Opportunities for Reducing CO_2 Emissions from Conventional and Unconventional Fuels using Oxyfiring: a Life-Cycle Perspective

Kerry E. Kelly, Adel F. Sarofim, and David W. Pershing
University of Utah

Abstract

The transportation fuel sector is under pressure reduce its greenhouse gas (GHG) emissions. For example, transportation fuels from unconventional fuel sources, such as heavy oil, oil sands and oil shale, face the challenge of carbon-based fuel standards. The refining industry, as the third largest stationary source of GHG emissions globally, is evaluating technologies for GHG reduction. Oxyfiring is a promising technology for reducing the CO_2 footprint from this industrial sector, but it requires a significant amount of energy to generate oxygen. This study examines oxyfiring for its potential to reduce well-to-pump, life-cycle GHG emissions from transportation fuels produced from crude oil and oil sands and the importance to a vehicle's life-cycle GHG emissions. It considers the additional GHG emissions associated with the power required for air separation and CO_2 handling; the fuel savings from oxyfiring compared to air firing; and the upstream GHG emissions associated with the additional fuel requirements. For a refinery, GHGs from the boilers, process heaters, and reformers are most readily captured, which results in approximately 40% of GHG emissions avoided. The upstream GHG emissions from recovery and transportation of the additional natural gas required for CO_2 capture would reduce GHGs avoided by approximately 1%.

Introduction and Motivation

Concern over GHG emissions and the resulting legislation, i.e., as low-carbon fuel standards, are motivating the transportation-fuel industry to evaluate strategies to reduce their carbon footprint. California enacted the first low-carbon fuel standard in 2007, which will begin to take effect in 2011 (CARB 2007). It requires oil refineries and distributors to ensure that the mix of fuel sold in the California does not exceed the limit of 86 g CO2 equiv./MJ energy released by 2020 for gasoline. This is a well-to-wheel (WTW) life-cycle standard and is based on GHG emissions from the extraction, processing, refining, distribution, and vehicle tailpipe emissions. In 2010, the EPA issued an expanded Renewable Fuel Standard that required renewable fuel volume increase from 12.95 billion gallons in 2010 to 36 billion gallons by 2022. The standard included mandatory life-cycle GHG emission thresholds for renewable fuel categories (US EPA 2010).   Other states and regions have proposed low-carbon fuel standards, but to date no other LCFS have been passed in the United States. Other countries and provinces have also approved carbon-based fuel standards, including British Columbia (2008), the European Union (2008), and the United Kingdom (2009).

When comparing emission-reduction strategies and fuels from different sources, it is important to consider the fuel's entire life cycle as illustrated in Figure 1, which shows GHG emissions from a typical fuel cycle for gasoline from a conventional source of crude oil. Figure 1 also illustrates the well-to-pump (WTP) cycle, which includes raw material extraction, transportation, processing (including upgrading), refining, and delivery to the pump, while the well-to-wheel (WTW) cycle also includes the fuel consumption and the resulting tailpipe emissions.

Figure 1. WTW and well-to-pump (WTP) GHG emissions from raw material extraction, processing/upgrading, refining and transportation, and consumption for gasoline produced from conventional crude oil. The GHG emissions in CO_2 equivalents include emissions of CO_2, CH_4, and N_2O.

Opportunities for Reducing Life-Cycle GHG Emissions

Because the fuel-consumption life-cycle stage is responsible for the majority of WTW GHG emissions (Figure 1), it generally presents the greatest opportunity for reducing the fuel cycle's carbon footprint, particularly for conventional sources of crude oil. For example, improving the average efficiency of a gasoline-powered passenger vehicle efficiency from 21.6 miles per gallon (MPG) to 28.6 MPG reduces the life-cycle WTW GHG emissions by 20% – equal to the average WTP GHG emissions in the US (US DOE 2009).

For conventional crude oil, refining is generally the second most GHG intensive life-cycle stage (Figure 1), and some incremental opportunities for improving the efficiency exist. For example, the efficiency of most refinery process heaters could be improved by 10% with air preheating and improved burner design (DOE 2006). However, the refining industry is mature, and these opportunities are more limited than for other life-cycle stages (DOE NETL 2009). Carbon capture is also an option for reducing GHG refining emissions. Van Straelen et al. (2009) report that approximately 40% of CO_2 emissions from a world-scale refinery are suitable for CO_2 capture using post-combustion capture methods; these capturable emissions tend to come from the larger, more concentrated CO_2 sources such as boilers and process heaters. Allam et al. (2005) performed a feasibility study of retrofitting their Grangemouth refinery's process heaters and boilers to oxyfiring for CO_2 capture (ca. 2 million tones/yr). They estimated that they could reduce their CO_2 emissions by approximately 50% at a CO_2 capture cost of $38/tonne and a CO_2 avoided cost of $43/tonne. CO_2 avoided is the difference between the CO_2 captured and stored, and the amount of CO_2, which would have been produced without capture.

