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#### ▶ To cite this version:

P Jean Valayer, Olivier Vidal, Noémie Wouters, Mark C M van Loosdrecht. The full energy cost of avoiding CO 2: A clean-energy booking provision for a vigorous energy transition. Journal of Cleaner Production, 2019, 10.1016/j.jclepro.2019.117820. hal-02396609

## HAL Id: hal-02396609 https://hal.science/hal-02396609

Submitted on 25 Oct 2021

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## The full energy cost of avoiding CO<sub>2</sub>: a clean-energy booking

#### provision for a vigorous energy transition.

P. Jean Valayer<sup>1, 2</sup>\*, Olivier Vidal<sup>1</sup>, Noémie Wouters<sup>2,3</sup>, Mark C.M. van Loosdrecht<sup>4</sup>

<sup>1</sup> ISTerre, Université Grenoble-Alpes, 1381 Rue de la Piscine 38041 Grenoble, France

<sup>2</sup> The Carbon Promenades a.s.b.l., Rue Alphonse Renard, 29, 1050 Brussels, Belgium

<sup>3</sup> Ghent University, UGent Campus Ostend, Wetenschapspark, 1, 8400 Ostend, Belgium

<sup>4</sup> Technical University Delft, Building 58, Van der Maasweg, 9, 2629 HZ Delft, The

Netherlands

\* Corresponding author <u>jean.valayer@univ-grenoble-alpes.fr</u>

Total word count: 7071, including figure captions, excluding references and abstract. Abstract: 211 (vs 258 old)

#### Manuscript Valayer, Vidal, Wouters, van Loosdrecht

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### Abstract

Carbon tax, emission trading schemes and externality disclosures have not provided the incentive to replace fossil-carbon sourced energy as envisioned at the Paris Agreement 2015. Much of the enforcement of these schemes is outside the fossil hydrocarbon producer's control. As an alternate to these schemes, this paper proposes an inventive evaluation and accounting procedure, based on the energy penalty cost of decarbonizing fossil fuels. Such cost can be internalized within the producer's books, and provide the required incentives, including provisions for the deployment of carbon-free fuels. In the inspiring thermodynamics of hydrocarbon to hydrogen conversion in a closed system using hydrogen combustion to decompose the hydrocarbon, we find a penalty of 0.56 Joule for each Joule available in the original hydrocarbon. Applying energy market price range of 150-500 \$/t methane and molecular mass-conversion to CO<sub>2</sub> equivalent, results in costs ranging from 60 to more than 200 /t CO<sub>2</sub>. They are well above current carbon tax or emission trading schemes prices. They quantify the required incentives to cleaner (C-free) production yielding prompt emission reduction in the producers' market. We show how similar penalties accrue from a broad spectrum of industrial hydrogen production processes using hydrocarbons. Among those, methane pyrolysis produces carbon-free energy from fossil fuels, with non-combustion promising applications for its carbon production.

#### Keywords

Carbon dioxide emission; emission avoidance cost; fossil clean energy; emission booking; energy booking; energy currency.

#### Declarations of interest: none

#### 1. Introduction

In the Paris Agreement 2015, the United Nation Climate Change 21st Conference of Parties (COP21) committed to holding the increase in global temperature to below 2°C above pre-industrial levels (UN-FCCC, 2016) and nations have provided incentives to curb CO<sub>2</sub>, carbon tax (CT), or emission trading schemes (ETS, 2019). Green House (GHG) Gas Emission disclosures (OECD, 2011), and Standards of reporting have been established with the Kyoto protocol (UNFCCC, 2008) and encouraged (ISO, 2014). Le Quéré et al. (2018) regularly publish the "Carbon budget", which updates anthropogenic CO<sub>2</sub> emissions, and their redistribution among the atmosphere, ocean and terrestrial biosphere. To estimate the remaining carbon budget to stay below a given temperature limit, they suggest integrating scenario data from current time into the future, as proposed by Millar et al. (2017)- correction (2018). These authors conclude that delivery of stronger pledges than those currently being enforced are necessary, at least to achieve the 1.5°C targets. Each scheme supporting the current pledges focuses on CO<sub>2</sub> quantities emitted, either, as the hydrocarbon burns to produce energy, or as the energy carrier gets de-carbonized at the process level. A per-tonne CO<sub>2</sub> emission penalty affects the corresponding economics. Such schemes, it was expected, would provide sufficient incentives to encourage Carbon Capturing and Sequestering (CCS). In the case of power generation, the Intergovernmental Panel on Climate Change (IPCC) disclosed CCS-based CO2 avoidance costs up to 270 \$/t CO2 (IPCC-WGIII, 2005), which is well above current penalties. In future energy scenarios of the United Kingdom national grid, CCS (or CCUS, carbon capture and usage) are considered, but its current costs "are such that it is not commercially viable to extract carbon as part of the electricity

generation process" (Stewart, 2017). A typically considered CCU is the production of methanol by catalytic reaction of CO<sub>2</sub> with hydrogen. A thermo-economic analysis, performed under MefCO<sub>2</sub> H2020, concludes that a significant outlet for oxygen at current market price is necessary for its viability (Bellotti et al., 2017). The hydrogen of this process is hydrolysisproduced. In a similar study, where hydrogen is sourced at its market price, and methanol sold at market price, viability is achieved for CO<sub>2</sub> value well above 200 €/t (Pérez-Fortes et al., 2016). While public low fault tolerance is feared for CCS environment risks (Krüger, 2017), CCS cost, technical and governance challenges do exist, and are progressively being addressed. Thus, analysing the mismatch between the sense of urgency and the slow implementation of CCS, the Dutch CCS research community identified 26 action plans in need of execution to implement large scale CCS, in governance, project facilitation, economics, and the very role of CCS (Hendriks and Koornneef, 2014). The development of a sizable pipeline grid for CO<sub>2</sub> disposal carries technical and investment challenges, requiring global cooperation (Onyebuchi et al., 2018). According to the International Energy Agency (IEA), CCS might become competitive after 2030 for hydrocarbon-based hydrogen production for CO<sub>2</sub> prices around 90 \$/t (IEA, 2015).

