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Quantifying vented by-product hydrogen: a case study in China

Abstract

The International Energy Agency estimated that by-product hydrogen constituted 16 per cent of global hydrogen production in 2022, primarily through naphtha reforming during oil refining.

[1] However, this definition of by-product hydrogen is quite narrow since it can also be generated through many other industrial and chemical processes like chlorine, coke, propylene or ethylene production. While some industries use a portion of this by-product hydrogen produced in the waste streams within their operations, a significant proportion has been vented into the atmosphere for decades, a practice that has been largely unnoticed by the public.

However, the venting of hydrogen can have adverse climate consequences. Recent studies analyzing hydrogen leakage have demonstrated that hydrogen's global warming potential over 20 years could be as high as 40 times that of carbon dioxide.[2] Consequently, estimating vented by-product hydrogen and investigating ways to mitigate this problem are important for the burgeoning hydrogen economy and to prevent any unintended climate repercussions.

By-product hydrogen is particularly significant in China, due to the strong presence of and high industrial and chemical output from the industries mentioned above. This report estimates China's annual by-product hydrogen production from nine major industrial and chemical processes and uses a range of venting ratios to calculate the amount of hydrogen directly discharged into the atmosphere. Our analysis suggests that around 13-16 million tons (Mt) of by-product hydrogen are being produced annually in China through various industrial processes; meanwhile 1.6 to 8.1 Mt of that hydrogen is estimated to be vented into the atmosphere. The uncertain but potentially significant scale of venting hydrogen would make it a comparable or even larger source than hydrogen leakage from the whole hydrogen supply chain (estimated to amount to 2.4 Mt/y in 2020 in the world).[3]

However, these estimates are subject to significant uncertainty due to data gaps and divergent estimates across different industrial processes. Assessing, addressing hydrogen's fugitive emissions and promoting sustainable hydrogen consumption requires regulating by-product hydrogen's production and prioritizing its capture and utilization. This includes assessing the feasibility and costs of by-product hydrogen usage.

Insight: 140

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Introduction

China is currently the largest hydrogen producer and consumer, well ahead of the United States (10 Mt) with production estimates for 2020 ranging between 26 to 33 Mt.[4] The range stems from the varying estimates of by-product hydrogen in statistics. Derived as an unintended or secondary product of industrial processes and often mixed with other gases, by-product hydrogen is not always fully accounted for in hydrogen reviews and statistics. The International Energy Agency (IEA) attributes a substantial proportion of Chinese hydrogen production to coal gasification (21 Mt) and natural gas (5 Mt), with a notable portion (7 Mt) classified as by-product hydrogen.[5]

Hydrogen leakage has been attracting attention over the past year with various estimates given on its current and future significance. But most studies on this topic focus on hydrogen leakage from traditional production methods such as coal gasification, steam methane reforming and electrolysis, which produce pure hydrogen, as well as from storage, transportation and use of hydrogen, overlooking by-product hydrogen.[6] Meanwhile, the direct venting of by-product hydrogen is a long-standing practice documented across various countries including the United States, Europe, China, and Jordan, driven by economic constraints and the absence of regulatory classification as to whether it is an air pollutant or indirect greenhouse gas (GHG), despite available extraction and purification technologies.[7] [8] [9] [10] [11]

While many countries' hydrogen strategies overlook by-product hydrogen, China's approach recognizes it as a source of supply but does not adequately address venting or the associated climate implications.[12] This research aims to estimate the annual amount of by-product hydrogen released into the air in China from nine key industrial processes, as the scale of vented by-product hydrogen from industrial activities has never been fully assessed. It will employ a combination of desk research and data analysis to estimate the amount and sources of by-product hydrogen, and the amount that is currently being vented. By doing so, this study seeks to shed light on the scale and potential climate impact of vented by-product hydrogen from industrial activities, and highlight the importance of capturing and utilizing this valuable resource to promote a sustainable low-carbon hydrogen economy. The findings of this study may have relevance to other regions grappling with similar challenges, as the issue of hydrogen venting is not limited to China alone.

