

Carbon neutral hydrocarbons

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Reducing greenhouse gas emissions from the transportation sector may be the most difficult aspect of climate change mitigation. We suggest that carbon neutral hydrocarbons (CNHCs) offer an alternative pathway for deep emission cuts that complement the use of decarbonized energy carriers. Such fuels are synthesized from atmospheric carbon dioxide (CO₂) and carbon neutral hydrogen. The result is a liquid fuel compatible with the existing transportation infrastructure and therefore capable of a gradual deployment with minimum supply disruption. Capturing the atmospheric CO₂ can be accomplished using biomass or industrial methods referred to as air capture. The viability of biomass fuels is strongly dependent on the environmental impacts of biomass production. Strong constraints on land use may favour the use of air capture. We conclude that CNHCs may be a viable alternative to hydrogen or conventional biofuels and warrant a comparable level of research effort and support.

Keywords: air capture; transportation; hydrocarbons; mitigation; hydrogen

1. Introduction

Stabilizing atmospheric levels of carbon dioxide (CO₂) will eventually require deep reductions in anthropogenic emissions from all sectors of the economy. Managing CO₂ emissions from the transportation sector may be the hardest part of this challenge. In sectors such as power generation, several options are currently available including wind power, nuclear power and carbon capture and storage (CCS) technologies. Each can be implemented, in the near term, at a scale large enough to enable *deep* reductions in CO₂ emissions at costs of under \$100 per tonne CO₂ (tCO₂) or an electrical premium of the order of \$37 (MW h)⁻¹, based on representative CO₂ emissions from a pulverized coal plant (IPCC 2005). It is recognized that in the last few years, the capital costs of constructing heavy equipment have escalated rapidly here and elsewhere; but we assume that recent capital cost increases are a transient phenomenon and use cost estimates prevailing in the 2000–2005 time window. Adding the premium to the lowest cost of electricity, subcritical coal at \$48 (MW h)⁻¹ (Breeze 2008), we establish a

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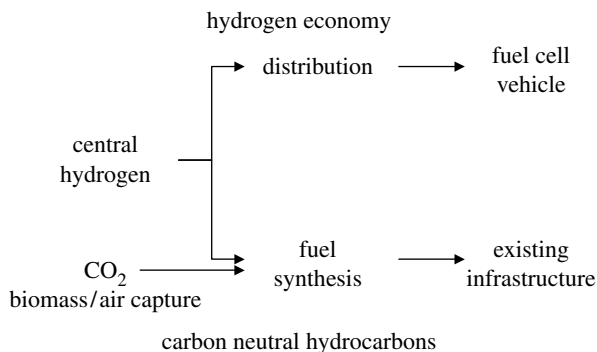


Figure 1. Two pathways for using centrally produced hydrogen in the transportation sector.

total electricity cost of $\$85 \text{ (MW h)}^{-1}$. All of the options listed by Breeze are below this threshold with the exception of expensive wind power sites. The transportation sector does not have such low-cost solutions. While there is ample opportunity for near-term gains in overall vehicle efficiency, these improvements cannot deliver deep cuts in emissions in the face of increasing global transportation demand.

Beyond efficiency, deep reductions in emissions from the transportation sector will require a change in vehicle fuel. Changes in fuel are challenging owing to the tight coupling between vehicle fleet and refuelling infrastructure. Economic network effects and technological lock-in arise because users demand ubiquitous refuelling, yet investments in new fuel infrastructure are typically uneconomic without a large vehicle fleet. Moreover, each of the three leading alternative fuel options, hydrogen, ethanol and electricity, faces technical and economic hurdles precluding near-term, major reductions in transportation emissions using these technologies.

We consider a fourth alternative: carbon neutral hydrocarbons (CNHCs). Hydrocarbons can be carbon neutral if they are made from carbon recovered from biomass or captured from ambient air using industrial processes. The individual capture technologies required to achieve CNHCs have been considered elsewhere; our goal is to systematically consider CNHCs as an alternative and independent route to achieving carbon neutral transportation fuels. We compare various methodologies for producing CNHCs, in terms of dollars (\$) per gigajoule (GJ) of delivered fuel, using hydrogen as a reference case. We argue for the development of CNHC technologies because they offer an alternative path to carbon neutral transportation with important technical and managerial advantages. We do not claim that CNHCs are ready for large-scale deployment or that they will necessarily prove superior to the three leading alternatives. We do argue that they are promising enough to warrant research and development support on a par with efforts aimed at advancing the alternatives.

CNHCs are effectively an alternative method for using carbon-free hydrogen, as shown in figure 1. Converting CO_2 into fuel by adding hydrogen can be viewed as a form of hydrogen storage (Kato *et al.* 2005). Once the hydrogen is produced, a choice exists between distribution and incorporation into a hydrocarbon fuel. The latter is potentially attractive because the energy cost of centrally produced hydrogen is inexpensive compared with crude oil or gasoline at the pump. Even

with CCS, hydrogen can be produced from coal or natural gas at costs ranging from $\$7.5$ to 13.3 GJ^{-1} (IPCC 2005), whereas the current cost of crude is $\$17 \text{ GJ}^{-1}$ (at $\$100/\text{barrel}$) and the cost of gasoline exceeds $\$20 \text{ GJ}^{-1}$ (neglecting taxes). The barrier to the use of hydrogen in transportation systems is distribution and vehicle design rather than the cost of central hydrogen. When CNHCs are considered, the competition is between developing a new distribution and use infrastructure or capturing CO_2 and synthesizing a hydrocarbon.

2. Carbon neutral hydrocarbons

(a) Overview

We define CNHCs as those whose oxidation does not result in a net increase in atmospheric CO_2 concentrations. Hydrocarbon fuels can be made carbon neutral either *directly* by manufacturing them using carbon captured from the atmosphere, or *indirectly* by tying the production of fossil fuels to a physical transfer of atmospheric carbon to permanent storage. The indirect route allows for a gradual transition from the current infrastructure, based on petroleum, to a sustainable system based on atmospheric sources of carbon.