Indeed, mitigation still requires significantly more R&D and investment incentive to deliver the COP21 pledges. Incentive values have been based on  $CO_2$  damage externality evaluations; they provide little encouragement for such pledge delivery. Zhao et al. (2017) found that public perception has ranked  $CO_2$  emission in a lower priority than particulates, NOx or  $SO_2$  emissions. They also found that the environmental cost of China coal-fired plants is 0.3 yuan, i.e. 0.05 kWh; attributing the total to  $CO_2$  would amount up to 150 \$/t  $CO_2$  using IPCC conversions (IPCC, 2006). Social Cost of Carbon of 40 \$/t have been used by the Obama administration, including a discount factor of 3%/year for long-range impact (Gles, 2017). Tax willingness to pay, and to accept by the operators has also been considered. In a hydropower scheme, US households are willing to pay only 3.66 \$/year to prevent GHG (Jones et al., 2017). However, when wealth

disparities occur, wealthier populations are willing to contribute to ecosystem services (Wang et al., 2017). A monetizing environmental impact of coal use of 21  $\pm 1 CO_2$  has been proposed in China (Chen et al., 2015), which includes a global Value Added Tax (VAT) reduction to offset its burden upon the overall economy. VAT reduction on "green" products has been preferred over pollutant taxation in a case study in Denmark (Nguyen et al., 2016). Finally, only a fraction of the taxes derived from the existing schemes is directed towards funding the energy transition (Carl and Fedor, 2016).

The above-mentioned approaches internalize hydrocarbon combustion externalities through an emission cost penalty paid to the community. They are insufficient to bring the needed incentives. Yet, Millar et al. (2017) identify encouraging pathways, one limiting warming to  $1.5^{\circ}$ C if a yearly rate of atmospheric CO<sub>2</sub> emissions reduction of 0.6 Gt CO<sub>2</sub>/yr/yr is achieved, and maintained linearly from 2020 onwards, further referred in this paper, as "Millar pathway". This objective requires a strong and probably unrealistic shift from hydrocarbons to renewable and nuclear energies, or drastic energy savings. Decarbonizing hydrocarbons is another option. Using hydrogen instead of hydrocarbons is possible in most applications, including transportation. Such an approach would take advantage of the Oil and Gas (O&G) engineering experience, resource expertise and infrastructure, capable of addressing the related logistic challenges, such as storage.

Wang et al. (2016) have shown that the transformation methane into hydrogen plus solid carbon by a pyrolysis process consumes energy. Givingup the energy value of fossil carbon would result in zero CO<sub>2</sub> emission externality and definitely curb the rising CO<sub>2</sub> content in the atmosphere, but it would create another externality instead, an energy penalty affecting hydrocarbon producers. Internalizing this penalty within the producer's accounting process can constitute an undisputable and universal "carbonenergy-penalty" framework, traceable all the way to the producer profit and loss line. Such a framework should encourage emission free hydrogen production solutions virtually at hand like thermal decomposition of methane itself (Keipi et al., 2018). As those authors point out, valuing the carbon produced is critical to the economic viability of thermal decomposition of methane.

The existing mitigation schemes internalise externalities, supported by emission damage estimates. None of them are based on the fundamental thermodynamics of avoiding combustible carbon containing fuels in the first place. Carbon-free fuel is truly a cleaner energy production fuel.

The objective of this paper is to innovate an approach designed to achieve Millar pathway at its source: fossil fuels production, decarbonized. The enabling invention will be an accounting method, providing the fossil fuel producing operators with a profit and loss incentive to supply decarbonized fuels, in an accelerated future.

A further objective of the paper is to test the impact of the method on the booked cost values, and compare the incentives generated with the existing schemes.

A final objective of the paper is to uncover key challenges and opportunities related to decarbonized hydrocarbon and avoidance penalty booking, such as hydrogen storage and non-combustion usage of carbons.

In our discussion, we shall scope out our next step: a "poof on concept".

## 2. Invention: the methodology

## 2.1 Determining the energy penalty in avoiding fossil carbon

A supplier can market hydrogen as a substitute to hydrocarbon. The substitution energy cost, can be estimated with appropriately selected energy performance indicators. Thermodynamically, the simplest indicator is the heat released by the combustion of the fuel. Higher Heat Value and Lower Heat Values refers to the energy released depending on whether the water is condensed or not in the final state. High Heat Value is appropriate in turbine power generation, where the water is fully condensed at the end of its process cycle. This is not the case in mobile application, where water vapour is expelled un-condensed through the exhaust. Considering the complete life-cycle of an energy producing system involves many more indicators. For example, energy pay-back ratio, or cumulative energy demands can be compared for various fuels, in standardized electricity producing systems (Modahl et al., 2013). Furthermore, the transition to new technologies faces the challenges of low experience-curve in high investment costs, and a several additional costly hurdles. Jones (2015) identifies among others, market adoption barriers and new technology financial risks. More recently, the specific example of variable renewable electricity has been explored by Hu et al. (2018). In an organized framework, they distinguish symptomatic barriers from the underlying fundamentals. They highlight the need for policy instruments that can deliver long-term visibility. In our paper, it is not proposed to provide an umbrella covering a diversity of investment situations. Instead, we propose to book, the bare minimum fundamental inevitable and predictable performance indicator that Hu et al. (2018) call for: the thermodynamic chemistry penalty of not using the carbon of the hydrocarbon for combustion. In this context, our candidate is the Higher Heat Value. It reflects the most recoverable energy of carbon-containing or decarbonized fuel. It is universal, and will not fluctuate in time or space. A fuel conversion cost based on HHV equivalency will represent the floor energy and other cost barriers our society has overcome to make further use of fossil sourced hydrocarbon. Choosing HHV rather than HLV, ensures that the full energy potential of the products is considered, without water state dependence variability. Thus, for the accounting procedure proposed in the present paper, it is assumed that hydrogen substitutes hydrocarbon on an HHV equivalent basis. A supplier can market hydrogen as a substitute to hydrocarbon in proportion to their respective HHV and the user buys the same amount of energy in form of hydrogen to supress CO<sub>2</sub> emission during combustion. The substitution of hydrocarbons by hydrogen is accomplished in a production unit, sourcing its feed from the inventory of hydrocarbon otherwise destined to the energy production market. To measure the

