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Abstract

The long-term impact of global warming and the resulting climate crisis, brought about by human-induced emission of greenhouse gases, is an imminent environmental concern. The Paris Agreement aims to limit global temperature rise to below 2° C over pre-industrial levels, to curb this impact. Meeting this limit necessitates reaching carbon neutrality by 2050, which imply no net transport of carbon dioxide to the atmosphere. The chemical process industry along with associated manufacturing industries such as iron and steel, cement and aluminum contributes significantly towards global carbon dioxide emissions. Mapping the precise routes of Carbon mobilization is the first step towards establishment of a sustainable, circular and Carbon neutral chemical industry. There exist no C flow models for aforementioned energy intensive industries. Current published literature also does not account for C mobilized to meet the energetic needs of global chemical processes. They also do not account for the emissions offset by material exchange between different production processes. In this work, we develop a steady state model of Carbon flow through chemical process and associated industries. Our model traces the flow of carbon from fossil feedstock, to energy carriers and chemical intermediates, and finally valuable products, by-products and emissions. This model makes use of process data, life-cycle inventories models developed by existing studies on the chemical and petrochemical industries, government databases, greenhouse gas emissions data and economy models. Fundamental laws like mass and energy balance are used in conjunction with stoichiometric calculations to estimate missing data and reconcile incorrect data. We represent this model as a Sankey Diagram to better facilitate visualization of the process network and identify scope of process improvement. We elaborate how this model helps the placement of process alternatives such as use of renewables, electrification, green hydrogen and carbon capture and storage in the value chain. These alternatives can be highly energy intensive, requiring a large amount of “net zero” electricity to function. The dependence of renewably sourced electricity on land area availability necessitates its efficient use. Thus, the integration of fossil alternatives in the model paves the path for their targeted and optimal usage towards decarbonization.

Keywords: Decarbonization, Modelling, Supply chain, Sustainability

1. Introduction

As global average temperature continues to rise and predictions for climate change turn more grim with every new assessment, closing the global anthropogenic carbon (referred to as “C” from here on) cycle has become more important than ever. Reducing the production of materials for consumption, infrastructure and healthcare in the face of a rising global population, or bringing about drastic reduction in consumptive behaviour overnight, is unlikely. Therefore, focussing on emissions reduction while still maintaining production volumes (or establishing a circular economy of materials) may arguably have better payoffs in the immediate future.

The efficiency (yield or selectivity) of conventional chemical processes cannot be increased indefinitely. Thus, there is a minimum C emission associated with all products. Any further reduction requires us to choose alternate pathways or retrofit mitigation technologies to conventional pathways. Many innovative technologies have been

developed to leverage both these options. [8, 7, 1, 10] The general idea behind carbon neutral technologies is to limit CO_2 emissions to the atmosphere. With prices of renewable electricity dropping steadily, electrically powered emerging technologies show promise in competing with incumbent routes of production. Examples of such processes include electrochemical means of converting CO_2 , that would otherwise be emitted to the atmosphere, to value added chemicals, or electrification of H_2 production. While renewables and emerging technologies may lower emissions to their credit, their usage does not absolve industries of all environmental concerns. C capture itself might increase energy needs of a process enough, to offset its C credits. Renewables also raise issues of waste management of noble materials, land use concerns. Thus, the application of these technologies needs to be weighed in with its tradeoffs to guide policymaking.

Attempts at large scale, sector-wide decarbonization imply the implementation of alternate low carbon pathways wherever possible, and C capture from exhaust gases elsewhere. This naturally requires a thorough knowledge of C flows, sources and sinks. A superficial knowledge of emissions from the chemical industry is not very useful in this regard. The contribution of different processes, pathways and fuels is needed to target processes with the highest decarbonization potential. The US EPA traces a majority of US greenhouse gas (GHG) emissions back to the transportation sector, followed closely by electricity generation and industrial sectors. Many existing works break down these emissions across manufacturing and process industries. These diagrams however, suffer from various inadequacies of their own. The diagram developed by Lawrence Livermore National Lab uses data from the US Energy Information Administration (EIA) and does not distinguish between different processes in the industrial sector. [3] The diagram by Global Climate and Energy Project (GCEP) at Stanford, while much more detailed still lumps all chemicals into one node and does not provide any insight into the individual consumption or emission of processes.[9, 2] The mass flow balance on the process network in the chemical industry developed by Levi et al. while comprehensive, does not have information on the energetic needs of these processes. Finally, there is a distinct need for and lack of distinction between the direct and indirect C requirements of a process. The decarbonization potential of a process changes significantly depending on whether C is required as feedstock for the process, or simply for its energy or heating needs. This insight is valuable and missing from the current literature.