It is vital to distinguish negative emissions achieved by permanent physical storage from economic offsets (carbon credits) or the sequestration of carbon in the active biosphere. While the use of carbon offsets such as those allowed under the clean development mechanism may have some benefits, they are not equivalent to non-emission (Wara 2007). There are also tangible benefits to increasing stocks of carbon in soils or standing biomass, but such organic stores are highly labile and may be quickly released back to the atmosphere by changes in management practices or climate. Geological storage reservoirs for CO_2 may also leak. However, the retention time for CO_2 in geological reservoirs is at least 10^3 times longer than that for carbon stored in the biosphere. In most cases, a very large fraction of CO_2 placed in geological storage is expected to be retained for time scales exceeding 10^8 years (IPCC 2005).

Direct and indirect routes to CNHCs both begin by capturing CO_2 from the atmosphere. Carbon can be captured from the atmosphere by either harvesting biomass from sustainable plantations or direct industrial processes referred to as air capture (Keith *et al.* 2006). Once captured, the CO_2 can be transferred to storage either in geological formations or other means such as mineral sequestration (IPCC 2005).

Alternatively, it may be returned to the fuel cycle through incorporation into a synthetic fuel or conventional biofuels. The synthetic fuel pathway depends on a source of primary energy to drive the required chemical reactions including the supply of hydrogen. As with hydrogen and electricity, these synthetic hydrocarbons are an energy carrier produced from a primary energy source such as wind, nuclear power or fossil fuels with CCS. Unlike hydrogen and electricity, they are carbonaceous fuels that are nevertheless carbon neutral as they were derived from the atmosphere. The relationship between all of the options is presented in figure 2.

We first review the technologies for capturing carbon from the air, using either biomass growth or air capture. The review is followed by discussions on transforming the carbon, in the form of high-purity CO_2 , into hydrocarbon fuels.

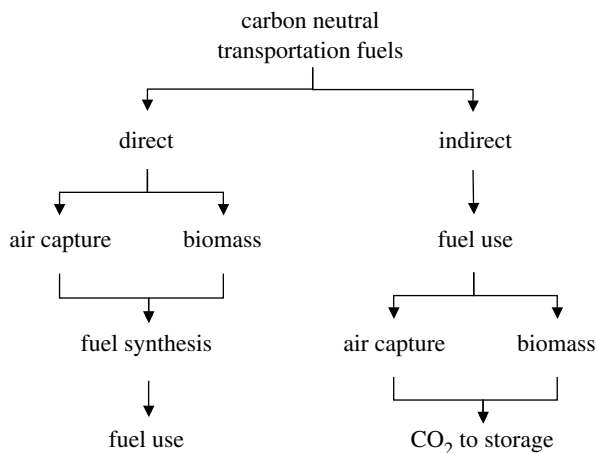


Figure 2. Schematic of routes to CNHCs.

The objective is to outline the important process steps so that they can be quantified in the economic comparison that follows. The comparison does not include fugitive emissions from individual process steps. These include emissions associated with harvesting and processing biomass, potential leakage from industrial air capture and CO_2 emissions associated with hydrogen production from fossil fuels (estimated at $7\text{--}28 \text{ kg CO}_2 \text{ GJ}^{-1}$; IPCC 2005). As such, the processes considered here will not be completely ‘carbon neutral’ unless accompanied by the removal of additional CO_2 from the atmosphere.

(b) Biomass systems

The large carbon fluxes between the atmosphere and the terrestrial biosphere (approx. 60 Gtonne carbon per year), in combination with our substantial control over terrestrial biotic productivity (Vitousek *et al.* 1986), grant us a powerful lever for manipulating atmospheric CO_2 . If biomass is cyclically harvested so that stocks of standing biomass are not decreased, it provides a means of simultaneously capturing both carbon and solar energy. As discussed below, once harvested biomass can be used to produce conventional biofuels or CNHCs; alternatively, the carbon can be permanently sequestered allowing for the indirect production of CNHCs.

Large-scale use of biomass presents enormous challenges and poses risks of substantial environmental, social and economic side effects. As noted by the IPCC (2007), ‘biomass production and use imply the resolution of issues relating to competition for land and food, water resources, biodiversity and socio-economic impact’. These competing issues make it very unlikely that conventional biomass fuels can be used as the dominant solution to emissions from the transportation sector. There is also a degree of risk associated with solving the climate change problem using a technology dependent on the climate (Fargione *et al.* 2008; Searchinger *et al.* 2008).

Estimates of biomass cost and availability vary widely. For example, the cost of switchgrass ranges from $\$33 \text{ tonne}^{-1}$ at a yield of $11 \text{ tonnes biomass ha}^{-1}$ to $\$44 \text{ tonne}^{-1}$ at 7 tonne ha^{-1} in Oklahoma (Epplin 1996). Walsh estimated

switchgrass costs at \$20–25 tonne⁻¹ depending on the location in the USA with woody crops (poplar) ranging from \$22 to 35 tonne⁻¹ (Walsh *et al.* 2003). Other researchers estimate the cost of short rotation crops in Sweden at \$89 tonne⁻¹ with forestry residues slightly more expensive at \$110 tonne⁻¹ (Gustavsson *et al.* 2007), using a conversion value of \$1.00 = €0.72 and an energy content for dry woody biomass of 20 GJ tonne⁻¹ (Khesghi *et al.* 2000). Alternative studies for combination biomass with CCS have assumed costs of \$50–54 tonne⁻¹ (Audus & Freund 2004; Rhodes & Keith 2005).

The dedication of large amounts of land to energy crops may also raise the price of agricultural products. Estimates vary from 10 per cent (Walsh *et al.* 2003) to 40 per cent (Searchinger *et al.* 2008). The current biofuel boom in North America appears to have increased agricultural prices significantly, even though its contribution to fuel supplies is minimal. This illustrates a negative impact of biofuel production, although it does not prove that larger scale biomass production could not succeed using better choices of crops and incentive mechanisms.

