

Carbon negative oil: A pathway for CO₂ emission reduction goals

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ABSTRACT

There is a carbon sequestration benefit to the ethanol manufacturing process if the CO₂ that is created in the fermentation process in an ethanol plant is geologically stored by an enhanced oil recovery (EOR) project. In order to recover one barrel of oil using CO₂-EOR, an equal or greater amount of CO₂ must be sequestered in order to recover the oil (~1.0–2.5 tonnes of CO₂ are stored for each tonne of CO₂ emissions resulting from combustion of the recovered oil). The oil produced from a CO₂-EOR sequestration project is therefore either carbon neutral or carbon negative if the CO₂ is sourced from the fermentation emissions from an ethanol plant. The 40.3 million metric tonnes of CO₂ fermentation emissions vented during the production of 53.4 million liters of ethanol per year in the U.S. could result in production of 40–100 million barrels of carbon negative oil annually. A carbon value chain (CVC) based on carbon credits could incentivize the construction of a CCS infrastructure in the United States that begins with the capture of corn ethanol CO₂ fermentation emissions. Utilization of biofuel fermentation emissions worldwide in bio-CO₂-EOR sequestration projects would help achieve global CO₂ emission reduction goals.

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1. Introduction

Atmospheric concentrations of carbon dioxide (CO₂) are higher than they have been for at least 800,000 years (NRC, 2010), driven by anthropogenic emissions related to expanding industrial activity and population growth. Mitigation is necessary to avoid severe, widespread, and irreversible impacts from climate change (IPCC, 2014). Mitigation pathways that can avoid detrimental climate change require substantial emissions reductions over the next few decades and near-zero emissions by the end of the century (IPCC, 2013). Transportation fuels comprise about 28% of manmade CO₂ emissions in the United States and about 13% of global emissions (EPA, 2014). Strategies to reduce CO₂ emissions from transportation fuels include the adoption of biofuels (ethanol, biodiesel) and other alternatives to liquid fossil fuels such as hydrogen, compressed natural gas (CNG), and electric vehicles (Farrell and Sperling, 2007a). The benefit of electric vehicles as a carbon mitigation measure depends on the reduction of the CO₂ emissions from power plants by the adoption of renewable energy sources such as wind power and solar power and the sequestration of CO₂

emissions from fossil-fuel power plants (Pacala and Socolow, 2004). Carbon sequestration is one of the most promising technologies that can be employed to dramatically reduce anthropogenic greenhouse gas emissions.

Carbon capture and storage (CCS) is the process of capturing CO₂ from stationary sources such as power plants, refineries, and other industrial sources, and storing these emissions in subsurface reservoirs where they can no longer contribute to global warming (Metz et al., 2005). The subsurface reservoirs that have been most extensively evaluated for CCS are depleted oil fields and deep saline reservoirs (Bachu et al., 2007). Saline reservoirs have a large capacity for CO₂ storage, and are commonly present beneath large CO₂ emission sources, such as coal-fired power plants near urban areas (NETL, 2010). The CO₂ storage potential of oil reservoirs is smaller than for saline reservoirs, and oil basins tend to be located far from urban areas where most of the anthropogenic CO₂ sources are concentrated (Folger, 2013a). The only CCS project under development in the United States involving sequestration of CO₂ from a coal-fired power plant into a saline reservoir is FutureGen 2.0 in Illinois (Folger, 2013b). The FutureGen 2.0 project was awarded US\$1.0 billion in funding by the US Department of Energy out of a total estimated project cost of US\$1.65 billion, with industrial partners expecting to contribute the other US\$650 million (DOE, 2014). In early 2015 the DOE withdrew its financial support after spending US\$202 million on the project, because of the cost of

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capturing CO₂ emissions from a coal-fired power plant and sequestering the CO₂ emissions in a saline reservoir proved to be much higher than originally anticipated (Martin, 2015; Mooney, 2015). There is a low likelihood that this “clean-coal” CCS technology can successfully be implemented in the near future without the benefit of oil production from the storage reservoir to economically assist the sequestration activity (Melzer, 2012). In anticipation of this outcome, the United States has started to develop a framework for CCS policy that involves the cooperation of the oil and gas industry (Pollak et al., 2011).

Carbon dioxide enhanced oil recovery (CO₂-EOR) is the most established and economical CCS method, since it has been employed to produce oil in West Texas for over 40 years. Carbon dioxide is used in the oil industry for tertiary recovery of oil, after the primary production and secondary water-flood recovery process is completed. In this enhanced oil recovery (EOR) process, CO₂ is compressed into a supercritical fluid and injected into depleted oil fields, where the CO₂ mixes into the oil and remobilizes the residual oil remaining in the ground. Once it is mixed with the oil above the minimum miscible pressure (MMP), the CO₂ increases the volume of the oil and lowers the viscosity of the oil, increasing the amount of recoverable oil in the reservoir (USDOE, 2013). In a typical project, the CO₂-EOR process is able to recover 10–20% of the original oil in place (OOIP); CO₂-EOR is therefore a means of recovering otherwise unobtainable oil from mature oil fields (ARI, 2006). If the reservoir pressure is below the MMP of the oil, then the CO₂ remains as a separate phase, resulting in an immiscible CO₂ recovery process. Although an immiscible CO₂-EOR project is capable of recovering incremental oil from the reservoir, the process is not as efficient as in a miscible CO₂-EOR project. In a CO₂-EOR project, the CO₂ is separated from the produced oil when it comes to the surface. The recovered CO₂ is then compressed and re-injected. The CO₂ is recycled multiple times through the reservoir to recover more oil. A small portion of the CO₂ is lost during the production operations as fugitive emissions, but about 95% of the CO₂ remains permanently sequestered in the subsurface reservoir (Marriot, 2013).

CO₂-EOR was responsible for 6% of the oil produced in the United States in 2012 (EIA, 2014). About 20% of the 62 million metric tonnes of CO₂ supplied to EOR operations in 2012 were from industrial sources (Kuuskraa et al., 2013). The source of CO₂ for EOR is otherwise from natural sources of CO₂ recovered from subsurface reservoirs. This fossil CO₂ is extracted with wells and piped to oil fields. The production of oil makes CO₂-EOR more economical than storing CO₂ in saline aquifers, which generates no profits in the absence of any carbon credits or tax allowances (Hill et al., 2013). The CO₂ utilized in an EOR project is a valuable commodity that is in high demand by the oil industry. Obtaining a pure CO₂ stream for EOR is expensive and a CO₂-EOR project operator carefully manages the purchased CO₂. As a result, the captured CO₂ is rarely if ever vented during commercial CO₂ floods, and is instead recycled through the reservoir to preserve the value of the commodity where it can generate a profit in the subsurface oil reservoir. An additional benefit of CO₂-EOR is that oil and gas reservoirs are better known than saline aquifers, making storage capacity estimations more accurate (Bachu et al., 2007). CO₂-EOR has been performed successfully in the Permian basin of West Texas and eastern New Mexico, in the mid-continent basins in Kansas, Oklahoma and the Panhandle of Texas, in the Gulf Coast states of Mississippi and Louisiana, and in the Rocky Mountain basins in Wyoming, Colorado, Utah, and Montana (Murrell & DiPietro, 2013).