The current major scientific efforts in this field focus on development of decarbonization technologies. However, this reductionist approach may have rebound effects, whereby increase in consumptive behaviour offsets the marginal benefits of emissions reduction, and may hinder the longer scale goals of establishing a circular, sustainable chemical industry which is still carbon neutral. For example, attempts at electrification of ammonia, source hydrogen from electrolytic processes and attempt to electrify the operation of Haber Bosch process, to avoid releasing carbon dioxide as a co-product of fossil sourced hydrogen. A superficial analysis may reveal the abatement of a large fraction of greenhouse gas emissions when such production routes are taken. However, as we see in the results of our work, other processes like methanol, urea and acetic acid production are dependent on this carbon monoxide for their feedstock. Decarbonizing these sectors thus becomes much harder. This insight is easy to miss in traditional reductionist thinking and may lead us to grossly overestimating the emissions reduction. This incites the need of development of more holistic models which will accurately reflect the dependence of different processes in the network and avoid chances of shifting impacts and inadvertently increasing the environmental burden. In this work, we build a model that captures the co-dependence of different processes and outline a protocol for resolving the feedstock and utility C needs of the chemicals and material industries, while distinguishing between different processes and pathways of production.

2. Methodology

This model traces most conventional processes centering the chemical industry. We outline the C flows in the feedstock, product as well as that associated with energy requirement of the process. For all cases, we begin with a process description and a stoichiometric model of the ideal process. Yield and selectivity data collected from published surveys of operational plants lets us calculate realistic values of feedstock. Energy data is estimated

from specific energy consumption (SEC) values or from life-cycle data. C content of these material and energy flows is then determined. Finally, we put these intensive flows into global perspective using production tonnage of each material. [11, 12] These calculations are demonstrated below for methyl alcohol.

Synthesis	$CO + 2H_2 \rightarrow CH_3OH$	(1)
Coal/Oil POX	$CH_n + H_2O \rightarrow CO + \frac{n+2}{2} H_2$	(2)
NG SMR	$2CH_n + O_2 \rightarrow 2CO + nH_2$	(3)
WGS	$CO + H_2O \rightarrow H_2 + CO_2$	(4)
RWGS	$H_2 + CO_2 \rightarrow CO + H_2O$	(5)
SMR to methanol	$2CH_n + \frac{n-2}{3} CO_2 + \frac{8-n}{3} H_2O \rightarrow \frac{4+n}{3} CH_3OH$	(6)
POX to methanol	$2CH_n + O_2 + \frac{4-n}{3} H_2O \rightarrow \frac{2+n}{3} CH_3OH + \frac{4-n}{3} CO_2$	(7)

To estimate feedstock requirement of methanol production, we use chemical synthesis route as shown in Eq.(1). The feedstock for methanol synthesis are sourced from syngas. Syngas can be generated by steam methane reforming of natural gas or coal gasification or partial oxidation of oil, as shown in Eq.(2) and Eq.(3) respectively. The kind of fossil feedstock used, determines the ratio of CO and H_2 in syngas. This ratio can be corrected by water gas shift or reverse water gas shift reactions for direct use in the synthesis process, depending on which gas is in excess. This is illustrated in Eq.(4) and Eq.(5). The value of 'n' can be approximated as 0.456 for coal, 1.873 for oil and 3.951 for natural gas. Thus, while syngas produced from coal and oil have excess CO and need to be subjected to water gas shift, NG sourced syngas is lean in CO and is followed up with reverse water gas shift. The final equations for methanol production, combining syngas generation, WGS/RWGS and methanol synthesis can be represented as Eq.(6) for NG and Eq.(7) for coal/oil.[6]

As can be observed from Eq.(6) and (7), the SMR/POX reactions coupled with WGS/RWGS reactions have two sources of C flows. The first is associated with the fossil feedstock requirement and the second is process emissions of CO_2 . The coal/oil POX process emits CO_2 which is released to the atmosphere. On the other hand, the NG SMR process consumes CO_2 which we assume is sourced from ammonia plants nearby. Ammonia plants use only H_2 from syngas mixture. Thus, CO , which is generated as co-product of this H_2 , can be separated and oxidized, according to Eq. (4), to provide feedstock to the methanol plants.

