Petroleum refinery greenhouse gas emission variations related to higher ethanol blends at different gasoline octane rating and pool volume levels

Vincent Kwasniewski, Confluence Consulting LLC, Glenview, IL USA
John Blieszner, Jacobs Consultancy, Chicago, IL USA
Richard Nelson, Enersol Resources, Manhattan, KS, USA

Received February 26, 2015; revised September 16, 2015; accepted September 17, 2015
View online October 23, 2015 at Wiley Online Library (wileyonlinelibrary.com);
DOI: 10.1002/bbb.1612; Biofuels, Bioprod. Bioref. 10:36–46 (2016)

Abstract: Refinery GHG emissions were predicted for 10% and 30% ethanol blends at refinery blend-stock octanes between 77 and 89 AKI at any gasoline pool energy content between parity and constant gasoline pool volume. Linear programming analyzed how separate E30 blending scenarios of 2017 PADD 2-based refineries affect greenhouse gas (GHG) emissions relative to status quo gasoline (i.e., E10, 87 AKI and 93 AKI premium). The compliance synergy of higher ethanol blends illustrated here is pertinent to national policy goals and multiple environmental objectives. Study results have implications for CAFE Standards, US EPA Tier 3 fuel standards, and Clean Air Act regulations of stationary source CO2 emissions from refinery operations. Results varied by amounts and types of crude oil processed, refinery operations, refinery gasoline blendstock produced (and fuel ethanol blended), and produced refinery product composition and properties. Significant differences exist in total refinery GHG emissions (including emissions from purchased electricity and hydrogen) with the largest differences from coke burn in the fluidized catalytic cracker and refinery fuel gas combustion principally related to reformer operations. The concept of refinery GHG emissions intensity was introduced to differentiate between differences in refinery throughput (an extensive factor) and severity of refinery operations (intensive factors). Refinery GHG emissions decline 12% to 27% from a 2017 base case for the various 30% ethanol cases, highlighting a significant gap in current life cycle analysis (LCA) and supporting incorporation of this improved approach into LCA related to higher ethanol blends. This methodology can be adapted to other PADDs and/or for the USA. © 2015 The Authors. Biofuels, Bioproducts, Biorefining published by Society of Chemical Industry and John Wiley & Sons, Ltd.

Keywords: ethanol; gasoline blending; greenhouse gas emissions; octane; petroleum refinery; petroleum refining emissions
Introduction

Ethanol use is expected to increase worldwide over the next decade due to favorable gasoline blending economics and governmental policies aimed at reducing greenhouse gas (GHG) emissions, improving vehicle efficiency, and/or reducing petroleum imports. US ethanol use is projected to increase from 55.2 billion liters in the 2013/2014 corn-marketing year (MY) to almost 70 billion liters in MY 2022/2023.1,2

In the USA, the principal policy supporting this projected use is the Renewable Fuel Standard (RFS), which mandates 136.2 billion liters of qualifying renewable transportation fuel use by 2022.3 Renewable fuels qualify within the RFS by providing GHG emissions reductions over their entire life-cycle relative to statutorily defined petroleum-based standards. Corn starch-based ethanol life-cycle GHG emissions must be at least 20% less versus 2005 gasoline and depending on a number of factors such as land use change, provides reductions of between 19% and 48% when compared to gasoline (on a per unit of energy basis) while ethanol derived from other sources such as corn stover and select herbaceous energy crops can have even greater life-cycle emissions reductions.4

In addition to regulatory drivers, ethanol has certain performance attributes that can result in increased use, principal among them higher octane versus conventional 87 AKI gasoline. In the USA, gasoline octane postings reference the fuel’s Anti-Knock Index (AKI), an average of Research Octane Number (RON) and Motor Octane Number (MON). The majority (85%) of US gasoline sold is regular grade, which has an AKI of between 85 and 88 depending on geography.5 Premium gasoline has an AKI greater than 90 with mid-grades between 88 and 90, inclusive.

Higher levels of renewable fuel with current engine technologies could reduce GHG emissions. However, another more intriguing approach, deemed publicly by major US automakers to be a promising pathway for compliance with both increasing renewable fuel volume requirements under the RFS and progressively more stringent corporate average fuel economy (CAFE) requirements, is a transition to advanced engine technologies with greater use of ethanol to reduce GHG emissions.6 This approach involves using higher engine compression ratios (CR), direct injection, and potentially turbocharging in order to improve thermal efficiency and reduce engine weight without power loss, which translates into lower tailpipe GHG emissions and less fuel consumption per mile. Importantly, for these vehicles to perform acceptably and achieve higher efficiencies, a higher minimum octane fuel (well above 88 AKI) is required. For these vehicles to be accepted by consumers, that higher octane number fuel needs to be widely-available and cost-effective which will mean high-CR vehicles will perform adequately.