By-product hydrogen and its climate implications

By-product hydrogen, generated as an unintended product within the waste gas mixture of several industrial processes, is typically recycled, combusted on-site, within the facility's operation.[13] Yet, as mentioned before, a significant proportion has been discharged into the air without any treatment as a standard practice. Indeed, a lack of market opportunities and transport infrastructure for this industrial by-product hydrogen have rendered it economically unattractive.[14] This has resulted in limited government involvement and industry awareness of its actual availability. This lack of awareness is further compounded by the fact that by-product hydrogen is usually manufactured, handled, and disposed of within the same facility, and not available to neighbouring facilities in the absence of infrastructure.[15]

However, it is time for a reevaluation of this practice. The venting of hydrogen into the atmosphere can have negative climate consequences. When released into the atmosphere, hydrogen acts as an indirect greenhouse gas.[16] Its interaction with other atmospheric components can lead to increased concentrations of methane, ozone, and water vapour, all of which have significant global warming potential.

Research in the early 2000s demonstrated that the development of a future hydrogen economy (largely based on fuel cells at that time) would have a greenhouse impact.[17] [18] [19] This is because hydrogen is the smallest molecule and has a tendency to leak into the atmosphere during production, storage, transport, and usage. Once in the atmosphere, around 20–30 per cent is oxidized by reacting with the hydroxyl radical (OH).[20] This leads to an increase in the amounts of the following GHGs: methane, and ozone and water vapour.

- Methane concentrations in the troposphere increase as less OH is available to react with methane, leading to a longer lifetime for methane.
- When hydrogen is oxidized, the reaction produces atomic hydrogen which leads to the creation of ozone through a series of reactions.
- Finally, the oxidation of hydrogen also increases the amount of water vapour in the stratosphere.

While the global warming potential (GWP) of hydrogen has been primarily characterized using the GWP-100 metric, the results have been inconsistent. Moreover, the warming effects of hydrogen are transient, comparable to methane, and do not accumulate over time (unlike carbon dioxide). The maximum GWP occurs around seven years after the initial pulse of emissions, making the reporting of hydrogen's potency in GWP-100 less valuable in conveying the much larger relative climate impacts over shorter time horizons.[21] Recent studies have therefore included GWP-20 (Table 1).

Derwent et al found in 2020 that hydrogen has a global warming potential (GWP) of 5±1 over a hundred-year time horizon.[22] Meanwhile, Hauglustaine et al found a higher 100-year GWP of 12.8 and a 20-year GWP of 40.1 with an uncertainty range of 24.[23] Finally, Warwick et al in 2022 found that hydrogen has a GWP of 11 on a 100-year timescale and 33 on a 20-year timescale.[24] The disparity between the studies is likely due to the fact that the most recent analyses included previously ignored changes in water vapour in the stratosphere and ozone in the troposphere in the GWP calculations.[25] Despite these differences, they all concur on the potential of hydrogen to extend the lifespan of methane, a potent yet short-lived greenhouse gas that has been the focal point of climate mitigation efforts in recent years.[26] Considering the scale of projected hydrogen consumption in the future, leakage has the potential to significantly undermine the climate benefits of a hydrogen-based economy.[27]

Table 1: Estimates of hydrogen global warming potential

	GWP-20	**GWP-100**
Derwent et al 2006	-	5.8
Derwent et al 2020	-	5 ± 1
Field and Derwent 2021	-	3.3 ± 1.4
Hauglustaine et al. 2022	40.1 ± 24.1	12.8 ± 5.2
Warwick et al. 2022	33 +11/-13	11 ± 5
Sand et al. 2023	-	11.6 ± 2.8

Source: Derwent el al(a).[28], Derwent el al(b).[29], Field, A.& Derwent, R.G.[30], Hauglustaine et al.[31], Warwick et al.[32], Sand et al[33].

Addressing hydrogen leakage is crucial, especially as the hydrogen industry is on the brink of scaling up. However, none of the past studies looking at hydrogen leakage have considered by-product hydrogen, but only focused on the more traditional parts of the hydrogen economy, such as the production, storage, transport, and final consumption of pure hydrogen. The impact of by-product hydrogen released into the atmosphere from industrial activities in the past has not been evaluated, and estimates of vented by-product hydrogen have not been incorporated in existing literature on hydrogen's climate impact. These gaps highlight the need for further research on the impact of hydrogen leakage and the importance of including vented by-product hydrogen in future assessments.