Corn is a major agricultural product of the United States. One of the main uses of corn is to produce ethanol for fuel. The carbon in corn is derived from carbon dioxide (CO₂) in the atmosphere via photosynthesis. Corn cultivation therefore functions as a carbon sink and is a possible pathway for reducing atmospheric carbon dioxide concentrations (Xu et al., 2010). Corn ethanol manufacturing in the United States was developed to provide an oxygenating additive for gasoline to reduce nitrous oxide emissions from automobiles, as well as to reduce CO₂ emissions from transportation fuels. The corn ethanol manufacturing process produces large amounts of biogenic CO₂ fermentation emissions, as will be shown in this paper. Capturing the CO₂ resulting from the bio-

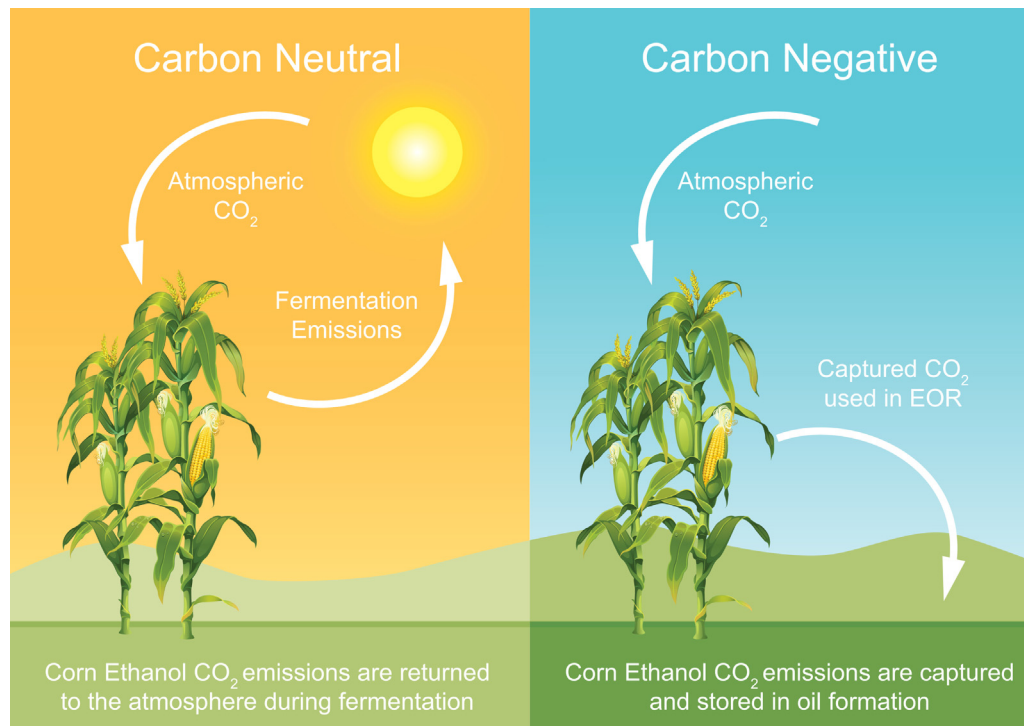


Fig. 1. Pathways for carbon from photosynthesis in corn cultivation through the corn ethanol manufacturing process to either carbon-neutral emissions of the CO₂ to the atmosphere (left) or carbon-negative CO₂ sequestration via enhanced oil recovery (right). From: Hornafius (2014).

Table 1
Net carbon sequestration calculation.

| | Beaver Creek | Salt Creek | Units of measure |
|--|--------------|------------|------------------------|
| CO ₂ e from burning a barrel of oil (Υ) | 0.43 | 0.43 | tCO ₂ e/bbl |
| CO ₂ utilization efficiency (ε) | 8.3 | 20.8 | Mscf /bbl |
| Volume to mass conversion (x) | 19.25 | 19.25 | Mscf/tCO ₂ |
| CO ₂ -EOR oil recovery efficiency (ε/x) | 0.43 | 1.08 | tCO ₂ /bbl |
| CO ₂ sequestration coefficient (S) | 1.0 | 2.5 | Sequestration Ratio |

The value of Υ is from the EPA (2014), ε was calculated from the Wyoming Oil and Gas Conservation Commission database (WOGCC, 2014), tCO₂ is metric tonnes of CO₂, Mscf is thousands of cubic feet at standard conditions, bbl is barrels of oil. From Eq. (4): this paper.

fuel fermentation process has been recognized as a way to achieve sustained net removal of CO₂ from the atmosphere (Lindfeldt and Westermarck, 2009; Xu et al., 2010; Laude et al., 2011; Koornneef et al., 2012). In most ethanol-manufacturing facilities, the CO₂ fermentations are vented to the atmosphere, resulting in a carbon neutral pathway for the carbon that is captured by the corn via photosynthesis in the corn cultivation process. If the CO₂ fermentation emissions are instead captured and stored in a CO₂-EOR project, then the CO₂ is permanently sequestered, resulting in a carbon negative CO₂ pathway (Fig. 1).

Carbon credit systems that mandate CO₂ emissions reductions provide a means to implement structural changes in energy consumption that enable market forces to find the lowest-cost method of achieving the desired result. California has pioneered this approach by enacting a low carbon fuel standard (LCFS), which mandates a 10% reduction in the carbon intensity (CI) of California's transportation fuels by the year 2020. The LCFS was designed to be performance based, allowing the market to determine how the carbon intensity of California's transportation fuels will be reduced (Yeh and Witcover, 2014). Other state and local governments have started to implement a low carbon fuel standard patterned after the California model, including Oregon, Washington, and British Columbia (British Columbia Laws, 2015; Oregon Clean Fuels Program, 2013; Pont et al., 2014).

This paper analyzes the carbon pathway in a CO₂-EOR process that utilizes CO₂ fermentation emissions captured from corn ethanol manufacturing (bio-CO₂-EOR). The paper begins by following the pathway of the carbon in corn through the corn ethanol manufacturing process. The carbon sequestration ratio for the bio-CO₂-EOR process is then analyzed, and the carbon intensity of the oil produced utilizing corn ethanol CO₂ is estimated. A life cycle analysis (LCA) of the gasoline resulting from the production and refining of bio-CO₂-EOR oil is then evaluated from the fermentation vent stack of an ethanol plant to the tailpipe of a petroleum-powered car. This paper concludes that implementation of bio-CO₂-EOR projects using corn ethanol fermentation emissions could play a significant role in reducing the carbon emissions from transportation fuels in the United States, and could finance the infrastructure for future CCS projects. Successful implementation of this technology on a large scale in the United States would provide a model for other nations to follow, as long as they

have oil fields, biofuel production and a favorable regulatory environment.

2. Methods

2.1. The carbon pathway of corn through the ethanol manufacturing process

There are two processes for producing ethanol from corn – wet milling and dry milling. Corn ethanol is produced in the dry mill process by first milling the corn kernels into flour know as meal. Water is then added to the corn meal to make a mash, and the starch in the mash is broken down to glucose by adding enzymes and treating at high temperatures. The mash is then transferred to a fermenter where yeast is added to the wet mixture and the glucose is converted to ethanol and CO₂. The wet mill process produces less ethanol (2.5 gallons of ethanol per bushel of corn versus 2.8 gallons per bushel in the dry mill process; Bothast and Schlicher, 2005), but enables other valuable food co-products to be produced. Over 80% of the ethanol manufactured in the United States is produced by the dry mill method. This paper focuses on the dry mill process.

The dry mill corn ethanol manufacturing process has three main outputs with the following carbon pathways:

- Ethanol: C₂H₅OH is used as a fuel and blended with gasoline. All of the carbon in ethanol is converted to CO₂ and H₂O in internal combustion engines and is returned to the atmosphere as vehicle exhaust.
- Carbon Dioxide: CO₂ from the fermentation of glucose in an ethanol plant is either vented to the atmosphere, captured for use in food processing (dry ice, carbonated beverages) or is geologically sequestered in CO₂-EOR projects (Xu et al., 2010). Only the CO₂-EOR pathway does not return the carbon to the atmosphere.
- DGS: Distillers grains and solubles are sold as livestock feed, either as WDGS (wet) or DDGS (dried). The carbon in DGS has a complex pathway through the farm, food and waste industry, but for the most part is ultimately returned to the atmosphere by respiration or decomposition as either carbon dioxide or methane. A small portion is sequestered in soils or in waste disposal facilities.