The raw material extraction and processing (including upgrading) life-cycle stages can be important contributors to the carbon footprint for unconventional fuels, such as oil sands, oil shale, and heavy oil.

It is interesting to note that as the United States moves toward more unconventional sources of crude oil, the baseline WTP GHG emissions of a barrel of crude oil is increasing (US DOE 2009). In addition, a good deal of variability exists in the WTP GHG profile depending on the source of crude (Figure 2). Canadian oil sands, Venezuelan bitumen, and

California heavy oil all have greater WTP GHG emissions than US conventional crude oil. However high WTP GHG emissions are not limited to unconventional fuels; Nigerian crude has the third highest WTP GHG emissions profile in Figure 2, primarily due the venting and flaring of nearly all of the co-produced natural gas (US DOE 2009).
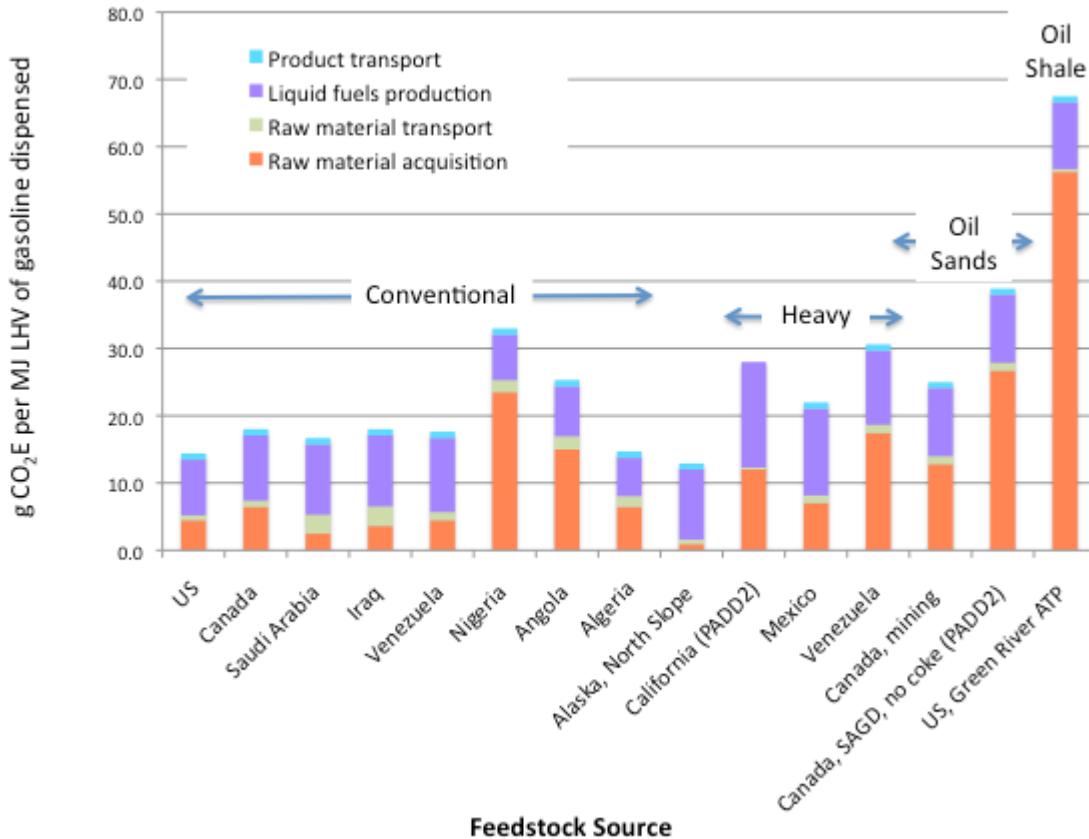

Figure 2. WTP GHG emission profiles for gasoline produced from various sources of crude oil (data from: Canada conventional, Canada SAGD, California heavy oil and Alaska North Slope (TIAX 2009); oil shale (Brandt 2008); and the remaining sources (US DOE 2009). PADD is the petroleum administration defense district, and PADD2 is the Midwest district. There is a good deal of uncertainty associated with Venezuelan crude and oil shale.