energy-cost impact of the substitution, we compare the energy-worth of the inventories required to satisfy a market with and without substitution. Furthermore, in an incremental approach, the energy production and delivery are transferred step by step from the original pool to the substitute. This allows the operator to sell both original and substitute at all times. It has the advantage of representing a realistic energy transition process. The original product is the same molecule, whether it is used as a feed for the substitution process, or directly sold to the energy market. It follows that, the combined product inventories and reactor can be considered as an independent production and delivery unit. While using energy units, rather than currency, the asset energy-worth evaluation is based on US Securities and Exchange Commission (SEC) corporate filings (SEC, 2018) where the O&G industry book their inventory (an asset) with the lowest cost or market value. Because only energy values are used in the present paper, and because the production-and-delivery unit is independent, lowest cost or market values are identical. Feed and sales are valued a single way: energy content. The substitution process will consume energy. Here, we calculate the residual retained energy after product substitution, a ratio r < 1 in relation to an original unit of energy **1** in Joule <sub>Out</sub>/Joule In. Four assumptions narrow the scope to our need [4A]: (i) the post-substitution inventory matches the pre-substitution energy demand (ii) the inventory end-use is a demand for a given energy amount in the form of a product, whether fully substituted hydrocarbon or not, (iii) The purpose of the substitution is strictly to abide to emission reduction as per Millar pathway, (iv) the substitution process may entail some CO<sub>2</sub> emission, sourcing its carbon from the hydrocarbon feed molecule, and may also entail some CCS to curb any CO<sub>2</sub> emission. From a process-unit accounting perspective, CO<sub>2</sub> emission actually "strands" the energy asset of the C-equivalent amount of hydrocarbon. The energy value of this asset will have to be written off, in the substitution process. This is explained in Fig. 1, where we express the accounting procedures, without and with CO<sub>2</sub> emission.

[Fig. 1] [See also Supplementary Fig. 1-S, more informative, less generic]

At the bottom of Fig. 1, is the source inventory of hydrocarbon, an inventory destined to respond to an energy demand. The operator may use decarbonizing processes, to abide to Millar pathway. His original inventory has  $E_{CpHq}$  energy value, in Joule. In the de-carbonization step above, the hydrocarbon is a mix, here, symbolically described with  $C_pH_q$  formula, where p represents the carbon number of each of its molecule. The operator keeps one part of his inventory to fulfil his demand as usual (on the right), and uses the other part as a feed to decarbonize. Without any  $CO_2$  emission, he produces *k* mole of hydrogen for each mole, the energy value of hydrogen is different from that of the original hydrocarbon. The residual energy-worth *r*, after de-carbonization is expressed in equation (1):

$$r = k \frac{E_{H_2}}{E_{C_p H_q}}$$
 (1) [ r = k(E(H\_2)/E(C\_p H\_q) ]

where  $E_{H_2}$  and  $E_{CpHq}$  the respective HHV J/mole values of hydrogen H<sub>2</sub> and the HHV per mole of the hydrocarbon feed C<sub>p</sub>H<sub>q</sub>. The trapeze shape illustrates the narrowing of the energy from original to residual.

In the substitution case, at the top, industrial processes result in  $CO_2$  emissions. This is the case of methane (or natural gas) reforming, the majority of US hydrogen production, according to US Department of Energy (DOE, 2019). The majority of this production, is a succession of two reactions.

 $CH_4 + H_2O + heat \rightarrow CO + 3 H_2$ ,

Where 2/3 of hydrogen are produced by the methane, followed by the water-gas shift (WGS) reaction:

 $CO + H_2O + a \text{ bit of heat} \rightarrow CO_2 + H_2$ 

where hydrogen comes from the water. As depicted in Muradov (2017), basis of our paper, the net reaction becomes:

 $CH_4 + 2 H_2O \rightarrow CO_2 + 4 H_2$ 

Except where mentioned otherwise, the mass balances used in the substitution case, are directly derived from Muradov (2017) publication. It discloses world average CO<sub>2</sub> emission per industrial H<sub>2</sub> produced. Muradov representation has the advantage of using industrial statistics to establish realistic mass balances without any simulation. CO<sub>2</sub> emissions record carbon use, and hydrogen production is also industry-wide recorded. Thus, net stoichiometric and real statistics can be used to compute theoretical and effective mass balances. A substantial amount of hydrogen comes from the water, at least stoichiometrically: 1/2. Water produced by the combustion of methane for process heat, can indirectly generate some methane-sourced hydrogen.

$$r = k \frac{E_{H_2}}{(1+n)E_{C_pH_q}}$$
 (2) [ r = k(E(H\_2)/[(1+n)E(C\_pH\_q)] ]

Substitution (2) entails the emission of one CO<sub>2</sub> molecule, per carbon atom of the feed, thus p CO<sub>2</sub>. As an illustration, naphtha, a popular hydrogen production feed in the O&G industry, C<sub>6</sub>H1<sub>4</sub>, emits 6 CO<sub>2</sub> mole/mole feed, into the checker box on the picture. Abiding to the Millar pathway, the producer can no longer sell a non-decarbonized hydrocarbon, in proportion to 6 moles of CO<sub>2</sub> emitted. Of course, 6 carbons is exactly the amount contained in one mole of naphtha. Therefore, one mole of naphtha used in the transformation process, forbids a direct sale of one mole of naphtha, valued at HHV. The balance is mole for mole. However, if the emitted CO<sub>2</sub> undergoes CCS, the direct hydrocarbon sales get penalized only to the extent of the remaining emission, n < 1. The forbidden inventory on the right, equal in size to "n", is stranded for energy usage. Its energy value is a loss for the operator. It is accounted together with the reaction feed 1, prior to the operation, totalling 1+n, although the process itself uses 1 only, further reduced by reaction inefficiency. Accounting-wise, this extended source inventory does not have to be assigned to one or the other segment of the final product, decarbonized, or not. It suffices to account for it as a waste of the original inventory. This waste results in a lower overall energy inventory, hence an overall lower asset, thus, a loss on the books. What happens concretely? As the production flow progresses, the inventory

replenishment is reduced by the "n" amount, the total inventory value is down accordingly, and the Millar pathway is respected with less emission producing products.