Table 2
Calculated CO₂ fermentation emissions from Kansas corn ethanol plants.

| Plant name | Ethanol capacity (millions gallons per year) | Ethanol production (thousands metric tonnes per year) | Calculated CO ₂ fermentation emissions from Eq. (1) (tCO ₂ e) | Reported non-biogenic emissions (tCO ₂ e) |
|-------------------------------|--|---|---|--|
| Arkalon Energy (Conestoga) | 110 | 328 | 313,830 | 111,086 |
| Bonanza Bioenergy (Conestoga) | 55 | 168 | 156,915 | 54,554 |
| East Kansas Agri Energy | 35 | 104 | 99,855 | 33,255 |
| Kansas Ethanol LLC | 55 | 168 | 156,915 | 55,442 |
| Prairie Horizon Agri Energy | 40 | 119 | 114,120 | 50,544 |
| Western Plains Energy, LLC | 45 | 134 | 128,385 | 45,017 |
| White Energy-Russell | 48 | 143 | 136,944 | 56,436 |

Ethanol production capacity reported by the Kansas Corn Growers Association (2014). The non-biogenic emissions are reported by the EPA (2014). tCO₂e is metric tonnes of CO₂ equivalent GHG emissions.

Table 3
Calculated CO₂ fermentation emissions from top ten ethanol producing states and U.S. total.

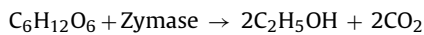
| State | Ethanol capacity (millions gallons per year) | Ethanol capacity (millions liters per year) | Calculated CO ₂ fermentation emissions from Eq. (1) (thousand tCO ₂ per year) | Calculated CO ₂ fermentation emissions from Eq. (1) (mmscfd) |
|---------------------|--|---|---|---|
| Iowa | 3,625 | 13,722 | 10,342 | 547 |
| Nebraska | 1,973 | 7,469 | 5,629 | 298 |
| Illinois | 1,486 | 5,625 | 4,240 | 224 |
| Minnesota | 1,129 | 4,274 | 3,221 | 170 |
| Indiana | 1,147 | 4,342 | 3,272 | 173 |
| South Dakota | 1,009 | 3,819 | 2,879 | 152 |
| Wisconsin | 504 | 1,908 | 1,438 | 76 |
| Ohio | 478 | 1,809 | 1,364 | 72 |
| Kansas | 411 | 1,556 | 1,173 | 62 |
| North Dakota | 393 | 1,488 | 1,121 | 59 |
| United States Total | 14,114 | 53,427 | 40,268 | 2,129 |

Ethanol production capacity reported by the Renewable Fuels Association (2012). tCO₂ is metric tonnes of CO₂. mmscfd is million of standard cubic feet per day.

An analysis of the carbon pathway through the dry mill ethanol manufacturing process shows that 22.7% of the elemental carbon in corn is release as CO₂ emissions, 45.4% is converted into ethanol, and the remaining 31.9% ends up as DGS, distillers corn oil, and other minor products (Hornafius, 2014). This paper analyzes the carbon pathway from the fermentation CO₂ vent stack at an ethanol plant through the CO₂-EOR process and the ultimate combustion of the produced oil. The carbon emissions associated with the ethanol manufacturing process and the resulting carbon intensity of the produced ethanol are not analyzed in this paper, since this topic is thoroughly investigated by other authors (Hsu et al., 2010; Wang et al., 2012; Unnasch et al., 2014).

2.2. Calculation of ethanol fermentation emissions

The conversion of glucose to ethanol and CO₂ occurs via the reaction:



The ethanol manufacturing process partitions the carbon in the glucose into ethanol and CO₂, with the atomic mass ratio for the carbon in these two end products being 2.0 (i.e., 2 g of elemental carbon in ethanol for each gram of carbon in a molecule of carbon dioxide). The molecular mass of ethanol is 46.07 and the molecular mass of carbon dioxide is 44.01, so 0.9553 kg of CO₂ fermentation emissions are created for each kilogram of ethanol produced. The quantity of CO₂ fermentation emissions (in units of mass, M_{CO_2}) can be calculated from the volume of ethanol produced (V_{ethanol}) using the equation:

$$M_{CO_2} = 0.9553 \times \rho_{\text{ethanol}} \times V_{\text{ethanol}} \quad (1)$$

The density of ethanol is 0.7890 kg/l, so 0.7537 kg of CO₂ are produced for each liter of ethanol. The output from a corn ethanol plant in the United States is reported in millions of gallons per year (1 gallon = 3.7854 liters), which is abbreviated MGY (e.g.,

Tables 2–4). The CO₂ output for commercial purposes in the US is therefore 2853 metric tonnes of CO₂ per million gallons of ethanol produced. In SI units the CO₂ output can be expressed as 753.7 metric tonnes of CO₂ per million liters of ethanol produced, or as 955.3 metric tonnes of CO₂ per thousand metric tonnes of ethanol produced (Tables 2–4).

2.3. CO₂ utilization efficiency (ϵ) in EOR

The measure of the efficiency (ϵ) of a CO₂-EOR project is the CO₂ utilization ratio:

$$\epsilon = \frac{V}{N} \quad (2)$$

where V is the volume of gaseous CO₂ injected into the reservoir and N is the quantity of oil recovered. Gas volumes are measured in the U.S. oil industry in thousands of standard cubic feet (1 Mscf = 28.3 m³) and N is measured in barrels (1 bbl = 42 US gallons = 159 l). In an EOR project, this ratio can refer to either the purchased CO₂ or the purchased plus recycled CO₂ that is injected. In this paper, only the CO₂ that is purchased from an ethanol plant is considered, because that is the quantity of CO₂ that is being sequestered.

The CO₂ utilization efficiency depends on the geological setting of the oil reservoir and the operational conditions of the EOR project. There are large regional variations in ϵ that are related to the ability of the surrounding layers to contain the CO₂ in the oil reservoir and how much of the CO₂ is lost to the saline reservoirs adjacent to the oil reservoir. The coefficient ϵ had an average value of 26 Mscf/bbl (4806 m³ CO₂/m³ oil) in CO₂-EOR projects in Mississippi and Louisiana in 2013 and had a long-term average value of 8.8 Mscf/bbl (1566 m³ CO₂/m³ oil) for CO₂-EOR projects in Wyoming and 9.2 Mscf/bbl (1638 m³ CO₂/m³ oil) for CO₂-EOR projects in West Texas (Murrell and DiPietro, 2013). These regional differences are related to the geology of the oil reservoirs and the bounding stratigraphy, and the ratio of miscible to immiscible CO₂-

Table 4
World Fuel Ethanol Production and potential avoided atmospheric CO₂ emissions.

| Country/continent | Ethanol produced (millions gallons per year) | Calculated CO ₂ fermentation emissions from Eq. (1) (thousand tCO ₂ per year) |
|----------------------------|--|---|
| United States | 14,114 | 40,268 |
| Brazil ^a | 6,267 | 17,880 |
| Europe ^a | 1,371 | 3,912 |
| China ^a | 696 | 1,986 |
| India ^a | 545 | 1,555 |
| Canada ^a | 523 | 1,492 |
| Rest of World ^a | 727 | 2,074 |
| Total | 24,243 | 69,167 |

^a World fuel ethanol production values source: USDA-FAS from RFA website (2014). CO₂ emissions calculated from Eq. (1): this paper.

