual pressure plant, at medium and high pressures
M/M	single pressure plant, at medium pressure
PE	polyethylene
PET	polyethylene terephthalate
PP	polypropylene
PVC	polyvinyl chloride
TPA	terephthalic acid
VCM	vinyl chloride monomer
VGO	vacuum gas oil
WRI	World Resources Institute

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