Evaluation of Oxyfiring in a Refinery

This study focuses on the refining life-cycle stage. Specifically, it examines oxyfiring for CO_2 capture for its potential to reduce WTP, life-cycle GHG emissions from transportation fuels produced from conventional crude oil. Firing boilers and process heaters with oxygen instead of air produces a concentrated CO_2 stream; however, oxyfiring requires an energy-intensive air-separation unit. This study builds on the work of Allam et al. (2005) who evaluated the conversion of seven boilers and thirteen process heaters to oxyfiring at British Petroleum's Grangemouth refinery. These boilers and process heaters produce relatively concentrated CO_2 streams, accounting for approximately 40% of the refinery's CO_2 emissions. Their study determined the power required to operate an air separation

unit, produced by a natural gas combined cycle plant, and the power required to purify, compress, and deliver the CO_2 to the fenceline.   They evaluated three oxy-firing cases.

Case 1: A gas turbine and associated steam production provides power for the air separation unit and CO_2 purification, compression, and transport.

Case 2: A gas turbine provides power to the air separation unit and other equipment, but steam from the turbine replaces a portion of the boiler steam. This results in a lower O_2 requirement, a smaller ASU, and less cooling water.

Case 3: The gas turbine is run in the precombustion decarbonisation mode with part of the oxygen being used for hydrogen production and CO_2 removal using amine scrubbing.

This study determined the GHG emissions (CO_2, CH_4, and N_2O) associated with the power generation required for the air separation unit as well as CO_2 purification, compression, and transport. Firing with oxygen instead of air also results in a small fuel savings.   The GHG emissions from the oxyfiring process are given by:

$$GHG_{ex} = GHG_{GT} - GHG_{,\,exp\,power} - GHG_{fuel\,sav}$$

GHG_{ex} = Excess GHG from oxyfiring for carbon capture
GHG_{GT} = GHG emissions from the natural gas turbine combined cycle power plant
$GHG_{exp\,power}$ = GHG emissions from excess power sold
$CO_{2,\,fuel\,sav}$ = GHG emissions from fuel saved in boilers and heaters associated with oxyfiring

In addition to the direct GHG emissions, this study also evaluated the additional upstream GHG emissions from natural gas extraction and transport associated with the natural gas required to power the air separation unit and ancillary equipment. The additional upstream data came from Argonne National Laboratory's GREET model (2009). Note that these estimates do not include GHG estimates for construction, decommissioning, or production of the amine used for amine scrubbing (case 3).

For comparison purposes, we evaluated the effect of improving process heater efficiency in a refinery from 83% to 93% using air preheat. These current and projected efficiencies are based on the current average process heater efficiency in the United States and projected efficiency improvements (US DOE 2006).

Figure 3 shows the results of our evaluation. Improving process heater efficiency reduces life-cycle GHG emissions by approximately 5%, and oxyfiring for CO_2 capture reduces life-cycle GHG emissions for fuel production by 28 – 34%. Although the air separation unit and CO_2 purification, compression, and transport requires additional energy, the GHGs emitted from this additional energy and the corresponding upstream energy requirements are much less significant than the GHG emissions saved through oxyfiring for CO_2 capture.
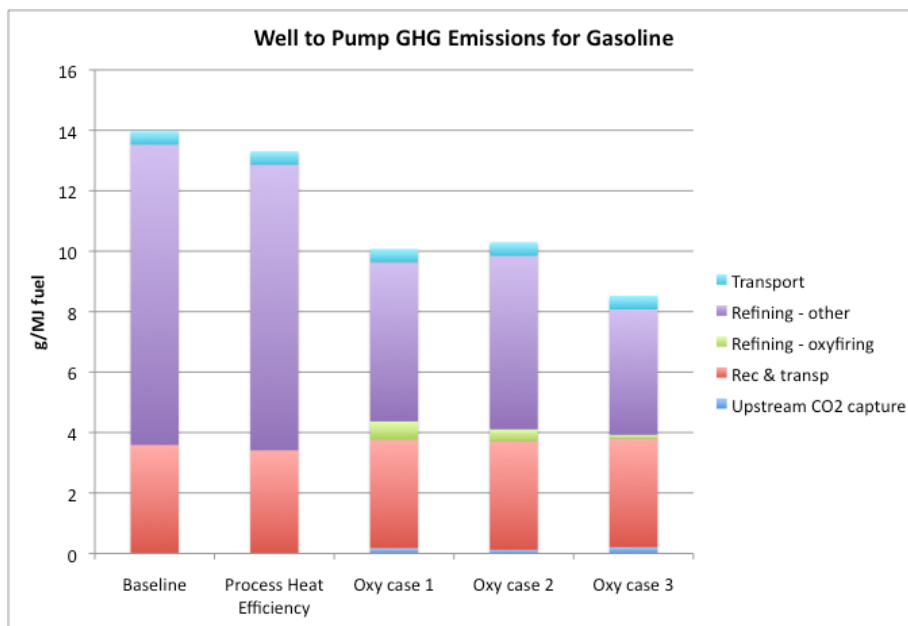