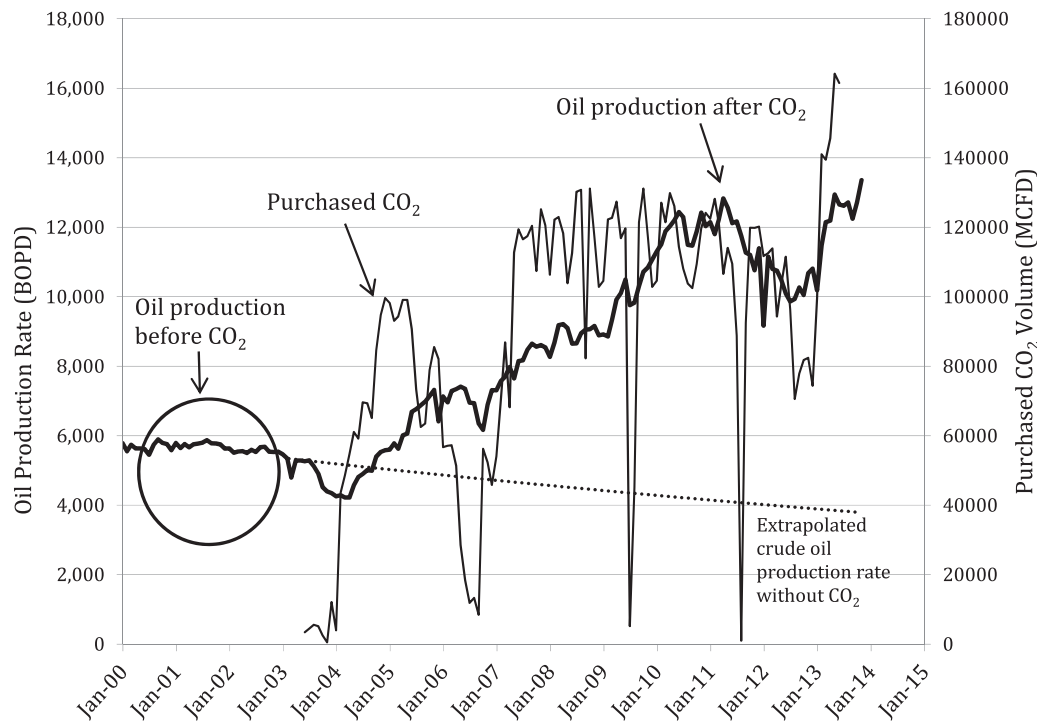


Fig. 2. Salt Creek oil field production response resulting from the injection of CO₂. The dotted line shows the extrapolated oil production decline curve without the injection of CO₂. The bold solid line is the actual oil production rate (in barrels of oil per day, BOPD). The incremental oil resulting from CO₂ injection is the difference between the extrapolated oil production rate and the actual oil production rate. Data from WOGCC (2014).

EOR projects in each geological basin. Individual projects within these basins display a range around these mean values, depending upon the geological circumstances that pertain to each reservoir.

The increase in oil production resulting from the CO₂ sequestration starts several months after the initiation of CO₂ injection. In order to calculate the incremental oil produced by the injected CO₂, the oil that would have been produced from the oil field without CO₂ injection needs to be subtracted from the total oil production after the start of the CO₂ flood. An example of the projected oil decline for a Wyoming oil field is shown in Fig. 2. The incremental oil that is produced is a function of both the amount of purchased

CO₂ that is injected into the oil reservoir and the amount of recycled CO₂ that comes back to the surface with the produced oil and is then recompressed and injected back into the oil reservoir. In the example from the Salt Creek oil field in Fig. 2, there is a correlation between purchased CO₂ injection volumes and the oil production rate. In the Beaver Creek oil field example in Fig. 3, there is a strong correlation between recycled CO₂ injection rates and oil production rates. In both cases, no CO₂ is being vented after it has been injected in the oil reservoir.

During the history of an EOR project, the CO₂ utilization ratio changes over time. For the first couple years a large amount of CO₂

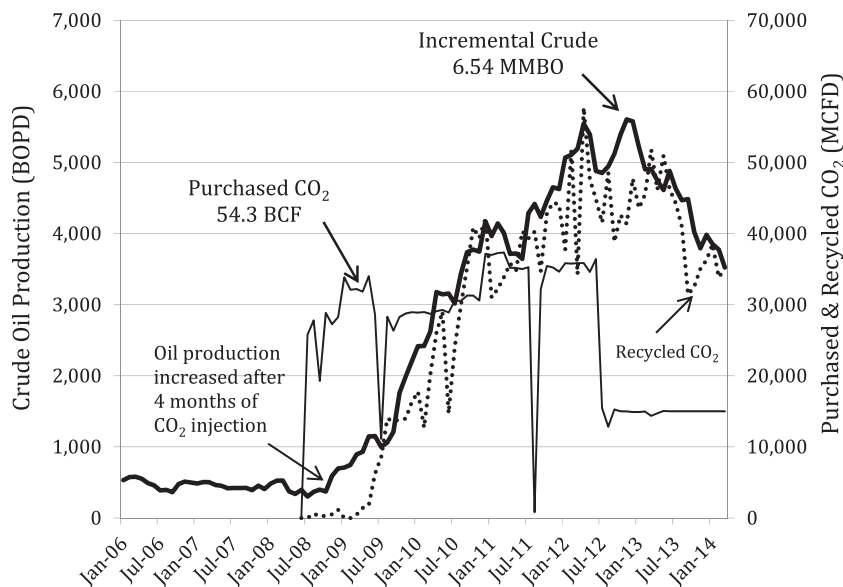


Fig. 3. Beaver Creek oil field production response resulting from the injection of CO₂. The bold solid line shows the oil production response from the injection of CO₂. Data from WOGCC (2014).

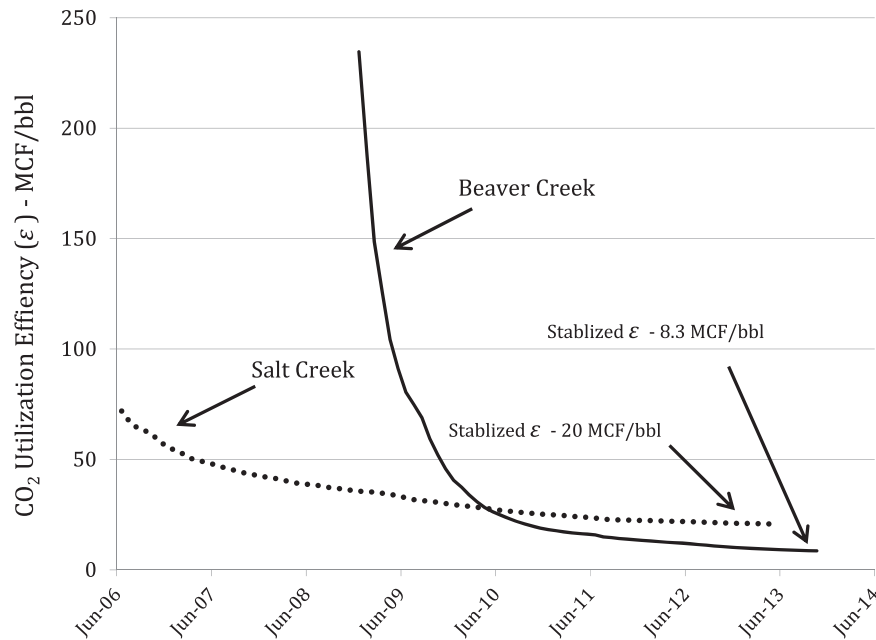


Fig. 4. Examples of the change in the cumulative CO₂ utilization efficiency (ϵ) for CO₂-EOR projects over time. The CO₂ utilization efficiency approaches an asymptotic limit towards the end of the project that is determined by the reservoir properties. Units are in thousands of cubic feet (MCF) per barrel of oil (bbl). Both of these oil fields are in Wyoming.

is injected into the subsurface reservoir with little recovery of oil. During this early period in a CO₂ flood the value of ϵ is very high (>50; see Fig. 4). During this period the CO₂ is mixing with the oil, but has not yet mobilized the oil so that it can flow to the producing wells. After a sufficient amount of CO₂ has been mixed in the oil, the oil production rate starts increasing and eventually a stabilized CO₂ utilization ratio can be established for the oil field. This stabilized value of ϵ is only established late in the life of a CO₂-EOR project, and cannot be accurately forecast before the project is initiated.