We assume an efficiency of 0.99 for the synthesis route (η_s) and 0.861 (NG), 0.808 (oil) and 0.76 (coal) for syngas generation steps (η_c). [6] Thus, the yield data along with stoichiometric information lets us calculate feedstock demand and C input thereof for methanol generation. [6] These calculations for process C of methanol are elucidated in Table 2 .

For energy requirement, we consider specific energy consumption (SEC) data for different feedstocks. Methanol generated from NG SMR has an SEC of 24 GJ/ton whereas partial oxidation of coal or oil lead to an energy consumption of 13.9 GJ/ton methanol. [5] To estimate the emissions associated with energy use, emission coefficients associated with each fuel are used. The final calculations are shown in Table 3.

	Feedstock	CO_2 input	η_c	η_s	n	Actual feed	Actual CO2
	$\frac{CH_n}{CH_3OH}$	$\frac{CO_2}{CH_3OH}$				$\frac{kg}{kgCH_3OH}$	$\frac{kg}{kgCH_3OH}$
Coal	$\frac{6}{2+n}$	$-\frac{4-n}{2+n}$	0.76	0.99	0.456	1.26	-2.004
Oil	$\frac{6}{2+n}$	$-\frac{4-n}{2+n}$	0.808	0.99	1.873	0.84	-0.763
Natural Gas	$\frac{6}{4+n}$	$\frac{n-2}{4+n}$	0.861	0.99	3.951	0.44	0.396

	SEC for feedstock use	Feedstock fraction	Emissions for energy use	Energy fraction
	$\frac{GJ}{ton CH_3OH}$	%	$\frac{kg CO_2}{MJ}$	%
Coal	24	20.5	0.091	50
NG	13.9	71	0.013	50

Finally, these intensive product flow calculations are scaled up for global production tonnages. Currently, the annual production capacity of methanol stands at 102 million metric tonnes. [4] Of this, we estimate 71% is sourced from natural gas derived, 8.5% from oil derived and the remaining from coal derived syngas. [6] The flows are scaled accordingly and thus we arrive at the total C flows associated with fulfilling the global demand of methanol. The treatment of process C follows a protocol illustrated by Levi et al. [6]

3. Results and Discussion

Fig 1 shows the mobilization of C in feedstocks for manufacture of major chemicals. All flows shown here correspond to mass units of C. Their relative values are scaled by their annual global production capacities i.e. the flows are extensive in nature. Therefore, in this case, the production tonnage and specific C consumption both dictate magnitude of the flows. Process flows resulting in output of C flows are shown to be released to the environment. Unreacted reactants or leakages are grouped together in a separate category as “loss”.

The diagram starts with fossil resources like crude oil, natural gas and coal. Refining processes yield primary hydrocarbons like olefins, aromatics, cyclic compounds and alkanes. Transformative reactions alter the relative production of these compounds. For example, toluene hydrodealkylation (THD) and toluene disproportionation (TDP) convert toluene to xylenes and benzene, ethylene and butene get converted to propylene via metathesis, and propane on dehydrogenation produces propylene. Alongside, we also show the synthesis of urea and methanol. The next stages show the production of platform chemicals like cumene, acrylonitrile, caprolactam, phenol, ethylene glycol, terephthalic acid, vinyl chloride monomer, acetic acid, formaldehyde etc from hydrocarbons. This is followed by production of polymers like polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, polystyrene etc. Finally, we track the end uses of some of these polymers to their major products. The diagram shows a large amount of C embodied in products used by the packaging industry, consumer goods and so on.

Large volume polymers like polyethylene, polypropylene, PET sequester C through their long half lives whereas C embodied in solvents such as acetone, ethylene glycol, toluene are either incinerated or disposed off. While attempts to circularize use of such stable plastics is underway, efforts can be made to source their feedstock C from non-fossil sources. While captured C or biogenic C can replace their fossil counterpart for use as feedstock, substituting the hydrogen or energy requirement of such processes presents a formidable task. Since captured C is only available as CO_2 , it does not have any value as fuel. While the diagram itself only represents C flows, co-product flows are captured in process models. This information is indispensable in searching for lower C pathways of production.

We also observe a significant amount of process loss, throughout the industry. This can be attributed to unconverted reactants or inefficient separation of products. When the consumption of process and energy C are compared, we see emissions distributed similarly across both categories. This points to the vast decarbonization potential of the chemicals industry whereby energy can be alternately sourced from non emitting resources.