The Chinese context: production, consumption, and venting

China, being the largest global producer of steel and chemicals, generates significant amounts of hydrogen as a by-product from various industrial processes, such as chemical, petrochemical, and metallurgical.[34] [35] This by-product hydrogen emerges from various processes, including:

- **Coke:** during the coking process, coal is heated in the absence of air to produce coke. This process releases various gases, including hydrogen. The gas mixture is often referred to as coke oven gas (COG), and it contains about 55 per cent of hydrogen.
- **Sodium chlorate ($NaClO_3$)**: produced by the electrolysis of sodium chloride (salt) solution. While the primary products are sodium chlorate and chlorine, hydrogen gas is released as a by-product at the cathode.
- **Chlor-alkali process**: involves the electrolysis of salt (sodium chloride) to produce chlorine and sodium hydroxide. Hydrogen is produced as a by-product at the cathode during this electrolysis.
- **Methanol**: typically produced from natural gas through steam methane reforming (SMR). During this process, methane reacts with steam to produce hydrogen and carbon monoxide. While hydrogen is used in the synthesis of methanol, excess hydrogen can be a by-product. The production of methanol is one of the current applications for hydrogen and existing use-case for by-product hydrogen.
- **Ammonia**: produced using the Haber-Bosch process, where nitrogen from the air reacts with hydrogen, typically derived from natural gas via SMR. The primary goal is to produce ammonia, but excess hydrogen can sometimes be generated. The production of ammonia is one of the current applications for hydrogen.
- **Semicoke**: produced by the pyrolysis of coal or oil residues. The pyrolysis process releases various gases, including hydrogen, as by-products.
- **Propylene**: can be produced through various methods, including steam cracking of hydrocarbons. During steam cracking, hydrocarbons are broken down into smaller molecules, producing ethylene, propylene, and other by-products, including hydrogen. In the process of propane dehydrogenation to propylene, while the product propylene is produced, the same molar amount of hydrogen is by-produced.
- **Refined oil**: during oil refining, various processes like hydrocracking and desulfurization require hydrogen. These processes can produce excess hydrogen as a by-product.
- **Polyvinyl chloride (PVC)**: PVC is produced by polymerizing vinyl chloride monomer (VCM). VCM is produced from ethylene and chlorine. While hydrogen is not a direct by-product of PVC production, the production of chlorine (used in making VCM) through the chlor-alkali process generates hydrogen as a by-product.

The absence of a well-developed hydrogen market primarily contributes to by-product hydrogen's waste.[36] In China, like in the rest of the world, hydrogen generation and consumption typically occurs within the same facility, leading to a weak linkage between by-product hydrogen producer and potential consumer(s).[37] Limited economic incentives exist for companies to separate and sell by-product hydrogen as the associated purification costs can be substantial.[38] Additionally, the available infrastructure for hydrogen storage and transport remains underdeveloped.[39]

Estimation of by-product hydrogen production and venting in China

Estimation of annual volume of by-product hydrogen produced in China

In order to estimate the total amount of by-product hydrogen, we have used the total production volumes of these various industrial and chemical products mentioned above, and a waste gas production ratio, allowing us to calculate the volumes of waste gas. While some of these processes generate a high purity stream of hydrogen as a by-product, others produce hydrogen mixed with impurities and other gases. For example, the electrolysis of brine produces hydrogen up to 99.9 volume/per cent in purity during the production of sodium chloride production (chlor-alkali process), while coke production generates coke oven gas with up to 59 per cent hydrogen content but containing impurities such as tar and sulphur compounds.[40] The presence of impurities can impede the purification process, making it more challenging to extract by-product hydrogen. Based on typical percentages of hydrogen in waste gas (against impurities), we can estimate volumes of by-product hydrogen produced for each process (Table 2).