2.4. Net CO₂ sequestration ratio (S) for bio-CO₂-EOR

The ratio of the amount of CO₂ that is sequestered in a bio-CO₂-EOR project versus the amount of CO₂ created by combustion of the oil is expressed by

$$S = \frac{B}{\Upsilon} \quad (3)$$

where S is the net CO₂ sequestration ratio (a dimensionless number), B is the mass of biogenic CO₂ sequestered by the CO₂-EOR project (in metric tonnes) per volume of oil produced, and Υ is mass of CO₂ emitted by burning the oil (~0.43 metric tonnes CO₂ per barrel for a high-quality oil; EPA, 2012). The value of Υ must be empirically determined for each oil. If the value of S is 1.0, then the oil produced is carbon neutral. Oil with an S value over 1.0 is carbon negative, since more biogenic CO₂ is sequestered in recovering the oil than is emitted by burning the oil. Oil produced by primary production or oil produced in a CO₂-EOR project that uses fossil CO₂ would by definition have an S value of zero, since no atmospheric CO₂ is being sequestered in the process.

The value of B can be expressed in oil field units, in which case

$$S = \frac{\epsilon/x}{\Upsilon} \quad (4)$$

where ϵ is the CO₂ utilization ratio and x is the conversion ratio for CO₂ from volume to mass (545 m³/tonne or 19.253 Mscf/tonne at 70 °F and 1 atm). For biogenic CO₂, such as from an ethanol plant, S will be greater than 1.0 and the EOR process carbon negative for any

values of epsilon (ϵ) greater than 8.3 Mscf/bbl (1478 m³ CO₂/m³ oil) (see the example calculations in Table 1).

2.5. Carbon negative oil and carbon credit systems

The added value that a unit volume of low-carbon-intensity bio-CO₂-EOR oil would attract from a credit market can be expressed by

$$\text{Creditvalue} = S \times \Upsilon \times \text{Creditprice} \quad (5)$$

For example, if the carbon-credit price is \$10 per tonne of CO₂ and the oil has a value for Υ of 0.43 metric tonnes of CO₂ per barrel, then the credit value that would be assigned to a barrel of carbon neutral oil ($S = 1.0$) would be \$4.30 per barrel.

2.6. Assigning a carbon intensity (CI) to bio-CO₂-EOR gasoline

Carbon intensity (CI) is the GHG emissions associated with the production, transportation, refining, distribution, and consumption of a transportation fuel measured in grams CO₂e per megajoule (g CO₂e/MJ) (Yeh et al., 2009; Wang et al., 2012). Argonne National Laboratory has produced a model that calculates the energy consumption and emissions associated with a fuel production pathway, known as the GREET model (Argonne, 2012), also called a wells-to-wheels (WTW) analysis. The California Air Resources Board (CARB) has modified this model in order to assign a CI to the petroleum and ethanol that is used as feedstock for the liquid transportation fuels in the state (CA-GREET), as well as other alternative fuels like hydrogen and biodiesel (CARB, 2013a). Ethanol is the main generator of carbon credits for this program, but an innovative oil production methods pathway has also been established that recognizes reductions in the carbon intensity of petroleum fuels that are achieved by better production methods. Two technologies under consideration as innovative oil production methods are solar steam thermal enhanced oil recovery (TEOR) and carbon dioxide enhanced oil recovery (Brandt and Unnasch, 2010). This carbon credit system financially incentivizes the production

of fuels that have low-CI values, with the goal of promoting the development of low-carbon-intensity technologies.

The carbon intensity of gasoline is calculated by summing the components of the production, transportation, refining and combustion processes using the following equation:

$$CI_{\text{total}} = CI_{\text{vehicle}} + CI_{\text{production}} + CI_{\text{transportation}} + CI_{\text{refining}} \quad (6)$$

The CO₂e emissions resulting from the combustion of gasoline (CI_{vehicle}) is 74 g per megajoule (MJ) of energy produced (74 g CO₂e/MJ). The CO₂e emissions resulting from the energy consumed in recovering the oil ($CI_{\text{production}}$) is in the range of 3–26 g CO₂e/MJ for crude oils currently refined in California (CARB, 2012, 2015). The additional CO₂e emissions resulting from the energy required to transport the oil to California refineries ($CI_{\text{transportation}}$) is less than 2 g CO₂e/MJ and the emissions resulting from refining gasoline (CI_{refining}) is estimated to be 10 to 12 g CO₂e/MJ. The total carbon intensity of the gasoline consumed in California is therefore in the range of 89–114 g CO₂e/MJ, depending upon the source of the crude oil (CARB, 2012). The resulting average reformulated gasoline in California (CARBOB) has a CI of 99.2–100.5 g CO₂e/MJ, depending upon the average crude oil supplied to California refineries and average California refinery efficiencies in each year (CARB, 2012, 2013b, 2014).

There is currently not a fuel pathway for CO₂-EOR projects approved by the California Air Resources Board, but a rule making process has started, and a pathway should be completed by 2017. Each project will have a different carbon intensity rating, due to the variable amounts of energy required to compress, dehydrate, transport and recycle the CO₂ in each oil reservoir and the different energy requirements to process the oil and transport it to a refinery. The National Energy Technology Laboratory has estimated the carbon intensity for the $CI_{\text{production}}$ term in Eq. (6) for CO₂-EOR projects in West Texas that use fossil CO₂ sources to be 19.3 g CO₂e/MJ (NETL, 2013). Once the other terms in Eq. (6) are added, the CI_{total} for gasoline produced from most of the CO₂-EOR projects in West Texas is estimated to be 102.1 g CO₂e/MJ (Marriot, 2013). This is about 2% higher than the estimate for the CI of the average gasoline consumed in California, because the energy requirement to recover the crude oil is slightly higher than the average of other crude oils refined in California.

The carbon intensity of gasoline refined from a CO₂-EOR project that uses biofuel fermentation emissions can be expressed by

$$CI_{\text{total}} = 74 \text{ g CO}_2\text{e/MJ} + CI_{\text{production}} + CI_{\text{transportation}} + CI_{\text{refining}} - S \times 74 \text{ g CO}_2\text{e/MJ} \quad (7)$$

Gasoline produced from carbon negative oil could have a positive CI if the term $S \times 74 \text{ g CO}_2\text{e/MJ}$ is less than the sum of the other terms on the right-hand side of this equation. If the term $S \times 74 \text{ g CO}_2\text{e/MJ}$ is greater than the sum of the other terms on the right-hand side of this equation, then the CI of the gasoline is negative. In this case ($CI < 0$), there is carbon dioxide being withdrawn from the atmosphere as the gasoline is being consumed, on a total life-cycle analysis (LCA). This provides a mechanism for decarbonizing the atmosphere, if the technology is employed on a large enough scale.

3. Results

3.1. Emissions from Kansas corn ethanol plants

The Kansas Corn Growers Association reports the volume capacity of ethanol plants in Kansas (KCGA, 2014). The CO₂ fermentation emissions from some of these facilities were calculated using Eq. (1). These CO₂ fermentation emissions are compared in Table 2 with the EPA reported non-biogenic emissions from these facilities. The

non-biogenic emissions are due primarily to natural gas consumed by these facilities during the ethanol manufacturing process and drying the DDGS. The unreported CO₂ fermentation emissions are two to three times as large as the non-biogenic emissions reported to the EPA. There is no requirement to report the CO₂ fermentation emissions because they are biogenic in origin, and therefore carbon neutral (see Fig. 1). Nevertheless, these CO₂ fermentation emissions represent a significant opportunity for carbon capture and storage, because these biogenic emissions are nearly pure (>98% CO₂) and are therefore readily captured at comparatively low cost. The high purity of CO₂ fermentation emissions eliminates one of the major barriers for CCS deployment, which is the cost of cleaning up diluted CO₂ streams from other anthropogenic sources (Bachu, 2008).