Ethanol has a higher octane rating than conventional gasoline. Consequently, higher blend levels could significantly increase a finished gasoline’s octane rating. In addition, engine researchers have determined ethanol’s high heat of vaporization provides a cylinder ‘charge cooling’ effect. Due to these two desirable properties, fuels with higher levels of ethanol could allow for design and use of direct-injection, spark-ignition engines with higher CRs and greater thermal efficiency.7

Recent studies examined increased ethanol content in gasoline and its impacts on engine performance with favorable results. Jung et al.8 tested splash-blended E10, E20, and E30 fuels in a Ford 3.5L EcoBoost direct injection turbocharged engine at CRs of 10.0:1 and 11.9:1. Results showed E30 (101 RON) at a 11.9:1 CR reduced CO₂ emissions by 5% and 7.5% on the EPA M/H (Metro Highway) cycle and US06 Highway cycles, respectively, while volumetric fuel economy was 3% lower on the M/H cycle and approximately equal on the US06 Highway cycle, compared to E10 fuel at a 10:1 CR. Taking advantage of ethanol’s higher octane rating and charge cooling effect, engine designs can be optimized to offset ethanol’s reduced energy content, thereby reducing vehicle fuel consumption and tailpipe CO₂ emissions relative to current engine designs. Splitter and Szybist6 concluded CO₂ reductions could be achieved without a decrease in miles per gallon with an intermediate ethanol blend providing reduced knock and tolerating a higher CR. Anderson et al.7 estimated a possible RON increase of four to seven points with 20–30% ethanol blends into current supplies resulting in a possible E30 RON of 98.6. Increasing the minimum RON requirement for E10 to 92 would mean an E30 RON of over 100. These studies indicate higher ethanol blends could have positive results on light duty vehicle fuel economies and reduce tailpipe greenhouse gas emissions.

Other national environmental policy objectives could be furthered with higher ethanol blends in conjunction with higher finished gasoline octane rating requirements. The US Environmental Protection Agency (US EPA) has recently set a 10 ppm sulfur ceiling for gasoline in 2017 due to concern over air quality-related public health concerns (Tier 3).9 Tier 3 also allows for updating specifications of the emission test fuel to demonstrate compliance with this new standard that incorporates current and
expected ethanol contents in the US gasoline pool and is also affiliated with the EPA’s GHG standards for light-duty vehicles which begins in 2017. While not the express subject of this study, given that sulfur and aromatics levels in ethanol are near zero and increased levels of ethanol beyond 10% by volume could allow for reduced levels of high octane aromatics-rich fossil gasoline blendstocks in finished gasoline, blending higher levels of ethanol would likely make compliance with Tier 3 gasoline requirements easier. Also, the US EPA recognizes manufacturers may wish to design vehicles to utilize higher octane ratings (e.g. 30%v ethanol, increased CR) as a means of improving overall vehicle efficiency and will allow them to test fuels with a minimum octane rating of 91 AKI which provides a significant market incentive for advancing beyond current E10 levels.9

Clearly, higher ethanol blends could simultaneously address multiple environmental policy objectives: reducing total life-cycle GHG emissions (RFS), increasing light duty vehicle efficiencies (CAFE), and improving air quality (Tier 3). It is rare to find such a compelling synergy, particularly for an approach that is deployable today without the need for an all too often elusive technology advancement. Given this possibility, it is important to develop a more complete body of knowledge around the impacts of blending increased volumes of ethanol with reduced levels of refinery blendstock (BOB), including consideration of the GHG emissions associated with the refining process, so policy-makers have the data to inform their decision-making. Anderson et al.7 specifically mention this point.

This study builds that body of knowledge focused specifically on changes in GHG emissions of a petroleum refinery to select ethanol blend levels and octane rating changes in finished gasoline streams. This study did not consider GHG emissions associated with crude oil exploration/production, inbound crude oil logistics, outbound product logistics, vehicle use, or ethanol production. Although ethanol referred to in this study was not designated from any particular source/feedstock, this study is particularly relevant to renewable fuels given that the ethanol would most likely be derived from biomass sources such as corn, sugarcane, or lignocellulosic crops, all renewable sources of fuel ethanol based on earlier LCA analyses.4

Linear programming (LP) has been demonstrated to optimize petroleum refinery operations involving crude oil input scheduling, output product qualities (e.g. octane number and aromatic content), energy utilization, and finished product blending.10-13 Hirschfeld et al.14 performed an LP analysis of the national (aggregate) US PADD-based refining sector to assess the additional cost per gallon of increasing octane ratings as higher ethanol blends are incorporated into the U.S. gasoline supply. They found gasolines with 10 and 30%v ethanol (95 to 100 RON, respectively) could be produced at a cost between one and five cents per gallon higher than corresponding blends at status quo octane ratings. They further found increases in ethanol content decreased refinery CO2 emissions at constant RON while increases in RON at constant ethanol content result in increased refinery CO2 emissions. Speth et al.15 performed a well-to-wheels economic and environmental analysis and found using high-RON gasoline in the US light-duty fleet would reduce CO2 emissions and decrease gasoline consumption by 3.0~4.4% between 2012 and 2040. They used an LP-based refinery model with a typical US Gulf Coast refinery and current US petroleum product slate.

A major outcome of this study is that it will provide renewable fuel life-cycle modelers looking at other GHG emissions aspects of higher ethanol level blends a reference point enabling incorporation one of the consequential effects of changes to BOB specifications caused by increased ethanol levels, specifically, reduced (or increased) levels of petroleum refinery emissions. Additionally, as the US EPA begins to regulate CO2 emissions from stationary sources (i.e. the Tailoring Rule),16 the broader understanding of petroleum refinery CO2 emissions provided by this study would definitely be applicable.