Ignoring the negative side effects of biomass harvesting discussed above, we assume that the cost of large-scale biomass delivered to centralized facilities ranges from \$40 to 80 per dry tonne or \$2 to 4 GJ⁻¹. It seems plausible that negative non- and macro-economic impacts of biomass production might limit biomass availability. Since we have no basis to estimate the effects of such impacts, we treat them parametrically, calculating the biomass price that would make biomass more expensive than air-capture routes to CNHCs.

(c) Biomass-based fuels

Biomass contains both carbon and energy. Production of ethanol from biomass uses the energy content of the biomass to drive the conversion process. In order to provide process energy, most of the carbon in the input biomass stream is oxidized and released to the atmosphere as CO₂. Even in advanced cellulosic ethanol production, which has not yet been applied at a commercial scale, only about one-third of the carbon content in the input biomass ends up in the fuel. As a means of recycling atmospheric carbon to liquid fuels, these processes make inefficient use of biomass carbon.

Here, we consider only the production of CNHCs from biomass using external energy inputs to make more efficient use of the carbon captured in the biomass. This choice is based on the assumption that land-use constraints will be the most important barrier to biomass-based fuels and the observation that the cost of large-scale carbon-free energy at a biomass processing plant is substantially less than that of delivered fuel energy. For example, hydrogen and heat might be supplied from coal with CCS at costs substantially less than those of delivered CNHCs or conventional gasoline. The use of external energy/hydrogen can convert a larger fraction of the input carbon to hydrocarbon fuel and reduce land use by a factor of 2–3 when compared with systems based on biomass alone (Agrawal *et al.* 2007).

There is a large suite of methods that might be employed to produce CNHCs from biomass. Examples include the following:

- electricity production with CO₂ capture followed by CO₂ hydrogenation using externally supplied H₂; the CO₂ capture step might use oxy-fuel, post- or pre-combustion capture;

- gasification to produce synthesis gas followed by production of CNHCs using the Fischer–Tropsch (F–T) process and CO₂ hydrogenation using externally supplied H₂; and
- biological processing to produce hydrocarbons or alcohols combined with carbon capture followed by CO₂ hydrogenation using externally supplied H₂.

For simplicity, we examine only the first route since there have been several assessments of biomass electricity with CO₂ capture. Moreover, it allows a direct comparison with air capture allowing us to consider both direct and indirect routes from biomass to CNHCs. In reality, biomass co-firing or co-feeding with fossil fuels seems a more likely near-term prospect. Such methods would produce hydrocarbon fuels with reduced life-cycle CO₂ emissions, but will not produce CNHCs. One might consider these options as a blend of CNHCs with conventional fossil fuel use.

(d) Air-capture systems

The process of air capture comprises two components: absorption and regeneration. The absorption phase refers to dissolving the CO₂ contained in the atmosphere into solution or onto a solid sorbent, while the regeneration phase refers to producing a concentrated stream of CO₂ from the medium used for absorption. Most recently published work has addressed systems that use a strong base, typically NaOH, as the sorbent and chemical caustic recovery as the means of regeneration. Earlier works assumed an electrochemical system based on carbon-free electricity. The challenge with electrochemical methods is the electricity consumption during regeneration, 308 kJ_e mol⁻¹ CO₂ (Bandi *et al.* 1995), which can be converted to a cost of \$100–200/tCO₂ for carbon neutral electricity costing \$0.05–0.10 (kW h)⁻¹.

The thermal process, as outlined in the literature, consists of four reactions: absorption; causticization; regeneration; and hydration (Baciocchi *et al.* 2006; Keith *et al.* 2006; Zeman 2007). The CO₂ is absorbed into sodium hydroxide to form sodium carbonate. The carbonate ion is transferred from sodium to calcium ions in the causticization process, which results in the precipitation of calcium carbonate. The CO₂ is regenerated by thermal decomposition of the calcium carbonate in a kiln while the lime produced is hydrated to complete the cycle. The absorption reaction is an established engineering technology dating back several decades (Spector & Dodge 1946). The other reactions are at the heart of the pulp and paper industry and can be directly applied to air capture with the addition of conventional CCS technologies (Keith *et al.* 2006), although conversion to an oxygen kiln significantly reduces energy demand (Baciocchi *et al.* 2006; Zeman 2007). Experimental work has shown conventional vacuum filtration technology sufficient for dewatering the precipitate and causticization at ambient temperatures to be feasible (Zeman 2008).

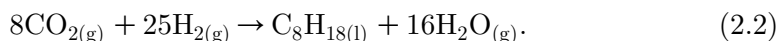
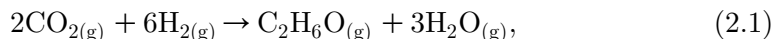
While technically feasible, the amount of energy consumed and its form are critical components in terms of neutralizing emissions from the transportation sector. The thermal requirements are dominated by the decomposition of calcium carbonate, which requires a minimum of 4.1 GJ/tCO₂ of high-temperature heat (Oates 1998) with the potential to recover 2.4 GJ/tCO₂ at lower temperatures via steam hydration (Zeman 2007). Using existing technologies, the actual thermal load

is 5.1 GJ/tCO₂ for an 80 per cent efficient kiln (Oates 1998). Some electrical energy is required to power blowers for air movement, pumps for sorbent circulation as well as oxygen production with load estimates varying from 126 to 656 kW h/tCO₂ (0.45–2.36 GJ_e/tCO₂; Zeman 2007). The cost of air capture was estimated, using technologies from other industries, for the system above at approximately \$150/tCO₂ (Keith *et al.* 2006). We note that this cost estimate was intended to be a minimum estimate for long-run costs and that it was based on a simplistic combination of existing technologies rather than on an integrated plant design. Other capture processes have been considered (Steinberg & Dang 1977) as well as advanced regeneration cycles based on titanates that reduce high-temperature heat requirements by approximately 55 per cent (Nohlgren 2004). In this work, we consider air capture costs ranging from \$100 to 200/tCO₂ recognizing that there are no *a priori* reasons why costs could not eventually be lower.