Having a residual energy  $\boldsymbol{r}$ , as per equations (1) or (2) the operator needs to respond to the original demand, hence deliver a unit-energy 1.

For one unit of energy-demand (*Out*), the conversion process requires an energy supply (*In*) of:

$$E_{In} = \frac{1}{r} J/J_{Out}$$
 (3) [E<sub>m</sub>=1/r)]

For each Joule produced (*Out*) the energy penalty of avoiding carbon is:

$$E_c = \frac{1}{r} - 1 = \frac{1 - r}{r}$$
 (4) [  $E_c = 1/r = (1 - r)/r$  ]

2.2 Booking the energy penalty, balance sheet.

A simplified double-entry energy-focused balance sheet can mirror corporate accounting (Fig. 2). Energy assets are included, fuel stocks in the short-term and mining reserves in the long-term.

#### [Fig. 2]

Three cases are represented: the two columns on the left reflect a typical fossil fuel operator asset and liability structure. The fossil carbon combustion energy value is implied in the assets, highlighted in dark. We are mindful that it cannot be a be accounted for as carbon combustion energy value. Indeed, it is chemically bound in the hydrocarbon molecule. However, whether cost or market-valued, the split between hydrogen and carbon can be in proportion of the combustion value balance before (with C) and after decarbonization (without C), as defined in paragraph 2.1. Thus, in the methane pyrolysis case, 56% is attributed to the carbon element. It is substantial in the long-term oil field reserves. Reserve inventories are currently valued using lowest cost or current market value (SEC, 2018). This accounting process must face the possibility that enforced emission

limitation might make such fields obsolete, stranded, if their products are not further decarbonized. The middle two columns address this nowfamiliar "stranded asset" potential, related to a loss of market for carbon containing material. They illustrate the loss of worth of the affected corporation producing carbon containing material. Less assets on the left of the two middle columns narrows the reinvestment and borrowing capacity on the right. The two columns on the right-hand side of Fig. 2 illustrate the booking of the CO<sub>2</sub> avoidance energy penalties of paragraph 2.1. As long the avoidance is not implemented, the total assets are intact (second from right column), with a carbon component explicitly valued in the proportions defined above, which actually equals its avoidance costs. While not incurred, this amount should also be booked at the same time on the liability side of the balance sheet (extreme right). There, it should constitute a provision for funding future carbon-avoiding fuel projects, or any other Cfree energy or regenerative processes. While equity is squeezed down by the intrusion of the provision, a strong financing capacity is preserved, but restricted for the exclusive benefit of C-free and regenerative developments. The sum of new equity and of the cost provision of the scheme might be higher than the equity, prior to the scheme implementation. Thus, the borrowing capacity of the operator might remain intact, at least book-wise; however, the technology risk associated with new developments funded by the provision will require shared consideration with the financing community.

## 3. Incentives: booked cost values (Results)

# 3.1 Methane thermal decomposition (MTD) and steam methane reforming (SMR).

MTD and SMR are used to illustrate the equations (1) and (2) of the methodology. MTD is not actually commercial, to our best knowledge, however it is being amply researched, and here, we chose an industrial simulation by Wang et al. (2016), which provides mass balances. In this case, n = o and the residual inventory value can be estimated directly by

applying the energy values (HHV) to the mass-balance of the simulated process from equation (1).

### [Fig. 3]

*Methane pyrolysis* produces a carbon-free combustible (hydrogen) and solid carbon instead of CO<sub>2</sub>. The heat value of produced H<sub>2</sub> is more than enough to entertain the pyrolysis reaction, with a final mass balance of k = 1.38 mole of H<sub>2</sub> delivered per mole of CH<sub>4</sub> input (Wang et al., 2016) (Fig. 3). The residual energy reads:

 $r = \frac{1.38E_{H_2}}{E_{CH_4}}$  (5) [ r = 1.38 E(H\_2)/E(CH\_4) ]

After HHV energy conversion from the mass balance, the residual energy available from the pyrolysis is r = 0.444 J/J. This assumes no further unaccounted-for energy losses in the final mass-balance of the simulation. On an exergy estimation basis, Wang et al. (2016) actually identified the residual energy to be 39%. "Exergy" is the maximum useful work in a process that brings the system into equilibrium with its environment. Thus, 0.444 is likely to be a maximum, yet to be demonstrated in industrial operation. The energy penalty incurred to avoid CO<sub>2</sub> is

$$E_C = \frac{1-r}{r} = 1.252$$
 (6). [EC=(1-r)/r = 1.252]

According to Macrotrend.net (2019), natural gas prices peaked around 19 \$/MMBTu in 2006. More recently, the fluctuations have been ranging from 2.6 to 4.7 \$/MMBtu. Applying the conversion factors proposed by (BP, 2017), the former period prices are close to 500 \$/t, and the recent ones to 150 \$/t. Further applying the formula (6) results in penalty of 626 \$/t of CH<sub>4</sub> for the 500 \$/t market value, and 188\$/t of CH<sub>4</sub> for the 150 \$/t CH<sub>4</sub> market value. As CO<sub>2</sub> weighs more than CH<sub>4</sub> by a factor of 44/16, the penalty of CO<sub>2</sub> extraction from CH<sub>4</sub> amounts to 228 \$/t [CO<sub>2</sub>] and 68 \$/t [CO<sub>2</sub>], respectively. These estimates assume that hydrogen and commercial hydrocarbons are fully substitutable, which is not the case yet. However, they provide minimum estimates of the true penalty of avoiding CO<sub>2</sub> in the combustion of fossil hydrocarbons, which is well above the value of exchanging pollution rights.

Fig. 4 illustrates a generic *SMR production*, with or without CCS. It includes the WGS reaction mentioned earlier. It also includes "pressure-swing adsorption" (PSA) variants, where remaining  $CO_2$  and other impurities are removed from the gas stream. Disclosed as industry averages by Muradov (2017), they are inclusive of the various variants of the SMR process, such as use of PSA. Stoichiometrically, 4 H<sub>2</sub> moles should be produced for each CH<sub>4</sub> mole. The industrial processes produce on average 2.44 H<sub>2</sub>. The CO<sub>2</sub> mole-emission mirrors the carbon containing moles used in the process, here one CH<sub>4</sub>.