Materials and methods

Petroleum Administration Defense Districts

Petroleum Administration Defense Districts (PADDs) are five separate multi-state areas in the USA used to analyze patterns of petroleum and finished product movement.17 The focus of this paper was on PADD 2 (Midwest) which had 27 operating refineries in 2013, producing 34% of the nation’s finished gasoline and including 170 ethanol plants with nearly 46 billion liters per year of operating production.18

Model development and calibration

For this study, a representative LP model (i.e., calibration case) was developed for PADD 2 using GRTMPS19 composed of high conversion refineries processing light and heavy crude oils and based on PADD 2 crude inputs and refinery products data for 2010 from the US Department of Energy’s Energy Information Administration (EIA).20,21
GRTMPS is a well-known optimization software system used extensively in the petroleum refinery sector and other industries to provide estimates of operational planning, scheduling, and economic forecasting.

Refinery capacity data and those of individual processing units (e.g. alkylation, hydrocracking) were taken from Oil & Gas Journal data. Capacities for all process units, which are maximum throughput constraints in the LP model, were summed for all PADD 2 refineries to obtain an aggregate representation of PADD 2 refining capability, including aggregate individual process unit capacities. No minimum throughput constraints were imposed since reduced aggregate throughput could in reality be achieved by shutting down entire units at individual refineries.

Upon configuration, appropriate 2010 mixes of light, medium and heavy crude oils and other feedstock inputs were evaluated and refinery product volumes calculated. Comparison of model predictions with the EIA’s 2010 production data allowed for calibration including crude types processed in the region. The model was run using six separate crude assays averaging 33.1 API and 1.3% sulfur. LP constraints were a plus or minus 3% (relative) on C5+ liquid products compared to actual PADD 2 operations. Additional screening was performed on the fluid catalytic cracker (FCC), hydrocracker, and coker. After minor model parameter adjustments, model predictions matched historical data within LP tolerances.

### Modeling PADD 2 in 2017

To represent 2017, the 2011 EIA Annual Energy Outlook was utilized for the refining volume forecast. EIA PADD data were not segregated, so PADD 2 volumes were assumed to grow from 2010 similarly to US projections overall. The specified differentiation between reformulated gasoline (RFG) for air quality non-attainment areas and conventional gasoline was retained and all gasoline in 2017 was assumed E10 with 87 AKI regular and 93 AKI premium (resulting in a gasoline pool average AKI of 88).

For conventional gasoline, it was assumed the current RVP waiver was eliminated. (Hirschfeld et al. report results with both elimination and retention of the RVP waiver.) LPG and butane volumes were constrained based on historical relationships to crude throughput and gasoline production.

In addition to product volumes, crude and product prices used in the LP were fixed at EIA forecast levels adjusted to a lower refining margin more realistic of past experience. Price inputs not provided in the EIA forecast were set using proprietary price relationships and know how developed from historical data. Pricing, however, had little effect on the resulting refinery operating plan, including refinery GHG emissions; therefore refinery profitability was not included in the scope of this study. Absolute operating and capital costs have been studied by others and were also not in scope.

For the PADD 2 model to converge with a feasible solution conforming to 2017 EIA volume projections, assumptions reasonable to the authors were made on crude, hydrocracking, and hydrotreating capacity investment from 2010 to 2017. Evolution of the refinery configuration from 2010 to 2017 was based on incremental investment incentive values generated by the LP, coupled with author experience. After evolving the refinery configuration to converge for E10 in 2017, the refinery configuration was not changed.

The major objective of this project was to analyze four separate E30 (i.e. 30% ethanol by volume) ethanol blending scenarios with several gasoline octane grades and supply volumes in the ‘aggregate’ Midwest-based petroleum refinery versus a common base case representative of status quo gasoline in 2017 to determine how GHG emissions from the refining process would change for 2017. Each E30 case varied by octane rating and gasoline pool volume. In all cases, the finished gasoline AKI was calculated as the volumetric weighted average AKI of the BOB and ethanol, assuming an AKI of 115.8 for ethanol and, as this study was initiated prior to Tier 3 sulfur specifications being announced, the older 30 ppm maximum sulfur specification in gasoline was used. All other constraints such as distillate production and fuel specifications were held constant across all 2017 cases. For each 2017 case, the refinery crude slate and operating conditions were determined by solving for the refinery economic optimum using the LP-model representation of the 2017 aggregate refinery. The methodology applied in this study is also applicable to the other PADD’s within the USA or could be potentially extrapolated to the USA as a whole.

Secondary objectives included showing how various refinery process unit operations would change with increased ethanol volumes, GHG emissions from those process units, resulting compositional changes in BOB, and determining if refinery operations would even be feasible and reasonable for the imposed gasoline specifications chosen.

The six cases analyzed were:

- Calibration – This E10 case uses actual 2010 data from petroleum refineries in Petroleum Administration Defense District 2 (PADD 2).
• **Base (B)** – This E10 case establishes a refinery configuration, crude slate, and operating conditions for the US Department of Energy – Energy Information Administration (EIA) projected finished product volumes for 2017 assuming all gasoline is E10 and the elimination of the 6.895 kPa (1 psi) Reid Vapor Pressure (RVP) waiver for conventional gasoline. Regular at 87 AKI and premium at 93 AKI are differentiated for both conventional and reformulated gasoline, resulting in a gasoline pool octane of 88 AKI.

• **88BV** – Similar to the Base case, also with differentiated gasoline grades having a pool octane of 88 AKI and with the various grades fixed at the same respective volume (V) levels, but at a 30% ethanol level (an E30 case).