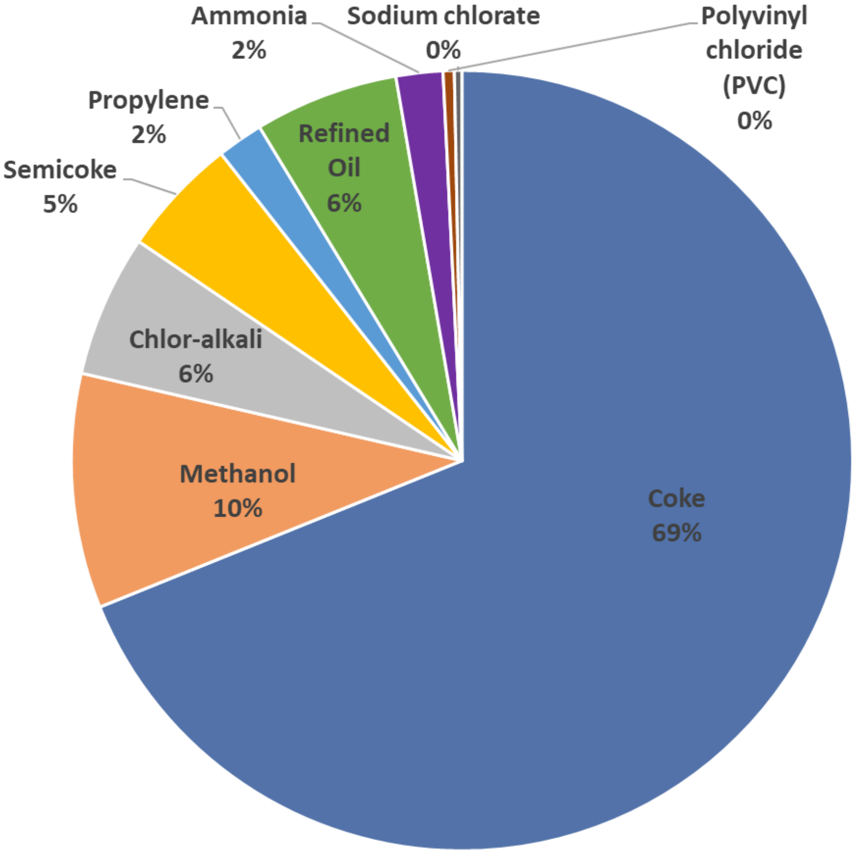
Table 2: Estimated by-product hydrogen production in China annually (2020)

Primary product	Primary product production volume (t/yr)	Waste gas production ratio (m3/t)	H2vol% in waste gas	Total by-product H2 (t)	Other components in the waste gas (in vol%)
Coke	471,000,000	430	54~59	9,829,834～10,740,004	CH4: ~ 25, CO: 6.5; CnHm: 2.5; CO2: 2, N2: 4, Sulfur
Methanol	49,840,000	480	60~75	1,290,130~1,612,663	CH4: 5 ~ 11, CO: 5 ~ 7; CO2: 2~13, N2: 0.5~20
Chlor-alkali [41]	36,730,000	270	98.5~99	877,979~882,435	N2: ~ 0.5 O2: ~1 Other
Semicoke	40,850,000	715	26~30	682,550 ~787,558	CO: 5~7; CH4: 7~8.5, CO2: 6~9, N2: 35~39
Propylene	7,370,000	500	80~92	264,966 ~304,711	C2H6: 1~2; C3H8: 0.5~1; N2: 1~2
Refined oil	674,000,000	*5% of total refined oil at density of 0.565 kg/m3	14~90	239,590 ~ 1,540,224	CH4: 3~25, C2+ :15~30 NH3 H2S
Ammonia	49,540,000	200~300	20~30	178,106~400,739	CH4:7~18, Ar: 3~8; N2: 7~25
Polyvinyl chloride (PVC)	20,740,000	62	50~70	57,787~80,902	C2H2: 5~15; C2H3Cl: 8~25; N2: 10~15
Sodium chlorate	850,000	620~660	92~95	44,998~47,902	O2: ~2.5 Other
Total				**13,465,942 ~ 16,397,138**	

Source: Chen et al [42], China EV100[43], Li, Y. & Huang, S. A[44], Liu et al [45], Tu et al [46], Wang et al [47]

The total production of by-product hydrogen in China was estimated to be between 13.5 to 16.4 Mt in 2020. This represents 40 to 50 per cent of China's reported hydrogen consumption (33 Mt) and 15 to 18 per cent of global hydrogen consumption (90 to 94 Mt).[48] This is also significantly higher than the 7 Mt previously reported as by-product hydrogen, which corresponds to the quantities collected and used and points to potentially significant quantities wasted – between 6.5 and 9.4 Mt of hydrogen.[49] It is noteworthy that around 65-70 per cent of total by-product hydrogen comes from coke oven gas, with methanol purge gas and chlor-alkali industry (for sodium chloride production) being the second and third sources (see Figure 1). Meanwhile, the six other processes represent a maximum of 11 to 19 per cent of total by-product hydrogen produced in China.