[Fig. 4]

We have selected three kinds of SMR processes described in the literature. The first one disclosed by Muradov (2017) allows the comparison, on the same basis, of a variety of processes reviewed further in this result section. The second and third cases, disclosed by Khojasteh Salkuyeh et al. (2017) compare SMR with and without CCS on identical bases. In the Muradov (2017) case, the ratio between the stoichiometric and actual production is estimated from hydrogen and emission statistics from world major hydrogen producers, while the Khojasteh Salkuyeh et al. (2017) cases use a simulation from the Aspen Plus V8.6 software. Industrial statistics based SMR, produces H<sub>2</sub> with a residual energy inventory value r = 0.39 J/J. The model-based SMR + CCS process delivers r = 0.51 J/J, when excluding transport and CO<sub>2</sub> injection energy costs. The latter vary considerably from site to site, and are far from negligible (Neal et al., 2017). The estimated CO<sub>2</sub> avoidance energy and financial penalty of H<sub>2</sub> production by SMR are listed in Table 1. Starting from the molecular reaction ratio at the top, energy values are attributed, computed to the residual energy values  $m{r}$  from equations (2). The last lines convert the yield findings into  $CO_2$  \$/t cost, as a function of the energy market values.

**Table** 1. CO<sub>2</sub> avoidance cost of SMR-produced H<sub>2</sub> with or without carbon capture (CC). Stoichio- and process mass balances (top) are then assigned HHV values: 1450 kJ/mole process-used + 1450 kJ/mole stranded by CO<sub>2</sub> emission. 4 moles H<sub>2</sub> deliver 1135 kJ.  $r=1135/(2 \times 1450)=0.39$  kJ/kJ.

Steam Methane Reformin	Muradov (2017) <sup>(a)</sup>	Khojatsteh (2017) <sup>(b)</sup>		
$\mathrm{CH}_4 + 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{CO}_2 + 4\mathrm{H}_2$	Unit	W/O CC	W/O CC	With CC
CO <sub>2</sub> /H <sub>2</sub> Theoretical stoichio	kg/kg	5.50	5.50	5.50
CO <sub>2</sub> /H <sub>2</sub> Proc. cond., incl. CC				2.70
CO <sub>2</sub> /H <sub>2</sub> Pr. cond. prior to CC		9.00	11.00	11.0
$CO_2/H_2$ (& $CH_4/H_2$ )(stoichio)	mol/mol	0.25	0.25	0.25
CO <sub>2</sub> /H <sub>2</sub> (process)		0,41	0.50	0.50
Process CH <sub>4</sub> /effective CH <sub>4</sub>		1.64	2.00	2.00
CH <sub>4</sub> unit HHV energy value	kJ/mol	886	886	886
CH <sub>4</sub> en. used per reacted CH <sub>4</sub>		1450	1772	1772
CO <sub>2</sub> CCS-captured, comprssd	mol/mol	0	0	0.75
Further penalty under Millar	kJ/mol	1450	1772	435
H₂ unit HHV energy value		284	284	284
H <sub>2</sub> per reacted CH <sub>4</sub>	mol/mol	4	4	4
$H_2$ energy per reacted $CH_4$	kJ/mol	1135	1135	1135
Residual stock value $m{r}$	kJ/kJ	0.39	0.32	0.51
CO2 avoidance energy penalty		1.56	2.12	0.94
CO <sub>2</sub> avoidance penalty	\$/t @	/t 778 1061 472		470
valued as $/t CH_4$ for the $CH_4$	500 \$/t			4/2
\$/t respective market values	\$/t @	000	019	140
"@500150"	150 \$/t	233	310	142
CO <sub>2</sub> avoidance penalty	@ 500	<sup>0</sup> 500		170
expressed as $/t CO_2$ for the	\$/t	203 300 172		
CH <sub>4</sub> \$/t respective market	@ 150	<b>9 •</b> •• • • • • •		
values "@500150"	\$/t	05	110	5 <sup>2</sup>

(a) (Muradov, 2017) (b) (Khojasteh Salkuyeh et al., 2017)

3.2 Quantification of energy  $CO_2$  avoidance penalty in a spectrum of hydrocarbon applications.

Table 2 extends the energy and financial avoidance costs across the industrial spectrum of hydrogen production, from left to right. The calculations are identical to those of Table 1, while not showing the intermediate steps. Regardless of the feed, the final energy penalty is expressed in \$/t of methane, translated into \$/t CO<sup>2</sup>. We reason that, while each feed delivers its own residual value r, its final link to the market place is assumed as methane (of NG) fuel to use a universally recognised energy value.

The net reactions involved are transcribed in Table 3. The main outcomes of the calculations are three-fold:

- Industry-favoured H<sub>2</sub> production processes (on the left of Table 2) are less attractive than  $CH_4$  pyrolysis (Pyrolysis = 44%) because they do produce an extra-penalizing  $CO_2$  emission along-side hydrogen, in a Millar pathway context.

- Translated into  $CO_2$  \$/t avoidance penalty, the outcome of all cases is consistently well above CT or ETD prices. Currently, except in Nordic countries (World\_Bank, 2018), neither carbon taxes nor carbon emission trading are close to reaching the minimum values needed to discourage any fossil-source hydrocarbon production having  $CO_2$  emission potential.

- Whether the process is steam or partial oxidation-based, and whether the raw material is actual methane (or natural gas), a light petroleum distillate (naphtha) or a heavy one (residual fuel), whether it is even a pyrolysis, more than half the energy available in the hydrocarbon is lost in avoiding carbon as a combustible. Loosing this energy is the price to pay to avoid the relentless and existential increase of deadly  $CO_2$  in the atmosphere.

Table 2. A spectrum of hydrogen processes yields similar  $CO_2$  avoidance values. Mass balance statistics by Muradov and Wang (top) lead to low relative energy value  $\boldsymbol{r}$  (lines 3, 4), high  $CO_2$  avoidance penalty per tonne of  $CH_4$  equivalent (5,6), high  $CO_2$  cost (7,8).