Figure 3. Comparison of baseline refining GHG emissions, refining emissions with improved process heater efficiency, and oxyfiring case 1 – case 3 (Allam et al. 2005). In the oxyfiring cases, the green bar and the darker blue bar indicate the excess GHG emissions associated with the power requirements for air separation, CO_2 purification, and CO_2 compression and with the natural gas extraction and transport, respectively.

Oxygen providers are working toward improved efficiency in air separation. The Allam study estimated that the air separation unit required 212 kW-hr/ton O_2. Near-term advanced air separation is projected to require 145 kW-hr/ton O_2 by 2015, so the GHG penalty associated with oxyfiring is likely to decrease in the near term.

References

R. Allam, V. White, N. Ivens, M. Simmonds, The Oxyfuel Baseline: Revamping Heaters and

Boilers to Oxyfiring by Cryogenic Air Separation and Flue Gas Recycle. Chapter 26 In *Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO2 Capture Project Capture and Separation of Carbon Dioxide from Combustion Sources*, David C. Thomas (ed). Elsevier 2005.

A. R. Brandt, Converting Oil Shale to Liquid Fuels: Energy Inputs and Greenhouse Gas Emissions of the Shell in Situ Conversion Process *Environ. Sci. Technol.*, 2008, 42 (19), 7489-7495.

A.R. Brandt, J. Boak, A. K. Burnham, "Carbon Dioxide Emissions from Oil Shale Derived Liquid Fuels" in Oil Shale: Solutions to the Liquid Fuel Dilemma, ACS, Chapter 11, pp 219–248.

ANL (Argonne National Laboratory) (2009) The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model, version 1.8c0, accessed July 2009, http://www.transportation.anl.gov/modeling_simulation/GREET/index.html

British Columbia Parliament (2008) Bill 16 – 2008, Greenhouse Gas Reduction (Renewable and Low Carbon Fuel Requirements Act, 4th Session, 38th Parliament, http://www.leg.bc.ca/38th4th/1st_read/gov16-1.htm, cited June 17, 2010.

CARB (California Air Resources Board) (2007) Final Regulation Order Subchapter 10. Climate Change Article 4. Regulations to Achieve Greenhouse Gas Emission Reductions Subarticle 7. Low Carbon Fuel Standard http://www.arb.ca.gov/fuels/lcfs/lcfs.htm, cited June 17, 2010.

European Union (2008) Monitoring and reduction of greenhouse gas emissions from fuels (road transport and inland waterway vessels, texts adopted 17 December 2008, Strasbourg.

TIAX LLC, Rosenfeld, J., Pont, J., Law, K. Comparison of North American and Imported Crude Oil Lifecycle GHG Emissions, July 6, 2009.

United Kingdom Renewable Fuels Agency, The Renewable Transport Fuel Obligations Order, amended 15 April 2009.

US DOE NETL, An Evaluation of the Extraction, Transport, and Refining of Imported Crude Oils and the Impact on Life Cycle Greenhouse Gas Emissions, March 27, 2009, Table A-1, pg A-3

US Department of Energy High Efficiency, Ultra- Low Emission, Integrated Process Heater System Final Technical Report, June 2006.

US EPA (2010) Renewable Fuel Standard, http://www.epa.gov/otaq/fuels/renewablefuels/index.htm, accessed June 21, 1010.

J. van Straelen, F. Geuzeboek, N. Goodchild, G. Protopapas, L. Mahony, CO2 capture for refineries, a practical approach, Energy Procedia 1 (2009) 179 – 185.