Figure 1: Estimated annual by-product hydrogen production in China (2020)



Note: The percentage of each product is calculated based on the average of the range of the estimated by-product hydrogen produced using data from Table 2.
Source: author calculations, based on Table 2.

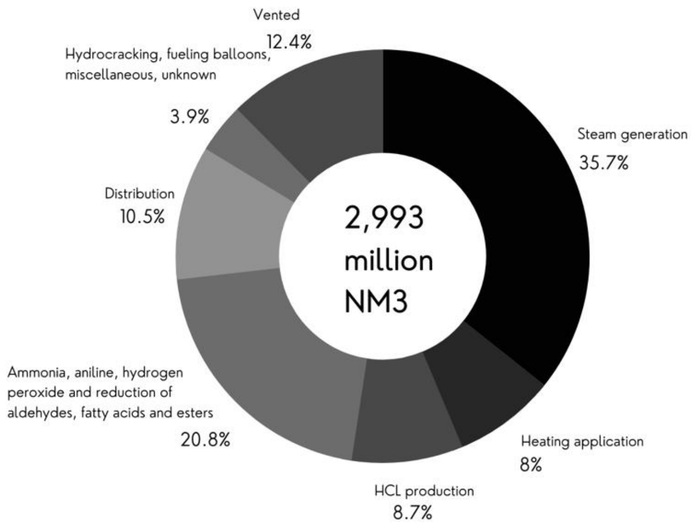
Estimation of annual volume of by-product hydrogen vented in China

Accurate data on the venting of by-product hydrogen is scarce. Some reports, such as Inner Mongolia's 5-year hydrogen development plan, mentioned that approximately 160,000 tons of by-product hydrogen were vented in 2020. The region's chlor-alkali and coking industries produced over 1.3 Mt of by-product hydrogen in total in 2020, implying a 12.3 per cent venting rate for the chlor-alkali and coking industries combined.[50]

Some industry-specific venting ratios are also available for coke oven gas and chlor-alkali processes in China due to their large-scale production. However, these venting ratios vary significantly; for coke oven gas, the ratios range from 20 per cent to 50 per cent, whereas for the chlor-alkali industry, they range between 30 and 40 per cent.[51] [52] [53] [54] In the U.S., up to 50 per cent of by-product hydrogen from chlor-alkali plants may be flared or vented, while in Europe, this figure has been much lower, around 10 to 15 per cent (Figure 2).[55] [56] [57] [58] Further investigation is required as there is currently no available data on the venting ratio of by-product hydrogen for production processes other than the chlor-alkali industry in the United States and Europe. Even for the part of that hydrogen that is recycled and used, some applications are rather 'low-grade' uses for the valuable hydrogen gas, such as steam generation and low-temperature heating, which can be easily substituted by other energy sources, while hydrogen use should be reserved for the hard to abate sectors where its use makes more sense. However, the costs of recovering, treating and transporting hydrogen to these sectors should be assessed versus these low grade uses.

Given the variability in venting ratios among industries and facilities and the limited data available, estimating the exact amount of by-product hydrogen vented in China is challenging. Despite these challenges, it is important to recognize the significance of the issue and to make reasonable estimates of the potential amount of by-product hydrogen vented. While the estimated ratio of by-product hydrogen vented in most remaining processes (ranging between 2.7 to 4.7 Mt) is unavailable, we have used venting ratios ranging from 12.3 per cent - based on data provided in the Inner Mongolia's 5-year plan, to 50 per cent - the top range ratio for coke oven gas, to estimate the total amount vented in China. Based on the 2020 estimated value for total by-product hydrogen produced in China, the total amount of by-product hydrogen vented could range between 1.6 to 8.1 Mt per year. The comparison between our estimates of total by-product hydrogen (13.5 to 16.4 Mt) compared to the IEA's estimate for by-product hydrogen used (7 Mt) was leaning towards the higher values for unaccounted (vented) by-product hydrogen (6.5 Mt to 9.4 Mt). These estimates are, of course, subject to significant uncertainties due to the variability in venting ratios across industries and facilities, and the limited availability of reliable data.