• **88BE** – An E30 case similar to 88BV, but with the additional gasoline production required to maintain the gasoline pool energy (E) content, rather than its volume, equivalent to the Base case.

• **97BV** – An E30 case also similar to 88BV, but with a single grade of conventional gasoline and a single grade of RFG, each having a practical maximum AKI of 97.

• **97BE** – An E30 case similar to 97BV, but with the additional gasoline production required to maintain the gasoline pool energy (E) content equivalent to the Base case.

In this model, all refineries in PADD 2 are represented as a single aggregated refinery having a capacity equal to that of the entire PADD, providing insight into the region as a whole and how specific refineries might respond under similar conditions. It can be seen as representative of a model average refinery in PADD 2.

### Results and discussion

In response to varying ethanol blending, finished gasoline octane rating, and finished gasoline pool volume constraints for the six scenarios, model results varied in amounts and types of crude oil processed, refinery operations required to process various crude oils, amounts of refinery gasoline blendstock produced (and fuel ethanol blended), the composition and properties of refinery products produced, and refinery GHG emissions.

### Refinery crude run and product slate

Refinery crude throughput was a combination of domestic and Canadian light, medium, and heavy sweet crudes.

The Calibration case was constrained to match 2010 supply/demand data with the 2010 refinery configuration and other cases were based on EIA projected 2017 supply/demand data, which did not include the significant increases in crude availability from the Bakken that has since materialized. All 2017 cases utilized the common ‘evolved’ refinery configuration. Higher finished product demands in 2017 require higher crude runs and product volumes for the Base case versus the Calibration case. In particular, distillate production is disproportionately higher (20%) than BOB (4%), causing the finished gasoline-to-distillate (G:D) ratio to decrease from 1.82 to 1.58. Despite the large change in both product volume and mix, the relative amounts of various crude types are virtually unchanged between the two cases.

E30 ethanol cases result in lower crude runs, by 9% to 15% between the four cases, on reduced BOB production with equivalent production of other ‘White Products’ (gasoline-range byproducts, jet fuel, and diesel and heating oil). Virtually no differences exist in relative amounts of the various crudes processed. Among the four ethanol cases, crude throughput is higher for the BE cases than BV cases; because of ethanol’s lower heating value, more gasoline is required for the BE cases to maintain gasoline pool energy equivalence to the Base case. For the 97 AKI cases relative to their respective 88 AKI case, crude throughput is higher due to the greater level of gasoline “volume shrink” in refinery operations needed to produce blendstock required to meet a 97 AKI finished gasoline specification. Table 1 shows the total crude oil processed and the primary product slate.

### Unit operations and gasoline blending

Tables 2 and 3 show total refinery crude and unit throughputs for key White-Product-related unit operations, major energy-related purchased utility inputs, and finished gasoline composition and properties resulting from differing unit operations. The 28% increase in distillate-producing hydrocracker throughput seen for the Base case versus the Calibration case is much higher than the 7% to 8% increase in throughput for the gasoline-related unit operations (e.g. the fluid catalytic cracker, reformer, and alkylation unit) due to the lower G:D ratio in 2017 versus 2010.

In each ethanol case, however, the volume and octane rating impacts of displacing BOB affect reformer operations and reformate blending. The primary function of reformers is to make high octane number aromatic hydrocarbons in order to increase gasoline octane ratings, which they do at high operating cost and at the expense of...
Table 1. Total crude oil processed and primary product slate (000 m³ per day).

| Scenario Cases | Total Crude Oil Throughput | Calibration | Base | 88BV | 88BE | 97BV | 97BE |
|----------------|---------------------------|-------------|------|------|------|------|------|
| White Products produced and Ethanol Blended | | | | | | | |
| Blend Stock for Oxygenated Blends | | 297.0 | 308.0 | 239.0 | 256.0 | 239.0 | 255.0 |
| Reformate & Naphtha Sales | | 5.9 | 6.3 | 6.3 | 6.3 | 6.3 | 6.3 |
| Jet Fuel | | 32.3 | 36.6 | 36.6 | 36.6 | 36.6 | 36.6 |
| Diesel & Heating Oil | | 149.0 | 180.0 | 180.0 | 180.0 | 180.0 | 178.0 |
| Subtotal - Fossil White Products | | 484.2 | 530.9 | 461.9 | 478.9 | 461.9 | 475.9 |
| Fuel Ethanol (blended at Gasoline Racks) | | 33.5 | 34.8 | 105.0 | 112.0 | 105.0 | 112.0 |
| Total Blended White Products | | 517.7 | 565.7 | 566.9 | 590.9 | 566.9 | 587.9 |
| Fossil Gasoline-to-Distillate Volume Ratio | | 1.64 | 1.42 | 1.10 | 1.18 | 1.10 | 1.18 |

Table 2. Refinery throughput and key refinery unit operations and utilities.

| Scenario Cases | Refinery Throughput | | | | | | |
|----------------|---------------------|-------------|------|------|------|------|------|
| Total Crude Oil (000 m³ per day) | | | | | | | |
| Calibration | 511.8 | 574.5 | 493.0 | 510.2 | 519.1 | 525.9 |