Air capture, as opposed to biomass growth, is not limited by land area rather by the rate of CO₂ diffusion to the boundary layer, analogous to the physics that limits wind turbine spacing (Keith *et al.* 2006). Previous work has shown that air-capture rates are at least one order of magnitude larger than biomass growth (Johnston *et al.* 2003). This value reflects the large-scale limitations of CO₂ transport in the atmospheric boundary layer. Note that air-capture systems need only occupy a small portion of the land area in order to capture the maximum large-scale CO₂ flux, just as wind turbines have a small footprint yet capture much of the large-scale kinetic energy flux. The effective flux, based on the air-capture plant boundary, can be expected to be at least two and quite likely three orders of magnitude larger than biomass growth with the remainder of the land area available for other uses, such as agriculture.

(e) CO₂ fuels

The production of synthetic fuels via CO₂ hydrogenation requires hydrogen addition and oxygen removal (Inui 1996). We consider the production of octane (C₈H₁₈) as a simple proxy for synthetic fuels that could replace current automobile gasoline; in practice, fuels with a range of hydrocarbons of approximately this molecular weight would probably be produced. We also consider dimethylether (DME) as a replacement for diesel fuel, even though it is not technically a hydrocarbon. We note that DME synthesis commonly takes the form of methanol dehydration (Jia *et al.* 2006) and higher order hydrocarbons can be formed on composite catalysts that include zeolites with methanol as an intermediary (Kieffer *et al.* 1997). The synthesis reactions are listed in equation (2.1) for DME and equation (2.2) for C₈H₁₈:



The production of hydrocarbons from CO₂ and H₂ feedstock is a high-pressure catalytic process where the choice of catalyst, operating pressure and temperature affects the reaction products (Inui 1996; Halmann & Steinberg 1999). A summary of relevant reaction characteristics is presented in table 1. While the synthesis reaction is exothermic, producing high-purity streams of

Table 1. Comparison of synthetic fuels from CO₂ hydrogenation (HHV; Lide 2000).

fuel	ΔH_f°	energy content ^a		hydrogen efficiency	
	(kJ mol ⁻¹ CO ₂)	(kJ mol ⁻¹ CO ₂)	(GJ/tCO ₂)	ratio ^b	energy ^c
C ₂ H ₆ O	-62	730	16.6	3	0.85
C ₈ H ₁₈	-118	685	15.6	3.125	0.77

^aBased on heat of combustion.

^bMolar ratio (H₂/CO₂) of reactants in equations (2.1) and (2.2).

^cRatio of energy content in produced fuel over reactant H₂.

hydrogen and CO₂ requires a significant amount of energy. The choice of product does not significantly impact the ratio of reactants with 3 mol of hydrogen required for every mole of CO₂. The energy component of hydrogen efficiency reflects the energy embedded in the feed hydrogen lost to steam production. Typically, the reactors operate at temperatures of approximately 200–300°C and pressures of 20–50 bar. It is likely that a use would be found for the reaction heat (second column of table 1) in such a process, e.g. solids drying (in air capture) or its employment in a low-temperature Rankine cycle. It is worth noting that synthetic fuel production does not currently employ CO₂ as feed (Mignard & Pritchard 2006; Galindo Cifre & Badr 2007), although much experimental work has been performed (Inui 1996; Kieffer *et al.* 1997; Halmann & Steinberg 1999).

3. Economic comparisons

A systematic comparison is used to identify the most important cost drivers for the various methods of producing CNHCs. We have chosen a metric based on the cost of delivering the fuel to the end-user, measured in dollars per GJ energy content (\$ GJ⁻¹). We employ four different bases for comparison: indirect methods to offset conventional oil use; air capture to hydrocarbons; hydrogen for use on-board vehicles; and biomass CO₂ to hydrocarbons. The derivation is first given in the equation form, followed by a table listing relevant coefficients and then text explaining their use and origins.

(a) Conventional fuels with indirect CCS

The refining of crude oil produces the current transportation fuels of choice, gasoline and diesel. The existing transportation infrastructure is built around these fuels and their use in the immediate future is likely. Under these circumstances, CO₂ emissions would be neutralized using indirect methods. The cost of neutralizing oil can be estimated using equation (3.1) and table 2; the symbols used are described in the discussion below.

$$\text{cost}_{\text{fuel}} \left(\frac{\$}{\text{GJ}} \right) = C_{\text{oil}} \times f_{\text{O/G}} + (C_{\text{CO}_2} + 1.5 \times C_{\text{storage}}) \times f_{\text{C/E}} \times f_{\text{LC}}. \quad (3.1)$$

The cost per unit energy of neutralizing conventional fuels is determined, in equation (3.1), by adding the energy cost of the fuel to the cost of offsetting the resultant emissions through CCS. The energy cost of oil is the product of the cost

Table 2. Coefficients for offsetting emissions from conventional fuels.

coefficient	C_{oil}	$f_{O/G}$	C_{CO_2}	$C_{storage}$	$f_{C/E}$	f_{LC}
units	\$/barrel	barrel GJ ^{-1a}	\$/tCO ₂	\$/tCO ₂	tCO ₂ GJ ⁻¹	—
value	50–100	0.27–0.24	—	8 ^b	0.067	1.40
source	—	EIA (2008)	—	IPCC (2005)	EPA (2005)	Farrell <i>et al.</i> (2006)

^aData analysis of monthly costs for cost of oil (West Texas Intermediate) and refinery price of gasoline since October 1993 resulted in ($\$ \text{GJ}^{-1}$) = $0.223 \times (\$/\text{barrel}) + 2.11$ ($n=170$, $r^2=0.952$).