Fossil hydrocar carbon avoidan energy value los	bon ce ss	Muradov (2017) <sup>(a)</sup>			Wang (2016) <sup>(b)</sup>			
Source & Process		CH <sub>4</sub> SMR	Nap htha SNR	CH <sub>4</sub> PO	Resid SO₂G	CH <sub>4</sub> Plas ma	CH <sub>4</sub> M Mat bal.	IC-H <sub>2</sub> Exer -gy <sup>(c)</sup>
CO <sub>2</sub> /H <sub>2</sub> theoretical stoichiometric	kg/ kg	5.5	6.9	7.3	13.7	0.0	0.0	0.0
CO <sub>2</sub> /H <sub>2</sub> process conditions		9.0	10.5	9.5	19.0	12.0	0.0	0.0
<i>r</i> = relative inventory value change	kJ/ kJ	0.39	0.43	0.37	0.30	0.24	0.44	0.39
CO₂ avoidance energy penalty		1.56	1.31	1.69	2.36	3.08	1.25	1.54
$CO_2$ avoidance penalty as \$/t of $CH_4$ for the $CH_4$ \$/t	CH4 @ 500 \$/t	778	657	844	1182	1542	626	768
respective market values '@500150' \$/t	CH4 @ 150 \$/t	293	197	253	355	463	188	231
$CO_2$ avoidance penalty as \$/t of $CO_2$ for the $CH_4$ \$/t	CH4 @ 500 \$/t	283	239	307	430	463	228	279
respective market values '@500150' \$/t	CH4 @ 150 \$/t	85	72	92	129	168	68	84

<sup>(a)</sup> (Muradov, 2017) <sup>(b)</sup> (Wang et al., 2016) <sup>(c)</sup> Variant based on process-tracked exergy  $(H_2 + C)$  as per (Wang et al., 2016)

Table 3. Reactions and abbreviations involved in theoreticalstoichiometry of Table 2.

$\mathrm{CH}_4$	Steam Methane Reforming (SMR) <sup>(a)</sup>	Net reaction: CH <sub>4</sub> + 2 H <sub>2</sub> O $\rightarrow$ CO <sub>2</sub> + 4 H <sub>2</sub>	
Naphtha	Steam Naphtha Reforming (SNR) <sup>(a)</sup>	$C_6H_{14} + 12 \text{ H}_2\text{O} \rightarrow 6 \text{ CO}_2 + 19\text{H}_2$	
$\mathrm{CH}_4$	Partial oxidation (PO) <sup>(a)</sup>	$\mathrm{CH}_4 + \frac{1}{2} \mathrm{O}_2 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{CO}_2 + 3 \mathrm{H}_2$	
Resid	Steam/O <sub>2</sub> gasification (RSO <sub>2</sub> ) <sup>(a)</sup>	$CH_n + \frac{1}{2}O_2 \rightarrow x H_2O + CO_2 + yH_2$	
$CH_4$	Plasma pyrolysis(ª)	$CH_4$ + Electricity $\rightarrow$ C + 2 $H_2$	
CH <sub>4</sub>	Pyrolysis (MC-H <sub>2</sub> ) <sup>(b)</sup>	$\rm CH_4 \mathop{\rightarrow} C + 1.38 \ H_2$	
Naphtha =	Light petroleum fraction		
Resid =	Heavy residual fuel oil		

(a) (Muradov, 2017) (b) (Wang et al., 2016)

# 3.3 Booking and global impact of energy CO₂ avoidance penalty (and decarbonized hydrocarbon)

Looking at the balance sheet, short *term*, *giving up fossil carbon is giving-up energy*. Transition funding (clean energy or energy avoidance) has to be to make-up for this loss. About  $33.10^9$  tonnes of CO<sub>2</sub> are emitted globally each year (BP, 2017). It follows that the value of CO<sub>2</sub> booked at its true avoidance penalty cost corresponds to 2.3 to 8.2.10<sup>12</sup> \$/year at natural gas

market prices of 150 to 500 \$/t (i.e.  $CO_2$  prices 70\$/t to 250\$/t). Today, approximately 30.10° \$ are actually collected, either in the form of carbon tax, or through the emission trading system, of which about <sup>1</sup>/4 is directed to funding the transition (Carl and Fedor, 2016). Thus, up to 99.5% of the  $CO_2$ avoidance cost of our scheme is not redirected as a provision for the energy transition. Yet, according to Millar et al. (2017), if the atmospheric decarbonation starts being possible as of 2020, a rate of 0.6 10° t  $CO_2/yr/yr$ , reduction, each year, from the yearly rate of emission would project the same 1.5°C warming by 2100 as RCP2.6-2017. A  $CO_2$  price provisioned at 200 \$/t for 0.6.10° extra tonnes reduction every year would amount to more than 100.10° \$/yr, while the transition funding is estimated by Carl and Fedor, (2016), at less than 10.10°, one tenth.

Turning to "income statement", the actual energy and financial flows of a fossil energy operator, are respectively depicted at the top and bottom of Fig. 5. Natural gas (NG, at the very top) is extremely efficient, energy-wise, if no CO<sub>2</sub> avoidance penalty is applied. For 100 (any energy unit) delivered at sales point, 103 suffice at the entry point (Raugei and Leccisi, 2016). Transformed into hydrogen with the intention to avoid CO<sub>2</sub> emissions, natural gas requires much higher energy value at the well level. In the SMR case ( $2^{nd}$  line), 263 + is needed at the well level, CO<sub>2</sub> avoidance energy penalty included. In the cracking case, 234 + is needed. This number would diminish considerably, if valuable outlets were developed for the solid carbon produced by the cracker. In the fourth line, native hydrogen from natural geological formations is not be subject to any CO<sub>2</sub> avoidance penalty. Yet, the energy cost at the well level is not known. The sign + reflects the unknown associated with mass hydrogen storage. The financial flow at the bottom, tracks back the energy market value expressed in currency at a "100" reference value, up to its extraction from the field. Most of the cost is in royalties and taxes (60%), close to the energy penalty in the cracking process.