3.2. Potential carbon sequestration from ethanol fermentation emissions in the United States

The ethanol industry in the United States produced 53.4 billion liters in 2012 (RFA, 2012). This amount of ethanol production resulted in 40.3 million metric tonnes of biogenic CO₂ emissions (Table 3). This is equivalent to 2.2% of CO₂ emissions by the transportation sector in the United States, which emitted 1830 million metric tonnes of CO₂ in 2012 (EPA, 2014). Other ethanol feedstocks are under development that could further expand the available CO₂ fermentation emissions available for capture, including switch grass, corn stover, wheat straw, and forest residue (Hsu et al., 2010). The Energy Independence and Security Act of 2007 mandated that approximately 136 billion liters per year (bLy) of ethanol be produced by 2022. This is equivalent to a CO₂ fermentation emissions rate of 102.5 million metric tonnes per year. An expanding ethanol industry could capture an amount of CO₂ fermentation emissions equivalent to as much as 10% of the amount of CO₂ emitted by the transportation sector in the United States by 2050, if CO₂ fermentation emissions were captured and stored by EOR projects.

3.3. Potential oil production from corn ethanol fermentation emissions in the United States

The large amount of oil that has been produced in the United States has created a substantial amount of pressure-depleted subsurface volume (voidage) that can be used for CO₂ sequestration. The potential of these sites for CO₂ storage are estimated to be 138 billion metric tonnes (NETL, 2010). There are 84 billion barrels of technically recoverable oil and 45 billion barrels of economically recoverable oil using CO₂-EOR, based on current oil and CO₂ prices (Ferguson et al., 2009). These oil reservoirs represent a large potential CCS target for utilizing CO₂-EOR technology.

The amount of oil that can be produced with corn ethanol fermentation emissions is dependent upon the CO₂ utilization efficiency (ϵ). If all of the existing corn ethanol CO₂ emissions were transported to regions with values of ϵ of 20 Mscf/barrel, like Louisiana and Mississippi, where CO₂-EOR projects have a low efficiency, then the 40 million metric tonnes of CO₂ fermentation emission produced annually would result in production of almost 40 million barrels of carbon negative oil per year ($S=2.5$). If the fermentation emissions are utilized in areas that have a value of ϵ of 8.3 Mscf/barrel, resulting in carbon neutral oil ($S=1.0$), then as much as an incremental 100 million barrels of oil per year could be produced. The United States produced 2.4 billion barrels of oil in 2012 (EIA, 2014), so this incremental oil production would increase oil production by 1.6% to 4.0% if all current US fermentation emissions were utilized.

A total of 16 million metric tonnes of CO₂ fermentation emissions are produced per year by ethanol plants in Nebraska and Iowa alone (Table 3). The closest oil producing state to these corn-belt states where CO₂-EOR is being widely implemented is Wyoming.

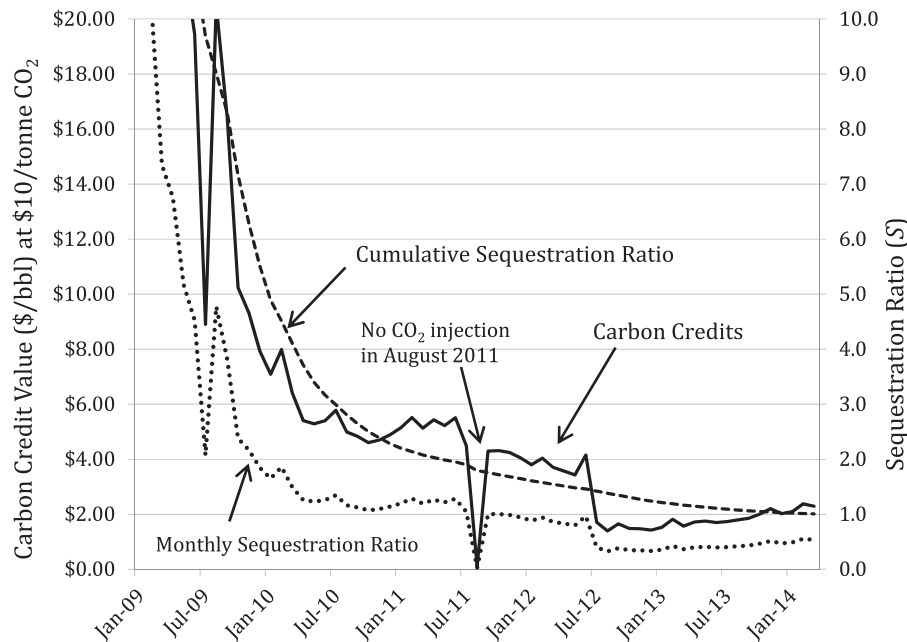


Fig. 5. Relationship between the sequestration ratio (S) in a hypothetical CO₂-EOR project that stores ethanol CO₂ fermentation emissions and the carbon credit price of the produced oil. The value of S was computed from the value of ϵ in the Beaver Creek CO₂-EOR project in Wyoming from Eq. (4), if it had been supplied by corn ethanol CO₂ emissions. The carbon credit value was calculated from Eq. (5) using the monthly value of S and assuming a carbon credit price of \$10 per tonne.

The future oil production potential from CO₂-EOR projects in Wyoming is estimated to be 1.2 to 1.8 billion barrels, which would require up to 20 trillion cubic feet of CO₂ (Wo et al., 2009). At current fermentation CO₂ production rates of 845 million cubic feet per day in Nebraska and Iowa, it would require 65 years to recover this volume of oil. In order to implement this CO₂ sequestration project, a one-thousand-mile (1600 km) CO₂ pipeline system would need to be constructed. The oil produced would be either carbon neutral or carbon negative, if the CO₂ was sourced exclusively from corn ethanol plants.

3.4. Worldwide ethanol production and CO₂ sequestration potential

The United States is the largest producer of ethanol in the world, followed by Brazil, Europe, and China (RFA, 2014). If bio-CO₂-EOR were to be implemented globally, the opportunity for CO₂ emission reductions would be further amplified. Table 4 shows the amount of CO₂ fermentation emissions resulting from global ethanol production today. The size of international sink capacity for EOR projects is 370 billion metric tonnes of CO₂ (Kuuskraa et al., 2013; Stevens et al., 2001). At current ethanol production rates, this represents over 5000 years of available storage capacity for CO₂ fermentation emissions. Clearly the implementation of bio-CO₂-EOR projects can only serve to build the initial CCS infrastructure that other technologies will utilize in the future once these other technologies have been commercialized.

4. Discussion

4.1. Corn ethanol fermentation CO₂ used for EOR: the Kansas example

There are two examples of corn ethanol fermentation CO₂ being used for EOR in the United States. Both of these ethanol plants are owned by Conestoga Energy Partners, LLC, and are located in southwestern Kansas (Table 1). The Arkalon ethanol plant redirects up to 313,830 metric tonnes of CO₂ per year to the Booker and

Farnsworth oil fields in Texas, which are operated by Chaparral Energy. The Bonanza ethanol plant sends up to 156,915 metric tonnes of CO₂ per year to the Stewart oil field near Garden City, Kansas, and is operated by PetroSantander, Inc. Both of the ethanol plants use a mixture of sorghum and corn as the feedstock.

At both the Bonanza and Arkalon facilities the CO₂ is piped at close to atmospheric pressure from the ethanol plant through a water knock-out facility and is then sent through a series of compression stages (utilizing a 3000 horsepower compressor at Bonanza) until the CO₂ can be shipped in a liquid form through a pipeline to the oil fields. There is a 15-mile long pipeline that sends the CO₂ to the Stewart oil field from the Bonanza plant, and a 90-mile pipeline sends the CO₂ captured at the Arkalon plant to the Booker and Farnsworth oil fields in Texas (Chaparral, 2013a). These are the only examples of bio-CO₂-EOR in the United States and should be examined more closely as a case study.