^bRepresenting a range of \$3–12 per tCO₂.

per barrel and a conversion factor ($f_{O/G}$) that translates the cost into the appropriate units. The conversion factor ($f_{O/G}$), relating the cost of a gallon of gasoline from the refinery to a barrel of oil, was obtained by comparing the price data over the last 14 years and using a value of 130.8 MJ gal⁻¹ of gasoline (Keith & Farrell 2003). The cost of offsetting the emissions is the cost of capture and storage multiplied by the emissions per GJ of energy. The cost of capture (C_{CO_2}) refers to the cost of removing CO₂ from the atmosphere. Underground geological storage is projected to cost \$1–8/tCO₂ with transportation of the compressed CO₂ by pipeline costing \$2–4/tCO₂ for a 250 km run with an annual flow rate of 5 Mt CO₂ (IPCC 2005). The cost of storage is multiplied by a factor of 1.5, as air capture produces an amount of CO₂ equivalent to 50 per cent of the amount captured if coal is used in the regeneration phase (Zeman 2007). The use of other methods of producing high-temperature heat, e.g. nuclear, would reduce this factor. The tonnes of CO₂ released per unit energy contained in gasoline ($f_{C/E}$) are derived using an emission factor of 8.8 kg CO₂ gal⁻¹ (EPA 2005). The final coefficient (f_{LC}) relates the life-cycle CO₂ emissions to the energy content of the final fuel, gasoline. In this manner, we include the process CO₂ emissions associated with converting oil to gasoline.

Using the values listed in table 2 and the values of \$100–200/tCO₂ for air capture, the fuel cost ranges from \$24 to 44 GJ⁻¹. The cost of conventional gasoline ranges from \$13 to 24 GJ⁻¹ as oil prices fluctuate between \$50 and 100 per barrel. Given the assumptions above, air capture increases the cost of fuel by \$10–20 GJ⁻¹; alternatively, with oil at \$100/barrel and air capture at \$100/tCO₂, the cost of vehicle fuel increases by 42 per cent.

(b) Synthetic fuels using atmospheric CO₂

Producing synthetic fuels from CO₂ requires hydrogen and a high-pressure catalytic reactor to synthesize the fuel. The cost of producing hydrogen with CCS on an industrial scale has been estimated at \$7.5–13.5 GJ⁻¹ (IPCC 2005). The cost estimates for hydrogen vary depending on the price of natural gas, as steam reforming of methane is the dominant method for H₂ production (Ogden 1999; Galindo Cifre & Badr 2007). Thermochemical methods for production are expected to be more economical than electrolysis except under circumstances where electricity is available at prices below \$0.02 (kW h)⁻¹ (Ogden 1999; Sherif *et al.* 2005) combined with a 50 per cent reduction in electrolysis capital costs (Ogden 1999). Conditions favourable to renewable electrolytic hydrogen may exist, e.g.

Table 3. Coefficients for synthetic fuels from atmospheric CO₂.

coefficient	C_{CO_2}	$f_{\text{C/E}}$	C_{H_2}	$f_{\text{S/P}}$	$C_{\text{synthesis}}$	C_{storage}
units	\$/tCO ₂	tCO ₂ GJ ⁻¹	\$ GJ ⁻¹	kJ _{IN} kJ _{OUT} ⁻¹	\$ GJ ⁻¹	\$/tCO ₂
value	—	0.067	10.5	1.24	3.5	8
source	—	EPA (2005)	IPCC (2005)	Lide (2000)	Michel (1999) and Gustavsson <i>et al.</i> (2007)	IPCC (2005)

excess wind power during early morning hours, but any gains from low electricity costs must eclipse increased capital costs associated with intermittent use of the electrolyzers. We believe that only under exceptional circumstances would one form of secondary energy (electricity) be converted to another (hydrogen). We use a representative value of \$10.5 GJ⁻¹ for carbon neutral hydrogen. The CO₂ resulting from the production of hydrogen is stored underground with any CO₂ produced during the regeneration phase of air capture.

$$\text{cost}_{\text{fuel}} \left(\frac{\$}{\text{GJ}} \right) = C_{\text{CO}_2} \times f_{\text{C/E}} + C_{\text{H}_2} \times f_{\text{S/P}} + C_{\text{synthesis}} + 0.5 \times C_{\text{storage}} \times f_{\text{C/E}}. \quad (3.2)$$

The cost of producing synthetic fuels from atmospheric CO₂ is calculated from equation (3.2). The total cost is the sum of producing the CO₂ and hydrogen added to the cost of the synthesis reactors. Again, the cost of air capture is estimated while the emissions per GJ of fuel produced ($f_{\text{C/E}}$) are equated to gasoline. The values of $f_{\text{C/E}}$ based on table 1 are 4–10 per cent lower than that of gasoline, which is a small advantage. The cost of hydrogen, a representative value, is multiplied by a factor ($f_{\text{S/P}}$) representing the efficiency of transferring the energy to the fuel. The hydrogen usage factor is calculated as the average of the inverse of hydrogen energy efficiency in table 1. It represents the extra cost associated with H₂ feed lost to water formation, as shown in equations (2.1) and (2.2). The synthesis costs vary with the fuel produced as the operating conditions and choice of catalysts vary. We used a representative value for multi-reactor synthesis with CO₂ as feedstock (Michel 1999; Gustavsson *et al.* 2007). Using the values given in table 3 and air-capture costs of \$100–200/tCO₂, the production cost for synthetic fuels ranges from \$23.5 to 30 GJ⁻¹. Mitigating the fugitive emissions from H₂ production using air capture would add \$2–4 GJ⁻¹ to the total cost, based on 0.3 tCO₂ per tCO₂ used in fuel production.

(c) Hydrogen use in transportation

The use of hydrogen as a large-scale fuel for distributed road transportation requires a complete replacement of the associated infrastructure including production, distribution and fuelling stations. We consider only the cost to deliver hydrogen to the vehicle in \$ GJ⁻¹. On the one hand, this neglects the cost reductions that will arise where hydrogen enables the use of fuel cells that are more efficient than the conventional engines used with CNHCs, while on the other hand, it neglects the extra vehicle costs associated with hydrogen storage and hydrogen power plants.