[Fig. 5]

Critical impact factors are apparent in Fig. 5, hydrogen storage, natural hydrogen production, valuing large carbon applications and tax/royalties-crude prices.

*Hydrogen storage* is a necessity in amounts similar to natural gas strategic storage (EIA, 2019), 4 10<sup>12</sup> cubic feet close to 10<sup>6</sup> tonnes for the US alone. Unlike natural gas, which has stabilised over eons of maturing, hydrogen is fugitive, light and mobile (Panfilov, 2016). It is biologically reactive with methanogenic microorganisms present in geological strata, leading to challenging concentration oscillation (Toleukhanov et al., 2015). Nevertheless, storage in large underground porous media is raising increased interest and selection criteria have been scoped, concerning porous formation, pressures, cap rock, injection/extraction processes, among others, in China (Bai et al., 2014) and Germany (Henkel et al., 2014). At a significantly lower scale, cavern storage is now within reach. Thus Simon et al. (2015) conclude that identified salt caverns can technically provide storage of hydrogen produced in association with close-by wind farms. However, the economics depends on antipollution incentives. The business case of salt caverns has also been assessed in France (Le Duigou et al., 2017). With a high utilization rate of electrolysers, profitability in the mobility market is achievable.

*Valuing carbon* produced by pyrolysis is a broad field worth addressing. The quantities involved are considerable, considering that 1.10<sup>10</sup> tonnes Carbon are emitted each year by fossil fuels and industry (Le Quéré et al., 2018). Ample industrial usage of powder-carbon, is happening, or "in the pipe line". Carbon is candidate for water treatment. Chars from the carbonization of various biomasses already perform a variety of water contaminant removal such as dyes, pesticides, polynuclear aromatics, phenols (Mohan et al., 2014). Iron oxide dispersed on activated carbon is being developed to remove phosphate from water (Wang et al., 2014). High phosphate adsorption capacities are expected with granular-activatedcarbon coated with iron oxides nanoparticles (Suresh Kumar et al., 2017). Carbon is known for its gas adsorption capacity. Technology has been developing since several years to chisel reliable carbon nanotubes to store hydrogen for mobility applications (Darkrim et al., 2002). Carbon material applications, are broadening into activated carbon fibres, filtration, adsorption, electrochemical water treatment (Hassani and Khataee, 2017). Powdered carbon (carbon black) has also become a mechanical property enhancing component in metallurgy, in sinter mixes (Fujira et al., 2008). The above-mentioned applications have low to medium scale volume potential. High volumes can be sought in large scale civil engineering, particularly for land reclamation. Currently, a variety of disposable material are treated to improve their mechanical properties, in spite of their finegrain constitution (Guo and Wu, 2018). This might be a promising sector for methane carbon disposal. The geotechnical properties of carbon-sand mixes are actually under evaluation (Budihardjo et al., 2015). Carbon is being studied in active landfills (ICBA, 2016), as agricultural adjuvant (Gaunt and Lehmann, 2008) or as mulch (Harada et al., 2019).

*Pyrolysis and other sources of hydrogen can be considerable*. Coal pyrolysis or other types of coal gasification, have huge hydrogen production potential (Cagniant et al., 1988). Innovative approaches hold hopes of obtaining a CO<sub>2</sub>-free gas (Galvita et al., 2007), integrating the coal gasification process with an iron redox. Natural pyrolysis of organic matter caused by igneous intrusions is evidenced in multiple locations such as Scotland and Australia, respectively cited by George (1992) and Hutton and Henstridge (1985). Such intrusions have been associated with a natural hydrogen production well (Briere and Jerzykiewicz, 2017). Natural production of clean hydrogen (Deschamps et al., 2013) occurs by reduction of water percolating ultrabasic rocks in the vicinity of oceanic ridges. This reduction results from water-rock interaction, leading to the oxidation of Fe2+ from olivine into Fe3+ in magnetite (Merkulova et al., 2016). Natural seeps of methane/hydrogen mix are associated with similar reactions in many geological situations (Etiope et al., 2017).

*Taxes and crude royalties. The* 60% tax and crude portion of Fig. 5, once collected, will be used in processes involving energy, and very likely CO<sub>2</sub>

emissions. For example, state sponsored construction involves cement, the production of which emits considerable amounts of  $CO_2$ . Thus, a carbon tax, expressed in financial terms might be a poorly relevant way to curb emissions. By contrast, the C-avoidance provision in the O&G books proposed in this article avoids at least a portion of the diversion away from net-emission curbing.

## 4. Discussion

Key success factors are apparent, in our approach, and might constitute the design basis of a proof of concept.

First, a commercially functional pyrolysis for hydrogen production is a reality check. A limited implementation of our scheme should help fund completion of promising avenues (Keipi et al., 2018). The cost provision destination should follow a credible eligibility assessment evidencing potentially sound fossil C-free energy or regenerative economy projects. Inspiration from nature favours circular economy where the inevitable thermodynamic energy loss is compensated by solar energy. For instance, competitive constraints identified for macro-algal bio-refineries (Seghetta et al., 2016) are overcome when CO<sub>2</sub> price reaches the values identified in the present article. Biomass pyrolysis might become attractive (Gaunt and Lehmann, 2008).

Second, in the recognition of the fundamental energy rather than finance orientation of our scheme, "clean energy" expressed in decarbonized Joule rather than  $\mathbb{C}$ , might be the best tool to justify and monetize further developments. This will ensure that the provision will actually be used for its intended purpose, independent from crude and other energy market price fluctuations.

Third, is the practicality of carrying out the proposed accounting, and constructing consensual "clean energy" or "regenerative" project criteria. This will require specific financial risk tools adapted to the innovation nature of the transition project. Fourth, the O&G community maintain its activity, continuing delivering energy goods, at the heart of their expertise, while transitioning vigorously away from fossil carbon for energy use.