In the case of the Booker project, the forecast oil recovery is 1.1 million barrels from 11.5 billion cubic feet of CO₂ (Chaparral, 2013b), resulting in a cumulative CO₂ utilization efficiency (ϵ) of about 10.5 Mscf/barrel and a net sequestration ratio (S) of about 1.3, meaning 30% more CO₂ is injected into the subsurface reservoir than the amount of CO₂ that is released into the atmosphere when the produced oil is burned. The resulting oil is carbon negative.

4.2. Pipeline infrastructure required to capture and store corn ethanol fermentation emissions

One challenge that must be overcome in order for the U.S. to exploit bio-CO₂-EOR technology is to create a pipeline infrastructure to transport the CO₂ from the corn-growing regions to oil basins suitable for CO₂-EOR. Transportation of CO₂ by pipeline is considered a mature technology that already has proven safe and efficient in CO₂-EOR operations. Pipeline transport is a lower cost option than transportation by truck or rail (Bonijoly et al., 2009). Most U.S. ethanol plants are located in the Midwest, where there are no nearby oil fields available to flood with CO₂ (Fig. 6). A CO₂ gathering and transportation system will therefore need to be constructed to the adjoining states that do have hydrocarbon basins suitable for

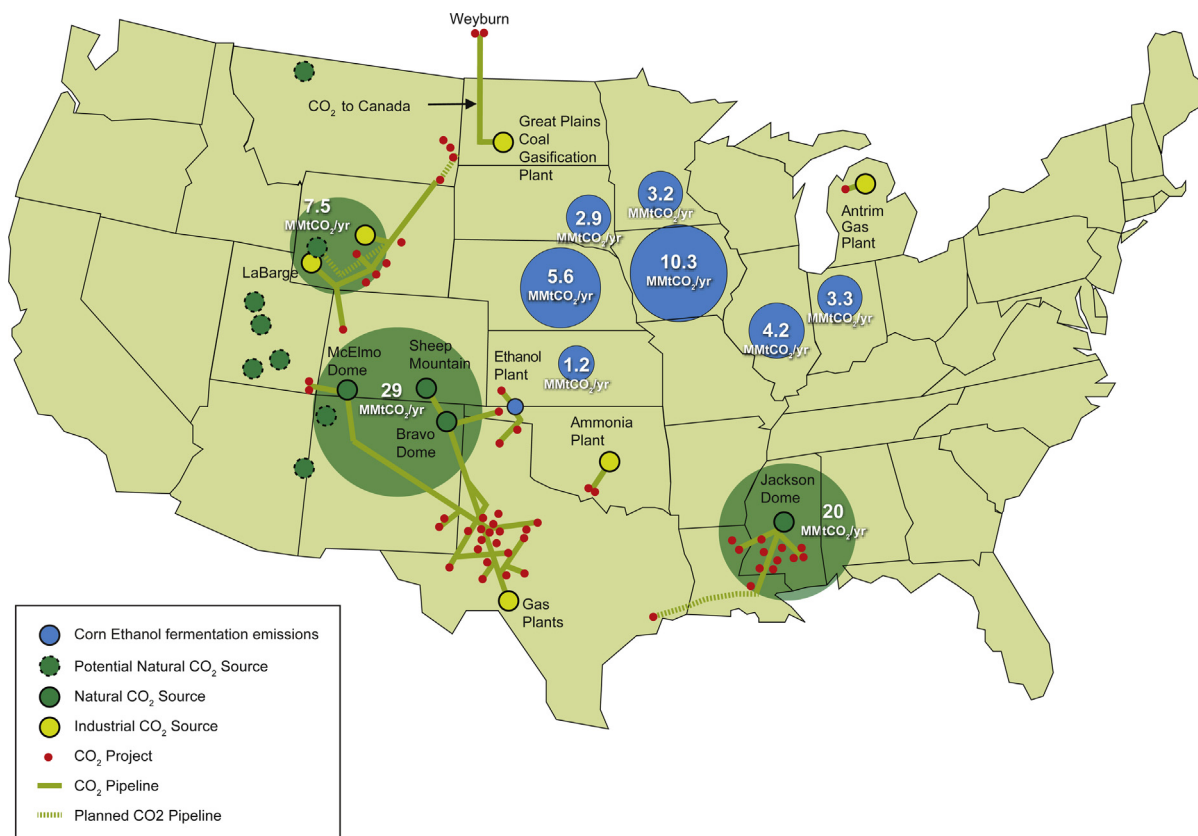


Fig. 6. Carbon dioxide emissions by state from corn ethanol fermentation emissions (blue) and natural sources of fossil CO₂ extracted from underground sources (green) in million metric tonnes per year. Fermentation emission totals are calculated from Eq. (1) (Table 3). Natural source totals are from Kuuskraa et al. (2013).

CO₂-EOR (Hill et al., 2013). Construction of this infrastructure will require a large amount of capital investment that needs to come from the private sector. Incentives to support these investments could come from Federal tax incentives, or from regional carbon reduction initiatives, such as the Low Carbon Fuel Standard that was enacted in California in 2007 (CARB, 2015; Yeh et al., 2009). This infrastructure could be financed with carbon credits generated by capturing CO₂ fermentation emissions from the corn ethanol plants in the Midwest. Once the infrastructure is built, it is available for utilization by other CCS projects, when these technologies have become commercially viable.

4.3. Comparison of CI values for transportation fuels

Wang et al. (2012), CARB (2013a, 2015) and Boland and Unnasch (2014) have estimated the carbon intensity (CI) of transportation fuels that can be commercialized in the United States. The benchmark for these studies is gasoline, which has an average CI in the United States of 94 to 100.5 g CO₂e/MJ after accounting for the GHG emissions resulting from the oil recovery process, transportation, refining, distribution and combustion. By comparison, corn ethanol has a CI rating of 73–121 g CO₂e/MJ when land use change (LUC) is included in the calculation (CARB, 2012; Unnasch et al., 2014). Sugarcane ethanol has a lower CI of 45–79 g CO₂e/MJ because the production process is more energy efficient (CARB, 2012; Hsu et al., 2010). The California Air Resources Board has assigned a CI to each of these fuels that is dependent upon the production methods, which results in a range of CI ratings that vary with the production pathway (e.g., wet mill versus dry mill for corn ethanol, coal versus natural gas for electric power, natural gas versus renewable feedstock for hydrogen, etc.). The widest range in CI estimates is for hydrogen vehicles (76–142 g CO₂e/MJ) depending upon the source

of the hydrogen (CARB, 2012). Electric and hybrid vehicles rely on electricity from the power grid and have different CI values across the United States depending upon the fuel sources used to generate the electricity (33–88 g CO₂e/MJ; Anair and Mahmassani, 2012; Yang, 2012).

The CI of gasoline made from bio-CO₂-EOR oil can be calculated from Eq. (7). The likely values for each of the terms in Eq. (7) for a bio-CO₂-EOR project are about 20 g CO₂e/MJ for the production term, 2 g CO₂e/MJ for the transportation term, and 12 g CO₂e/MJ for the refining term, which sums to 34 g CO₂e/MJ. If the net sequestration ratio (*S*) has a value of 1.3 in Eq. (7) (slightly carbon negative oil), the carbon intensity of the gasoline would be 12 g CO₂e/MJ (e.g., the Booker bio-CO₂-EOR project in Texas). This compares favorably with the CI of other technologies that are being advocated to reduce the carbon intensity of transportation fuels (Fig. 7). For oil that is moderately to extremely carbon negative (*S* = 1.5–2.0), the CI would be in the range of –3 to –40 g CO₂e/MJ. A carbon credit system that incentivizes bio-CO₂-EOR projects would allow this negative CI technology to be implemented.