Table 4. Coefficients for hydrogen transportation systems.

coefficient	C_{H_2}	C_{dist}	C_{station}
units	\$ GJ ⁻¹	\$ GJ ⁻¹	\$ GJ ⁻¹
value	10.5	10–22.5	5
source	IPCC (2005)	Yang & Ogden (2007)	Ogden (1999)

Our hydrogen cost assumptions are based on large-scale central-station hydrogen production using fossil fuels with CCS, since this is the most immediately available technology. Currently, over 90 per cent of hydrogen production is derived from the steam reforming of methane at production scales of up to 100 million standard cubic feet of hydrogen per day (Ogden 1999; Sherif *et al.* 2005; Galindo Cifre & Badr 2007). The estimates often use a purchase price of less than \$6 GJ⁻¹ for natural gas, which may not reflect prices for large-scale hydrogen production. Above this price point, production costs are similar for coal costing \$1.5 GJ⁻¹.

The cost of hydrogen fuels delivered to the vehicle is estimated using

$$\text{cost}_{\text{fuel}} \left(\frac{\$}{\text{GJ}} \right) = C_{H_2} + C_{\text{dist}} + C_{\text{station}}. \quad (3.3)$$

Using the values given in table 4, the cost of hydrogen fuels delivered to the vehicle ranges from \$25.5 to 38 GJ⁻¹. The range is strongly dependent on the cost of distributing the hydrogen to fuelling stations, which is in turn dependent on market penetration of hydrogen vehicles (Yang & Ogden 2007). The range in table 4 reflects penetration levels of 5 per cent (\$22.5 GJ⁻¹) and 50 per cent (\$10 GJ⁻¹) where market penetration is taken as the proportion of vehicles using hydrogen fuel. These values are taken from the ‘base case’ of Yang & Ogden; the cost of other scenarios varies from –22.5 to +37 per cent for the 50 per cent market penetration and –17 to +70 per cent for 10 per cent. Equation (3.3) does not include any CO₂ removal from the air to compensate for the fugitive emissions associated with H₂ production from fossil fuels, as mentioned in §2*a*. Using an air-capture cost of \$100/tCO₂, the additional cost ranges from \$1 to 3 GJ⁻¹ including storage.

(d) Carbon neutral fuels from biomass

As discussed in §2*d*, there are many ways to convert biomass to CO₂ and fuels. We focus on fuel synthesis in a manner similar to that described in §3*b* using CO₂ derived from a biomass power plant. The cost of CO₂ derived from such a plant is a function of the cost of biomass and the difference between the balance of system costs for the biomass plant and the cost of a carbon neutral fossil plant. The cost for the balance of system is the difference between the cost of biomass electricity with CCS and the fuel cost. The fuel cost is obtained by dividing the biomass cost with the energy content; the result is then divided by the thermal efficiency of the plant. The cost of carbon neutral electricity was taken as \$0.073 (kW h)⁻¹ (IPCC 2005).

The ideal case is where the revenues generated from the sale of electricity offset the cost of the plant and capture system. The cost of CO₂ is then the cost of biomass divided by the tonnes of CO₂ produced per tonne of biomass or

$\$/\text{tCO}_2 = 0.59 \times (\$/\text{tonne}^{-1})$, based on the chemical formula for woody biomass (Petrus & Noordermeer 2006). In practice, the relationship will depend on the capture efficiency and the specific technology. Using studies from the literature, we establish two relationships for the cost of CO_2 and the cost of biomass based on steam gasification (Rhodes & Keith 2005), equation (3.4), and oxygen gasification (Audus & Freund 2004), equation (3.5). The CO_2 and dry biomass costs are expressed in $\$/\text{tonne}^{-1}$:

$$C_{\text{CO}_2} = 1.07C_{\text{bio}} - 16, \quad (3.4)$$

$$C_{\text{CO}_2} = 0.69C_{\text{bio}} + 55. \quad (3.5)$$

Steam gasification is the most cost-effective method for the biomass cost range used in this work. The resulting cost for CO_2 ranges from $\$27$ to $70/\text{tCO}_2$. The cost of producing carbon neutral fuels by indirect methods, as per equation (3.1), using these values ranges from $\$16.5$ to 31.5 GJ^{-1} . By comparison, direct methods based on equation (3.2) produce a delivered cost of fuel ranging from $\$18.5$ to 21 GJ^{-1} . These costs are lower than the associated values for air capture using both indirect (28–33%) and direct (23–30%) methods.

Biomass can be converted directly to hydrocarbon via the F–T synthesis, labelled here as biomass F–T. This technology has reached the commercial stage with a plant in Freiburg, Germany, producing $15 \text{ ktonnes yr}^{-1}$. The cost of these fuels has been estimated at $\$21 \text{ GJ}^{-1}$ (Fairley 2006). The process uses biomass residues and the sensitivity to increasing feedstock prices, owing to increased demand for biofuels, was not discussed.

(e) Comparison of methodologies

A cost comparison of the various delivery methods for carbon neutral transportation fuels is presented in figure 3. The figure contains the upper- and lower-bound estimates, based on the previous sections, for the different methods. The total cost has been divided into subsections (oil, air capture, biomass, hydrogen, oxygen, fuel synthesis including reforming and fuel distribution including fuel stations) to illustrate the relative importance of each component.

Reviewing figure 3, we observe that the cost of oil, ranging from $\$50$ to 100 per barrel, has a strong effect on the cost of indirect methods. The cost of oil accounts for 56–55 per cent of indirect routes using air capture and 80–77 per cent of costs for biomass-based systems. Direct routes are characterized by the need for hydrogen. The contribution from hydrogen production ranges from 56 to 43 per cent for air-capture systems, 71 to 61 per cent for direct biomass systems and 41 to 28 per cent for hydrogen-based systems. The lower percentage for the hydrogen infrastructure highlights its dependence on a hydrogen distribution system and fuelling stations. At oil costs above approximately $\$150$ per barrel oil substitutes win out, and direct routes to CNHCs are uniformly preferred to indirect routes.

The choice of mitigation technology will not, of course, depend simply on cost due to the strong path dependency in the coupled development of vehicle technologies and refuelling infrastructures. Considering costs alone, and ignoring the large uncertainties in technology, we can nevertheless draw some interesting conclusions about how the relative cost competitiveness of various routes to CNHCs depends on the cost of carbon, biomass and crude oil.