## 5. Conclusion

We have illustrated an innovated accounting scheme which fosters clean fossil-fuel production. The decarbonization required to achieve clean fuel, essentially hydrogen, is expressed in energy units. We have shown that the industrial cost of substitution of hydrocarbons by hydrogen and solid carbon allows one to capture carbon without CO<sub>2</sub> emissions and provides a carbon free fuel with a reasonable residual energy value. We found that the loss of value (the penalty) in their substitution into hydrogen is very similar, regardless of the feedstock and process used. The resulting CO<sub>2</sub> equivalent prices are all well above 70 \$/t, and in the 200\$/t range for higher energy market prices. We have also identified valuable non-combustion potentials for the carbon product, produced alongside the hydrogen. We can book the penalty on the liability side of the balance sheet, as a provision for accelerated C-free energy products. We thus discourage continued Ccontaining exploration, and protect against stranded asset risks. We found that the generated provision constitutes a magnitude higher potential than today's transition funding effort.

We have identified some essential key success factor to test in a proof of concept approach.

It has been recognised that primary energy is a key factor driving GDP and growth. However, there is a price to pay: taking care of emission. There is an un-dissociable link between pollution  $(CO_2)$  and the access to more than half the energy available in fossil fuel. Pollution externality could be replaced by a pollution avoidance cost, feasibly internalized in O&G books as an energy-justified provision to finance a broad range of pollution-free processes. This will ensure emission control at their root-source. Key initiatives will benchmark the next-step proof-of-concept: (i) pilot scale-demonstrate fundamental C-free hydrocarbon production, (ii) enlist private

and institutional funding agencies, designing the accounting, funding, and financial risk instrument associated, (iii) enlist at least one O&G operator as scale-up designer and developer, (iv) enlist a Carbon-non-combustion usage task-force, (v) enlist a social body empowered for biosphere/social contribution and integration, (vi) link-in the hydrogen development community.

The end product will be a full-scale project proposal, in solidarity with a financial and social community inspiring the energy transition, potentially including energy related monetary tools. For orders of magnitude, an energy-backed currency might require as much as 10<sup>10</sup> tonnes traceably clean hydrogen, if one were to equate the proportion of money supply backed by gold at Bretton-Woods' time, with today's global money supply.

## Acknowledgements

The first author acknowledges the Prof. Nazli Choucri (Massachusetts Institute of Technology), Drs Norman and Jane Li (NL Chemical Technology Inc., Chicago), and Helen and Joe Soussou (Watertown Massachusetts) for their intellectual and financial support. He also thanks Gauthier Chapelle (Brussels, Belgium), for his thoughtful comments and plight towards an entirely regenerative economy.

All authors are deeply thankful to the thorough and most valuable comments of the 3 anonymous reviewers, and the editing team.

## Authors

P. Jean Valayer: lead author, Olivier Vidal : scientific supervision, clarity and argumentation, Noémie Wouters, argumentation, Mark van Loosdrecht : focused clarity, and carbon perspective and usage extension.

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Fig. 1. Accounting for energy penalty in producing C-free fuels from fossil hydrocarbon.

The decarbonization (bottom) is accomplished through a thermal decomposition with hydrogen production (Equation 1 in the text). Solid carbon is the by-product. Substitutions reactions (top) involve carbon oxidation; CO<sub>2</sub> is released and forecloses a carbon for carbon amount of direct sales originally intended from the original inventory (Equation 2 in the text).



Fig. 2. O&G balance sheets, expressed in energy units.

Today (left) hydrocarbon assets imply carbon content without any related penalty. One can apportion the value or cost contribution of carbon according to the energy balance resulting from an H-C splitting process as in Fig. 3. Fossil carbon containing assets loose value, if stranded by regulations, squeezing out the corporate worth, equity and borrowing capacity (middle). The alternate (right), is to balance the carbon asset currently present, by an equal liability, provision to fund C-free fuel development.



Fig. 3. Methane decomposition into solid carbon and hydrogen.

A pyrolysis reactor uses a fraction of the produced hydrogen as a combustible. As 56% of the hydrogen heat value is used in the combustor for the pyrolysis, 44% of the heat value remains available for the fuel market.



Fig. 4. A generic Methane Steam Reforming generic process.

A first steam reforming step (CH<sub>4</sub> + H<sub>2</sub>O  $\rightarrow$  CO + 3 H<sub>2</sub>), is followed by the water-gas shift step (CO + H<sub>2</sub>O  $\rightarrow$  CO<sub>2</sub> + H<sub>2</sub>O) with possible CO<sub>2</sub> capture and gas separation via pressure and swing adsorption (PSA). The mass balance 1 CH<sub>4</sub>  $\rightarrow$  2.44 H<sub>2</sub> is deducted from the published world average CO<sub>2</sub> emission per industrial H<sub>2</sub> produced, inclusive of all variants, PSA or not.



Fig. 5. Comparing energy flows with the financial flows.

The-4-line flow chart at the top back-tracks 100 energy arbitrary units (on the right) back to its source. Natural gas (NG) required 103 at the well on the left. Decarbonized NG requires much higher values (in red), unless alternate use of carbon gets valued, e.g. as civil engineering material. Native hydrogen from natural deposits, might be attractive. The financial flow of an operator at the bottom illustrates 60% cost in tax and royalties.



Fig. 1-S. Chemical net reactions illustrate the energy flows of Fig. 1.

In the thermal decomposition case, at the bottom, partial produced hydrogen is burnt with oxygen to produce water and heat. Water, carbon and hydrogen are produced. In the reforming net-reaction at the top, hydrogen is produced, while carbon recombines with oxygen, and a  $CO_2$  mole is produced. As much as economically feasible,  $CO_2$  is sequestered (CCS), however, there remains a proportion n <1, which is not sequestered.



# Abandoning fossil carbon

= 56% energy loss

= externality from
the operator perspective:
CO<sub>2</sub> avoidance penalty

Pyrolysis of methane:

 $CH_4 \rightarrow C + 2H_2$ 

$$r = 1.38 \frac{E_{H_2}}{E_{CH_4}} = 0.44$$

Net steam methane reforming:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$
$$r = 2.44 \frac{E_{H_2}}{2E_{CH_4}}$$

Hydrocarbon substitution

$$r = k \frac{E_{H_2}}{(1+n)E_{H(C)}}$$



Alternate carbon use: Water treatment, agriculture Civil engineering, metalurgy