4.4. Carbon credit allocation for bio-CO₂-EOR projects

The CI assigned to bio-CO₂-EOR gasoline in this paper is for the carbon pathway that starts at the fermentation CO₂ vent stack of the ethanol plant and ends at the tailpipe of a petroleum-powered automobile. The CI assigned to corn ethanol by the GREET model includes the emissions involved with the growing, harvesting, and transportation of the corn and production of the ethanol, as well as the distribution and combustion of the ethanol, but assumes that the fermentation CO₂ is vented to the atmosphere and is not captured and stored. The CI of ethanol is therefore independent of the CI of the bio-CO₂-EOR gasoline calculated in this paper, because the

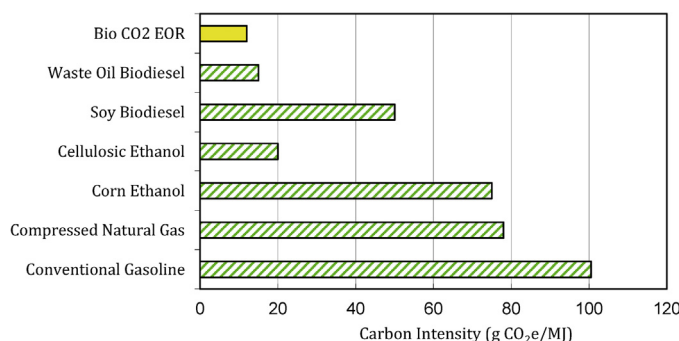


Fig. 7. Carbon intensity (CI) of transportation fuels that can be utilized on a large scale in the United States. The CI values are calculated on a wells-to-wheels basis, including feedstock recovery, refining, and fuel combustion, as determined by CARB (2014) and this paper. The value of 12 g CO₂e/MJ for bio-CO₂-EOR gasoline is for a bio-CO₂-EOR project with an S value of 1.3 (e.g., the Booker bio-CO₂-EOR project in Texas).

owner of the ethanol plant receives carbon credits for the ethanol under the assumption that the CO₂ is vented, rather than being captured and stored by a bio-CO₂-EOR project or a CCS project involving saline reservoirs.

For most liquid transportation fuels, the intrinsic carbon intensity of the fuel is constant through time. However, in a bio-CO₂-EOR project, the CO₂ utilization efficiency (ϵ) changes continuously throughout the life of the project (Fig. 4), so the value of the sequestration ratio (S) also changes over time. It is impossible to know the ultimate value for ϵ or for S in a CO₂-EOR project until the project is completed, so it would be difficult to establish a fixed carbon credit price for bio-CO₂-EOR oil over the life of the project. Instead, the carbon credit price would need to be established on a monthly or quarterly basis, from the value of S during that time period. An example of how the carbon credit value might change over the early life of a bio-CO₂-EOR project is shown in Fig. 5. Because the value of S is very high early in the project life, the credit value would also be high, but would decline rapidly as the project progresses. A way around this problem might be to assign the carbon credits to the ethanol producer, since the volume of CO₂ fermentation emissions is constant per unit volume of ethanol (Eq. (1)). A drawback of this approach is that the ethanol producer is not responsible for sequestering the carbon, and would have no obligation for maintaining the sequestered CO₂ in the oil reservoir after selling the credits. For this reason, the oil field operator is most likely to receive the carbon credits, in exchange for permanently retaining the CO₂ in the oil reservoir the after receiving the credits. Alternatively, the ethanol producer could receive the carbon credits and pay the oil producer for the service of sequestering the carbon, and include sequestration guarantees in the contract.

4.5. Environmental policy and industry involvement

The enactment of carbon markets in several regions across the United States has enabled the possibility of creating a carbon value chain (CVC) in which carbon credits incentivize the construction of the infrastructure required for the widespread implementation of CCS. California is leading the way in establishing a low-carbon-intensity fuels market. The California LCFS long-term goal is to reduce GHG emissions to 80% below the 1990 level by 2050 (Farrell and Sperling, 2007b). The program was created to incentivize new technologies like biodiesel and lower the carbon intensity of ethanol. In its first couple years of active trading the LCFS credit price rose dramatically due to uncertainty that the deployment of currently available technologies could reach the targets. If carbon negative oil (CNO) were recognized as a fuel that accomplishes these goals, the resulting credits would provide the necessary

financial incentives to build the pipeline infrastructure and conduct the CO₂ monitoring to ensure that the stored CO₂ remains sequestered. The idea of using CO₂-EOR to fund the necessary CCS infrastructure to reduce CO₂ emissions in the United States has been extensively studied (e.g., MGA, 2011), but little progress has been made because of a lack of financial incentives for CO₂-EOR operators in the oil producing states to switch to biogenic CO₂ over subsurface fossil CO₂ sources.

In a scenario where carbon credits are allocated to bio-CO₂-EOR oil to provide financial incentives for collaboration between the oil and ethanol industries to build the necessary CCS pipeline infrastructure, the risk and reward will have to be fairly distributed between these two industries. If the oil industry receives all the credits and pays the ethanol plant for its CO₂, the oil industry takes all the risk regarding the fluctuating value of the credits. Conversely, if the ethanol industry receives the carbon credits and pays the oil industry for the sequestration costs, then the ethanol producers would assume the carbon-credit valuation risk. If the risk and cost allocation is balanced, the ethanol and oil industry could form a mutually beneficial relationship. In the CVC framework considered in this paper, the ethanol industry captures the atmospheric CO₂, the oil industry's EOR projects permanently geologically sequester the CO₂ and carbon credit systems like the California LCFS provide the financial incentives to produce the low-CI transportation fuels and fund the necessary infrastructure.

5. Conclusion

The implementation of CO₂-EOR projects using corn ethanol fermentation emissions could play a significant role in reducing the carbon emissions from transportation fuels in the United States. Life cycle analysis of gasoline produced from a bio-CO₂-EOR project, starting from the fermentation CO₂ vent stack of an ethanol plant, through the production and refining process, to the tailpipe of an automobile, shows that this fuel has a low carbon intensity, and could even be carbon negative. Low carbon fuel standard regulations like those enacted in California are the most promising mechanism for creating a market for carbon neutral and carbon negative bio-CO₂-EOR gasoline in the near term, because the LCFS regulations create carbon credits that could help finance CCS projects and related infrastructure costs. A carbon value chain could be created that utilizes ethanol plants to capture the carbon, CO₂-EOR projects to store the carbon, and the LCFS credits to help finance the capital investment required to construct the CO₂ pipelines from the ethanol producing states to the oil producing states. Forging a mutually beneficial relationship between the oil and ethanol industries will further strengthen domestic energy security by improving the financial viability of the bioethanol industry.

Increasing the diversity of low-carbon-fuel sources will help make the shift from fossil fuels to renewable fuels possible over the next several decades. The bio-CO₂-EOR technology that was analyzed in this paper could be implemented over the next decade, because the ethanol plants have already been constructed and the depleted oil fields already exist in several localities where CO₂-EOR technology is proven and is ready to implement. Establishment of a CO₂ pipeline infrastructure in the U.S. to transport biofuel fermentation emissions from states where there is a well developed agricultural economy to the states that have depleted oil fields that can serve as carbon sequestration sites would put into place a CCS infrastructure that could be utilized in the future when other technologies for carbon capture become commercially viable. Future carbon value chains that rely on LCFS trading schemes would facilitate the commercial development of advanced biofuels that rely on cellulosic ethanol fermentation processes after the necessary CO₂ pipeline infrastructure has been built. Successful commercial

demonstration of these carbon-negative CO₂ technologies in the United States that start with bio-CO₂-EOR projects would provide a model for worldwide implementation of these carbon mitigation measures.

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