Figure 2: European chlor-alkali industry's hydrogen applications in 2021 listed by Euro Chlor



Source: Euro Chlor [59]

Utilization of vented hydrogen in China: potential solutions and mitigation strategies

By-product hydrogen is seen as a hydrogen source for the near future to quickly expand the hydrogen applications in China. The national plan for the hydrogen sector, unveiled in March 2022, prioritizes the utilization of by-product hydrogen in the near term.[60] This is particularly evident in areas with high production levels, especially in provinces known for their extensive metallurgical and chemical outputs. Provinces such as Shandong, Shanxi, Shaanxi, Inner Mongolia, and Hebei consider by-product hydrogen as an economical means to strengthen the hydrogen industry.[61] [62] [63] [64] [65] Some regions have even established production goals for by-product hydrogen by 2025. [66]

Efforts have been made to improve by-product hydrogen utilization and reduce vented hydrogen. This is more common within the chlor-alkali industry due to the high purity level of by-product hydrogen produced. For instance, Yan et al.(2018) recorded how a chlor-alkali manufacturer modified its system to transport originally vented hydrogen through pipelines to Tangshan Ossia Chemical Co., Ltd., a silica manufacturer. [67] In their 2016 paper, Zhao et al cite a sodium chlorate manufacturer based in Inner Mongolia reported a series of modifications and upgrades to its hydrogen recycling device in order to collect hydrogen in its waste stream.[68] Wang and Yao (2014) reported that the Henan Shenma Chlor-Alkali Manufacturing firm constructed 370 meters of pipelines to send its by-product hydrogen to a nylon manufacturing plant across river.[69] Conversely, documentations of case studies on the collection of vented by-product hydrogen from other industrial processes remain scarce. These processes often result in a higher concentration of impurities, which in turns leads to increased costs and technical challenges associated with the purification and extraction of by-product hydrogen (see Table 2).

However, comprehensive data regarding the availability and management of by-product hydrogen, including the total amount produced, the fractions vented, combusted, and collected, remains limited.[70] The acquisition of more robust data is crucial to facilitate well-informed decision-making by policymakers and industry leaders regarding resource optimization and systematic reduction of hydrogen's climate impact.

Conclusion

The increasing interest in hydrogen as a potential decarbonization solution has renewed scientific inquiries into its possible climate impact. Our study highlights the need to better understand the venting of by-product hydrogen as an issue and obstacle to achieve a sustainable low-carbon hydrogen development. The lack of attention and comprehensive data on the venting of by-product hydrogen is a concern, given the potential climate impact of hydrogen leakage, as demonstrated by research conducted since the early 2000s. Therefore, it is essential to improve data collection on the production and venting of by-product hydrogen to better comprehend how much hydrogen can be prevented from being released into the atmosphere; the hydrogen recovered could be used in existing and new applications.

It is important to also recognize the indirect climate impact of hydrogen and take action to reduce vented hydrogen in the air, since the venting of by-product hydrogen has significant climate impact, with the estimated amount of hydrogen released resulting in significant CO_2-equivalent emissions per year. Moreover, the economic impact of this loss must be considered against the question of how much of this hydrogen could be economically recovered in the long run. The rate of decarbonization in the steel and chemical industries is expected to lead to a drop in by-product hydrogen availability in the future. However, in the short term, measures must be taken to control venting.

Encouraging the flaring of hydrogen within facilities that generate by-product hydrogen could result in lower greenhouse warming effects, but this process must avoid co-combustion of other impurities in the waste stream. The reduction of vented hydrogen would not only have immediate positive climate impacts, but would also benefit the long-term, as hydrogen leakage is a plausible concern in the emerging hydrogen economy. It is worth noting, however that by-product hydrogen produced in many of the nine processes covered is very often fossil-based. Some processes such as chlor-alkali may be in a position to produce low carbon hydrogen if they use clean sources for electricity.

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