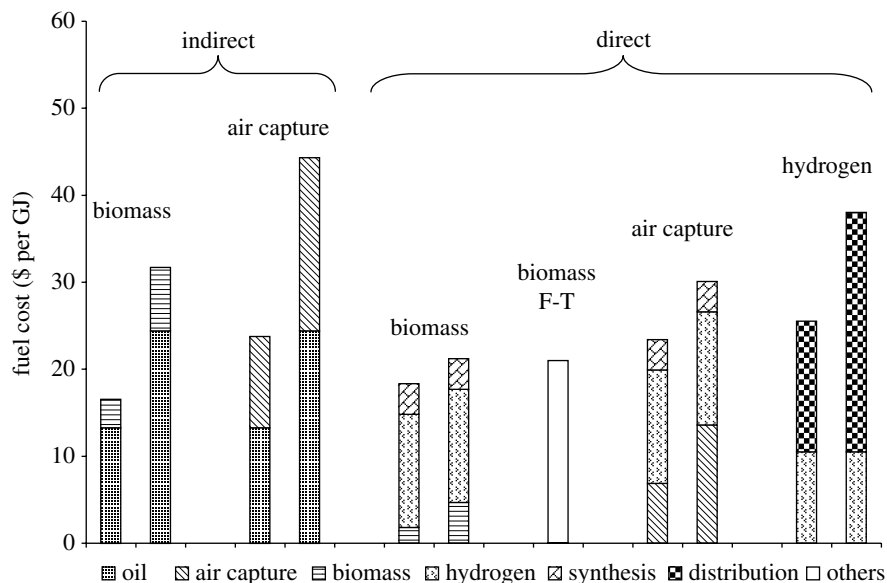


Figure 3. Comparison of delivered costs for carbon neutral transportation fuels.

We first consider the comparison between direct and indirect routes as a function of the cost of petroleum. We previously established, in §3*b*, that the cost of delivering synthetic fuel is approximately $\$24 \text{ GJ}^{-1}$ when air capture costs $\$100/\text{tCO}_2$ and H_2 costs $\$10.5 \text{ GJ}^{-1}$. Using the correlation from table 1 ($f_{O/G}$), we can convert this value to an oil cost of $\$96/\text{barrel}$. Thus, at higher oil prices, it is economical to produce synthetic fuels under the assumed conditions. This value does not include any price on CO_2 emissions. Based on the emission factor $f_{C/E}$ and the life-cycle factor f_{LC} , the combustion of the gasoline produces the equivalent of 0.288 tCO_2 per barrel of oil. The values define a line with a negative slope, as shown in figure 4, which also contains a vertical line whose abscissa represents the cost of air capture. Above the line, mitigation by direct air capture is the most economical option. At emission prices lower than the cost of air capture, the most economical option is to pay for the emissions, while at higher prices, indirect methods are preferable. The area bounded by low oil and emission costs refers to the ‘business-as-usual’ scenario. A similar graph can be produced for CNHCs using biomass by drawing a parallel solid line with the y -axis ordinate at $\$73.5/\text{barrel}$ ($\$18.5 \text{ GJ}^{-1}$) and a vertical dashed line with the x -axis abscissa at $\$27/\text{tCO}_2$ ($\$40 \text{ tonne}^{-1}$ biomass).

The balance between the cost of fuels using CO_2 produced from biomass and air capture can also be measured in this manner. In this case, the common metrics are the cost of hydrogen and fuel synthesis. The comparison, as shown in figure 5, contains curves for the ‘ideal’ case as well as steam reforming (Rhodes & Keith 2005) and oxygen gasification (Audus & Freund 2004). In the ideal case, the revenues from the sale of electricity exactly offset the capital and operating costs of the facility resulting in a direct relationship between the cost of biomass and CO_2 . The area where air capture is economical is below and to the right of the gasification lines. The intersection of the gasification curves occurs at a biomass price of $\$180 \text{ tonne}^{-1}$, beyond which it is more economical to use oxygen

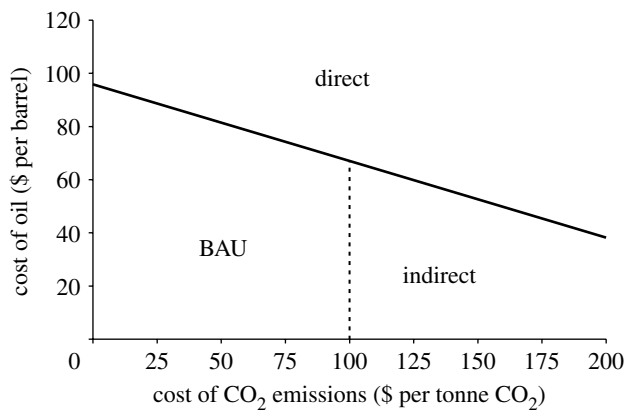


Figure 4. Mitigation options based on synthetic fuel production using $\$100/\text{tCO}_2$ air capture with $\$10.5 \text{ GJ}^{-1} \text{ H}_2$.

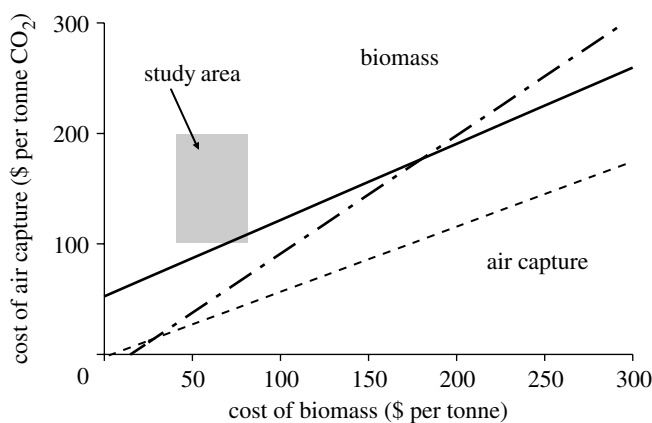


Figure 5. Effect of biomass cost on the cost of producing CO_2 for fuel synthesis (dashed line, ideal; solid line, Audus & Freund (2004); dot-dashed line, Rhodes & Keith (2005)).

gasification owing to the higher capture rate (85% as opposed to 55%). The study area can expand to the right if the external costs of biomass are included. The threshold for $\$100/\text{tCO}_2$ air capture is if the total cost of biomass, including non-market costs, rises above $\$105 \text{ tonne}^{-1}$.