Refinery Unit

| Scenario Cases | | | | | | | |
|----------------|---------------------|-------------|------|------|------|------|------|
| Isomerization Unit (000 m³) | | 25.9 | 32.4 | 31.3 | 32.1 | 32.4 | 32.4 |
| Alkylation Unit (000 m³) | | 33.5 | 31.5 | 17.1 | 18.3 | 20.7 | 27.3 |
| Fluidized Catalytic Cracker (000 m³) | | 149.0 | 160.0 | 101.0 | 108.0 | 112.0 | 117.0 |
| Hydrocracker (000 m³) | | 36.3 | 46.5 | 46.5 | 46.5 | 46.5 | 46.5 |
| Delayed Coker (000 m³) | | 49.9 | 58.0 | 40.7 | 42.7 | 43.1 | 44.7 |
| Reformer (000 m³) | | 100.0 | 108.0 | 19.7 | 19.2 | 119.0 | 125.0 |
| Severity (AKI) | | 92.5 | 90.0 | 90.0 | 90.0 | 100.0 | 100.0 |

Utilities

| Scenario Cases | | | | | | | |
|----------------|---------------------|-------------|------|------|------|------|------|
| Purchased Natural Gas (GJ) | | 1,160 | 1,250 | 1,090 | 1,110 | 1,040 | 1,070 |
| Purchased Hydrogen (thousand m³) | | 2,070 | 10,600 | 18,900 | 19,800 | 1,640 | 1,990 |
| Purchased Electricity (GW-hr) | | 17.1 | 18.9 | 14.5 | 14.8 | 17.1 | 17.8 |

gasoline volume. For the 88BV and 88BE cases, reformer throughputs decrease 82% and reformate blending into finished gasoline falls from 27% to less than 4% due to the large addition of incremental high octane ethanol reducing the need for octane number in the BOB to make an average 88 AKI finished gasoline. A side effect of reduced reformer throughput, which also reduces by-product hydrogen production, is higher purchased hydrogen volumes.

When the finished gasoline pool minimum octane specification increases from 88 to 97 AKI, the impact on reformer operations and reformate blending is reversed. The need for an 89.2 AKI BOB blendstock versus only 76.7 AKI for the 88BV and 88BE cases requires reformate blending at roughly the same 27% level as the Base case and reformer throughputs are increased by 10% to 16%. The need is for both higher reformate volume and higher reformate octane number, as reformer severities (a measure of conversion to high octane aromatic compounds, typically measured in octane number units) of 100 AKI were also required versus only 90 AKI for all other cases. Understandably, the 97BV and 97BE cases also showed the lowest purchased hydrogen volumes (83% and 90% lower versus Base case and 88 AKI cases, respectively).
but incremental ethanol takes the place of FCC gasoline, alkylate, and naphtha, all of which decline as a percentage of the blend. BOB blendstock octane ratings for the 97 AKI cases actually increase versus the Base case by over 4 AKI to where refineries needed to operate prior to the days of 10% ethanol blending.

Aromatic, olefinic, and sulfur contents of finished gasoline decline by over 50%, 30%, and 50%, respectively, for the 88BV and 88BE cases versus the Base case. For the 97BV and 97BE cases, aromatic content (principally from reformate) increases 5% to 6%, olefinic content (principally from FCC gasoline) declines about 27%, and sulfur content declines by 8% to 21%.

With respect to differences in refinery unit operations and gasoline blending between the two constant volume cases and their respective constant gasoline pool energy cases, throughputs increase modestly, but only small differences in gasoline blending occur.

### Refinery greenhouse gas emissions

Model results in Fig. 1 show significant differences in total greenhouse gas emissions from refinery operations including emissions from purchased upstream electricity (assuming 201 g CO₂/MJ) and upstream purchased hydrogen (assuming 5.5 kg CO₂/kg H₂). In all cases and for all

---

Table 3. Gasoline composition and properties.

| Component Blendstocks (vol%) | Scenario Cases |
|------------------------------|----------------|
| Ethanol                      | Calibration   | Base | 88BV | 88BE | 97BV | 97BE |
| Ethanol                      | 10.0          | 10.0 | 30.0 | 30.0 | 30.0 | 30.0 |
| FCC Gasoline                 | 25.1          | 26.1 | 17.2 | 17.1 | 18.8 | 18.4 |
| Reformate                    | 25.6          | 26.9 | 3.9  | 3.6  | 26.7 | 26.3 |
| Naphtha                      | 13.8          | 12.4 | 28.7 | 29.5 | 4.1  | 3.9  |
| Alkylate                     | 10.3          | 9.2  | 5.0  | 5.0  | 6.1  | 7.5  |
| Isomerate                    | 7.7           | 9.3  | 9.0  | 8.6  | 9.3  | 8.7  |
| Butanes                      | 7.5           | 6.1  | 6.2  | 6.1  | 5.1  | 5.3  |

**Key Properties of Finished Gasoline**

- **Octane Number (AKI)**
  - Calibration: 87.7, 87.7, 88.4, 88.4, 97.2, 97.2
  - Base: 87.7, 87.7, 88.4, 88.4, 97.2, 97.2
- **Aromatic Content (Volume %)**
  - Calibration: 21.6, 20.4, 10.0, 10.0, 21.7, 21.4
  - Base: 21.6, 20.4, 10.0, 10.0, 21.7, 21.4
- **Olefinic Content (Volume %)**
  - Calibration: 7.7, 7.8, 5.1, 5.1, 5.7, 5.6
  - Base: 7.7, 7.8, 5.1, 5.1, 5.7, 5.6
- **Sulfur Content (ppm)**
  - Calibration: 23, 24, 10, 12, 22, 19
  - Base: 23, 24, 10, 12, 22, 19