4. Conclusions

Visualization of the C Flow model points us to the industries with greatest C footprint and the best ways to retrofit decarbonization technologies to these specific cases. This model is a stepping stone towards possibly answering bigger questions about the deep decarbonization of the chemicals industry. The data used in this model, can be used in conjunction with data on emerging technologies to optimize the economics and electricity demand of a decarbonized chemical industry. Additionally, the need for innovation and the direction in which it is needed may also be investigated. Eventually, the need for a policy change to support and affect the shift to decarbonized technologies can be supported with models such as this one. Thus, this model is a foundation in the vision of a sustainable, circular and C neutral chemical industry.

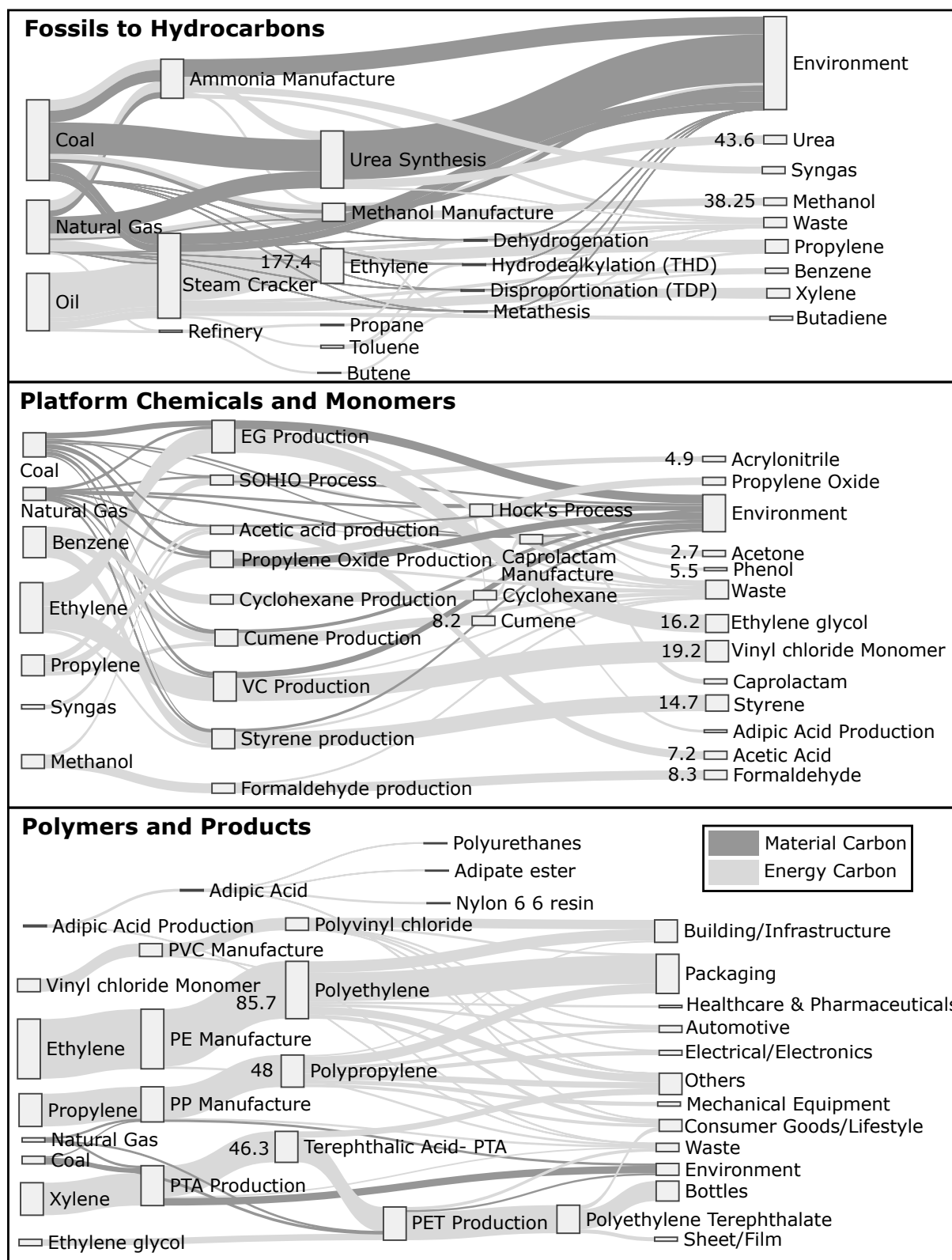


Figure 1: Flow of Fossil C through the Chemical Industry for in 2018 (in million metric tonnes of C)

5. Acknowledgments

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