Similarly, a comparison can be made between fuels produced using CO_2 from air capture with using hydrogen on-board vehicles. Given that the cost of producing the hydrogen is identical, the comparison is between producing the CO_2 and synthesis for air capture and distributing the hydrogen to fuelling stations, as shown in figure 6. We have not included the cost of fuelling stations, which would add $\$15/\text{tCO}_2$ for each $\$1 \text{ GJ}^{-1}$ of cost. The cost estimate for fuel stations used in §3 ($\$5 \text{ GJ}^{-1}$) would add $\$75/\text{tCO}_2$ to the allowable cost of air capture. Even without the fuelling stations, the required cost of air capture to be competitive with a fully developed hydrogen economy is not unreasonable. We investigated the effect of a 50 per cent reduction in the cost of fuel synthesis, shown as the dashed line in figure 6.

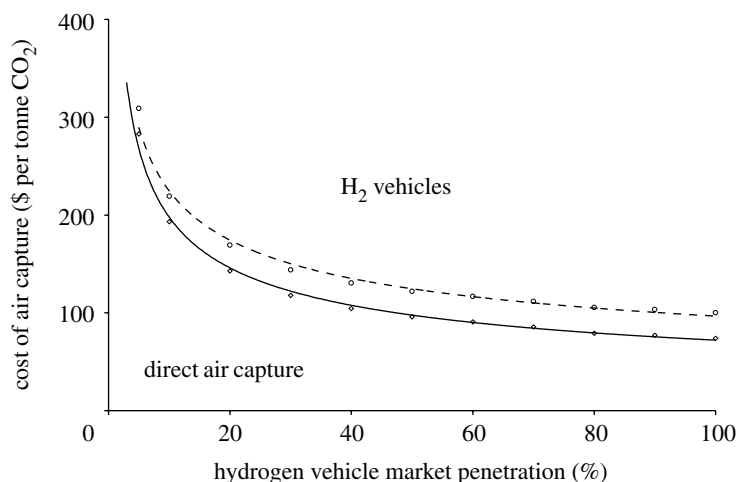


Figure 6. Effect of reduced cost of hydrogen distribution, as measured by market penetration, on the allowable cost of air capture.

4. Non-economic considerations

The work presented here has focused on estimating the comparative costs of various methods of producing and delivering carbon neutral transportation fuels. There are, of course, external factors such as food production and geopolitical realities, which will exert market pressures on the chosen method of fuel production. Some efforts have been made to quantify the effects of biofuel production on food prices (Walsh *et al.* 2003) and the effects of a global change to a Western, meat-based diet (Hoogwijk *et al.* 2003). These effects are difficult to quantify and also depend on the pathway. Projections to 2050 and beyond may reflect gradual changes but annual changes, such as switching crops, may have a dramatic impact on food prices. We will not delve into the food debate beyond raising the question of who gets to decide when it is time to grow food or fuel.

A carbon neutral fuel is of little use unless consumers purchase vehicles designed to use those fuels. Currently, the consumer and commercial vehicle fleet is dominated by hydrocarbon-based internal combustion engines. The large volume of vehicle sales, 20 million annually in the USA, has led to economies of scale in production that make introducing a new vehicle type more expensive. Some hydrogen vehicles are available but the cost is two orders of magnitude higher than conventional vehicles (Mayersohn 2007). Additionally, electric vehicles are at least one order of magnitude more expensive than gasoline-powered cars (Tesla Motors 2008, <http://www.teslamotors.com/buy/buyPage1.php>). While electric vehicles require a different infrastructure, the expected price of electricity with CCS, which ranges from \$0.05 to 0.07 (kW h)⁻¹ (\$14–20 GJ⁻¹; IPCC 2005), can be compared with the fuel costs in figure 2. Additionally, the consumer has come to expect certain attributes in a vehicle, including range and interior space, which may drive up the effective cost of alternative technologies. The premium afforded to hydrocarbon fuels may be quite substantial (Keith & Farrell 2003).

Land-use change is also an important consideration for carbon neutral transportation fuels. Recent work has highlighted the importance of considering emissions over the complete life cycle of the fuel production process including indirect emissions from land-use change as a result of biofuel production. Once included, the life-cycle emissions of food-based biofuels change from slight reductions (20%) to net emitters for at least 40 years (Fargione *et al.* 2008; Searchinger *et al.* 2008). Only cellulosic fuels from abandoned or degraded cropland do not result in an immediate release of carbon stores, although the potential carbon accrued through reforestation is not included. Cellulosic fuels were found to be the most economical in this work but their net greenhouse gas reductions must be subject to the same analysis as food-based fuels. Specifically, the carbon accounting must include roots and soil carbon as well as detritus from harvesting. Fargione *et al.* (2008) suggested that slash and thinning from sustainable forestry along with the use of carbonaceous wastes may provide the lowest net emissions. By contrast, CNHCs based on air capture, as well as hydrogen and electricity, are not dependent on the biosphere. They have the benefit of simple accounting with readily verifiable emission profiles as opposed to indirect emissions from biofuels, which may span the globe.

5. Conclusions

We have introduced a methodology for a systematic comparison of solutions to greenhouse gas emissions from the transportation sector. We focused on solutions built around the concept of CNHCs and compared these against the production and distribution of hydrogen for consumption in the transportation sector. We find that CNHCs may be a cost-effective way to introduce hydrogen into the transportation infrastructure in a gradual manner. The continued use of liquid hydrocarbon fuels will minimize the disruptions and delays caused by requiring a different transportation infrastructure. It is far from evident, however, that any of these solutions, including electric vehicles, will be the method of choice. The lack of a clear technological ‘winner’ warrants equal attention and funding on all potential solutions.

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