**Key Properties of BOB**

- **Octane Number (AKI)**
  - Calibration: 84.6, 84.6, 76.7, 76.7, 89.2, 89.2
  - Base: 84.6, 84.6, 76.7, 76.7, 89.2, 89.2
- **RVP (annual average) (kPa)**
  - Calibration: 74.1, 70.6, 75.3, 75.1, 75.5, 75.8
  - Base: 74.1, 70.6, 75.3, 75.1, 75.5, 75.8
- **Density (kg/m³)**
  - Calibration: 729, 727, 720, 720, 741, 740
  - Base: 729, 727, 720, 720, 741, 740
- **High Heating Value (GJ/m³)**
  - Calibration: 33.8, 33.9, 33.6, 33.7, 33.8, 33.8
  - Base: 33.8, 33.9, 33.6, 33.7, 33.8, 33.8
results presented, carbon dioxide was the only GHG modeled and no emissions of any kind from the production of ethanol are included. Higher product demands for the Base case increase refinery GHG emissions by 8% over the Calibration case. For the various 30% ethanol cases, ethanol displacement of BOB decreases refinery GHG emissions by 12% to 27% compared to the Base case.

Figure 1 also shows GHG emissions from refinery sources separated into coke burning in the FCC unit, combustion of refinery fuel gas (for process heat or other uses), combustion of purchased natural gas (for process heat, hydrogen production, or other uses), and purchased electricity and hydrogen. The largest differences occur in emissions from the FCC coke burn with reductions from 21% (97BE) to 42% (88BV).

Refinery fuel gas emissions also vary significantly. Considering changes in combined emissions from both refinery fuel gas and purchased natural gas, as they are interchangeable on an energy basis, GHG emissions reductions versus the Base case range from 9% (97BE) to 25% (88BV). Emissions from purchased electricity and hydrogen, combined on a relative basis are smaller (by 10% to 15%).

Relative differences among the various high ethanol cases and emissions sources within the refinery are understandable as refining more crude oil (88BE and 97BE) will produce more emissions versus a constant gasoline volume case with lower crude throughput (88BV and 97BV). Similarly, running the energy-intensive refinery unit operations needed to make octane number (97BV and 97BE) will produce more emissions than corresponding lower octane rating gasoline cases (88BV and 88BE).

Also clear from these results is the effect of reducing BOB production volumes on refinery GHG emissions is not accurately estimated by simply reducing life-cycle GHG emissions from BOB by a fixed standard amount per unit volume of BOB displaced by ethanol. Hirschfeld et al.14 and Speth et al.15 found similar results. The implicit assumption of that convention is life-cycle emissions from BOB are independent of ethanol blend percentage, finished gasoline octane ratings, and other gasoline blending properties. From results and discussion above, this clearly is not the case. Changes in refinery GHG emissions result from changes in the more extensive factor of refinery throughput and the more intensive factor of refinery operating conditions. By decoupling these two factors, it is easier to see the beneficial impact on emissions associated with ethanol’s gasoline blending properties (a more intensive effect) as well as its volume (a more extensive effect). This decoupling can be done in a variety of useful ways, presented in Table 4, by dividing total refinery GHG emissions for each case by various normalization factors such as crude throughput, produced product volumes, or the energy contained in produced products. We define these normalized, intensive measures of the GHG emissions associated with refinery operations as ‘Refinery GHG Emissions Intensities’.

The Base and Calibration cases on any GHG emissions intensity basis are essentially the same. Changes that do exist are due to changes in the G:D ratio, which appears
V Kwasniewski, J Blieszner, R Nelson

DOI: 10.1002/bbb

Biofuels, Bioproducts, Biorefining published by Society of Chemical Industry and John Wiley & Sons, Ltd.

© 2015 The Authors.

Table 4. Refinery greenhouse gas emissions intensities.

| Output Parameter | Calibration | Base | 88BV | 88BE | 97BV | 97BE |
|------------------|-------------|------|------|------|------|------|
| COTP (kg CO2eq/m³) | 219 | 214 | 181 | 182 | 203 | 206 |
| FWPP (kg CO2eq/m³) | 231 | 231 | 193 | 194 | 228 | 228 |
| FMGP (kg CO2eq/m³) | 377 | 399 | 374 | 364 | 441 | 426 |
| FWPE (g CO2eq/MJ) | 6.51 | 6.47 | 5.39 | 5.42 | 6.33 | 6.34 |
| FMGE (g CO2eq/MJ) | 11.2 | 11.8 | 11.1 | 10.8 | 13.0 | 12.6 |

Legend: COTP - Crude Oil Throughput Basis; FWPP - Fossil White Products Produced Basis; FMGP - Fossil Motor Gasoline Produced Basis; FWPE - Fossil White Products Contained Energy Basis; FMGE - Fossil Motor Gasoline Contained Energy Basis

more prominently in motor gasoline-based intensities since all incremental emissions from additional distillate production are assigned to smaller incremental production of motor gasoline.

However, large differences exist between the Base and ethanol cases. For the 88BV and 88BE cases, GHG intensities are roughly 15% lower than the Base case on a crude oil throughput, White Products produced, or White Products contained energy basis. This significant decrease highlights advantages of ethanol’s gasoline blending properties as refinery operations are decreased from units that generate a disproportionately high level of GHG emissions (e.g. the reformers and FCC unit).

The 97BV and 97BE cases also have roughly equal GHG emissions intensities (2% to 4% lower than the Base case). This is reasonable as high GHG-producing operations at the refinery are operated at higher rates versus the 88BV and 88BE cases. Thus, while the 97BV and 97BE cases do have lower total refinery GHG emissions shown in Fig. 1, most of that reduction is due to the extensive factor of running less crude oil, in contrast to the 88BV and 88BE cases that also have a large intensive factor improvement.

The results shown in Table 4 and Fig. 1 demonstrate the importance of accounting for refinery GHG emissions intensities in life-cycle analysis of higher-level ethanol fuels. While a complete, thorough life-cycle analysis of higher-level blends was beyond the scope of this paper, if only the extensive factor of a reduction in crude oil throughput were considered and changes in the crude oil-based GHG emissions intensity were omitted, a modeler would estimate refinery GHG emissions benefits of 30% ethanol blends at 88 AKI and constant gasoline pool volume to be a reduction of 17,700 metric tons per day for PADD 2. However, with the improved GHG emissions intensity associated with this case, the reduction would actually be nearly twice that value (33,700 metric tons per day). By including both extensive and intensive factors discussed in this paper along with other factors, such as carbon in the BOB blendstock, life-cycle emissions of the blended ethanol, and the efficiency of engines burning the fuel, life-cycle modelers will be able to perform a more complete analysis of some of the exciting fuel-engine options available to make meaningful reductions in transportation fuel GHG emissions in the near-term.

Conclusions

Several national environmental policy objectives could potentially be furthered with higher ethanol blends in conjunction with higher finished gasoline octane rating requirements. Specifically, the results of this study are directly related to furthering three national air quality policy objectives by offering a means of increasing vehicle efficiency (CAFE), reducing sulfur content and emissions in gasoline (Tier 3) and reduction of CO2 emissions (RFS).

An LP model was developed for an aggregate PADD 2 petroleum refinery and utilized to illuminate and dimension changes in GHG emissions of higher-level (30%) ethanol blends in gasoline for 2017 as compared to a 2017 Base case of E10 with no RVP waivers for conventional gasoline. The changes are significant on both extensive and intensive bases among the four ethanol blending cases and, in particular, depend on the specified octane rating requirements in finished gasoline. Using results of this study, refinery GHG emissions can be estimated for ethanol blends between 10% and 30% at BOB octane ratings between 77 AKI and 89 AKI at any gasoline pool energy content between parity and the lower level associated with a constant gasoline pool volume.

Results varied by amounts of crude oil processed, refinery operations required to process the various crude oils, amounts of refinery gasoline blendstock produced (and fuel ethanol blended), and finished gasoline composition and properties. Model results show significant differences.
in total refinery GHG emissions with the largest emissions differences occurring from the fluidized catalytic cracker coke burn and refinery fuel gas combustion related primarily to changes in reformer operations. In total, refinery GHG emissions decline by 12% to 27% from the 2017 Base case for the various 30% ethanol cases due to both the extensive effect of lower crude oil throughput and the generally-overlooked intensive effects of differences in the severity of refining operations.

Research conducted in this study as well as that by Hirschfeld et al. and Speth et al. highlight significant gaps in current life-cycle analyses and provide researchers, policymakers, and others investigating other GHG emissions aspects of higher ethanol level blends a reference point enabling incorporation of the consequential effects of reduced (or increased) levels of petroleum refinery emissions resulting from changes to BOB specifications caused by increased ethanol levels.

**Acknowledgement**

We wish to thank the Illinois Corn Marketing Board for its support of this project.

**References**

1. FAPRI, US Baseline Briefing Book – Projections for Agricultural and Biofuel Markets MU Report #01-13. [Online]. Food and Agricultural Policy Research Institute. Available at: http://www.fapri.missouri.edu/outreach/publications/2013/FAPRI_MU_Report_01_13.pdf [February 25, 2015].

2. US EIA, Annual Energy Outlook 2013. [Online]. US Energy Information Administration, Washington, DC. Available at: http://www.eia.gov/forecasts/aeo/pdf/0383%282013%29.pdf [February 25, 2015].

3. US Congress, Energy Independence and Security Act of 2007. [Online]. US Baseline Briefing Book – Projections for Agricultural and Biofuel Markets MU Report #01-13. [Online]. Food and Agricultural Policy Research Institute. Available at: http://www.fapri.missouri.edu/outreach/publications/2013/FAPRI_MU_Report_01_13.pdf [February 25, 2015].

4. Wang M, Han J, Dunn J, Cai H and Elgowainy A, Well-to-wheels analysis of ethanol–gasoline blends: Quantifying the potential benefits in the United States. Fuel 97:585-594 (2012).

5. Pinto JM and Moro LFL, A planning model for petroleum refineries. Braz. J. Chem. Eng. 17:4-7 (2000).

6. Zhang BJ and Hua B, Effective MILP model for oil refinery-wide production planning and better energy utilization. J Cleaner Prod 15(6):439-448 (2007).

7. García CA, Grossmann I, Harjunkoski I and Kaboré P, A simultaneous optimization approach for off-line blending and scheduling of oil-refining operations. Computers & Chemical Engineering 30(4):614-634 (2006).

8. García A, Gautami G and Khanam S, Hydrogen distribution in the refinery using mathematical modeling. Energy 35(9):3763-3772 (2010).

9. Hirschfeld DS, Kolba JA, Anderson JE, Studzinski W and Frusti J, Refining economics of U.S. Gasoline: octane ratings and ethanol content. Environ Sci Technol 48(19):11064-11071 (2014).

10. Speth R, Chow E, Malina R, Barrett S, Heywood J and Green W, Economic and Environmental Benefits of Higher-Octane Gasoline. Environ Sci Technol 48: 6561–6568 (2014).

11. US EPA, Clean Air Act Permitting for Greenhouse Gases. [Online]. US Environmental Protection Agency, Washington, DC. Available at: http://www.epa.gov/nsr/ghgpermitting.html [February 25, 2015].

12. US EIA, Petroleum & Other Liquids - Product Supplied. [Online]. US Energy Information Administration, Washington, DC. Available at: http://www.eia.gov/dnav/pet/pet_cons_products/9-grtmps [February 25, 2015].

13. US EPA, Tier 3 Vehicle Emission and Fuel Standards Program. [Online]. US Environmental Protection Agency, Washington, DC. Available at: http://www.epa.gov/otaq/tier3.htm [February 28, 2015].

14. US EIA, Petroleum & Other Liquids - Company Level Imports. [Online]. US Energy Information Administration, Washington, DC. Available at: http://www.eia.gov/petroleum/imports/companylevel/archive/ [February 25, 2015].

15. US EIA, Petroleum & Other Liquids - Monthly Archives. [Online]. US Energy Information Administration, Washington, DC. Available at: http://www.eia.gov/petroleum/imports/companylevel/archive/ [February 25, 2015].

16. US EIA, Fuel economy and CO2 emissions of ethanol-gasoline blends: Quantifying the potential benefits in the United States. Fuel 97:585-594 (2012).

17. Jung HH, Leone TM, Shelby M, Anderson J and Collings T, Engine load range and downsize downspeed opportunity. SAE Int. J. Engines 6(1): 422-434 (2013).

18. US EIA, Tier 3 Vehicle Emission and Fuel Standards Program. [Online]. US Environmental Protection Agency, Washington, DC. Available at: http://www.epa.gov/otaq/tier3.htm [February 25, 2015].

19. GRTMPS, Haverly Systems, Inc., Denville, New Jersey. Available at: http://www.ethanolrfa.org/pages/2015-highlight-significant-gaps-in-current-life-cycle-analyses-and-provide-researchers-policymakers-and-others-investigating-other-ghg-emissions-aspects-of-higher-ethanol-level-blends-a-reference-point-enabling-incorporation-of-the CONSEQUENTIAL-EFFECTS-OF-REDUCED-OR-INCREASED-LEVELS-OF-PETROLEUM-REFINERY-EMISSIONS-RESULTING-FROM-CHANGES-TO-BOB-SPECIFICATIONS CAUSED-BY-INCREASED-ETHANOL-LEVELS.

20. Oil & Gas Journal. OGJ Survey Downloads. [Online]. Oil and Gas Journal, Tulsa, OK. Available at: http://www.ogj.com/ogj-survey-downloads.html [February 25, 2015].

21. US EIA, Petroleum & Other Liquids - Product Supplied. [Online]. US Energy Information Administration, Washington, DC. Available at: http://www.eia.gov/petroleum/imports/companylevel/archive/ [February 25, 2015].

22. Oil & Gas Journal. OGJ Survey Downloads. [Online]. Oil and Gas Journal, Tulsa, OK. Available at: http://www.ogj.com/ogj-survey-downloads.html [February 25, 2015].

23. US EIA, Annual Energy Outlook 2011. US Energy Information Administration, Washington DC. Available at: http://www.eia.gov/forecasts/archive/aeo11/index.cfm [February 25, 2015].

© 2015 The Authors. Biofuels, Bioproducts, Biorefining published by Society of Chemical Industry and John Wiley & Sons, Ltd. Biofuels, Bioprod. Bioref. 10:36–46 (2016); DOI: 10.1002/bbb
Vincent Kwasniewski
Currently an independent business-technology consultant, Vincent Kwasniewski earned his PhD in chemical engineering from the University of Minnesota and his BS in chemical engineering from Northwestern University and has over twenty years of work experience in biofuels, petrochemicals, and oil refining.

John Blieszner
John Blieszner is a Group Manager at Jacobs Consultancy. He is responsible for developing, leading, and performing engagements in management and technical consulting and developing economic and industry forecasts. His areas of expertise are in energy and greenhouse gases, oil and gas production, oil sands/upgrading, refining, and petrochemicals, as well as in technical and financial risk management, strategy development, and quantitative decision analysis.

Richard Nelson
Richard Nelson is founder of Enersol Resources, a private consulting firm specializing in energy, environmental, and agricultural assessment and analysis. He has over 25 years experience in the biomass and bioenergy field and has served as a consultant to the US Department of Energy, the Western Governors’ Association, the National Biodiesel Board, and other additional public and private entities and agencies. He has also been a member of biomass and bioenergy-related task forces and working groups for the California Air Resources Board, the Western Governors’ Association, the US Environmental Protection Agency, and the International Energy Agency and is a primary or collaborative author on more than 20 peer-reviewed publications as well as numerous technical reports focused on renewable energy, sustainability, environmental quality, and agriculture. Dr. Nelson holds degrees in both mechanical and agricultural engineering from Oklahoma State University. He was formerly at Kansas State University with the Center for Sustainable Energy.