

# Combustion Emissions from Refining Lower Quality Oil: What Is the Global Warming Potential?

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The greenhouse gas emission intensity of refining lower quality petroleum was estimated from fuel combustion for energy used by operating plants to process crude oils of varying quality. Refinery crude feed, processing, yield, and fuel data from four regions accounting for 97% of U.S. refining capacity from 1999 to 2008 were compared among regions and years for effects on processing and energy consumption predicted by the processing characteristics of heavier, higher sulfur oils. Crude feed density and sulfur content could predict 94% of processing intensity, 90% of energy intensity, and 85% of carbon dioxide emission intensity differences among regions and years and drove a 39% increase in emissions across regions and years. Fuel combustion energy for processing increased by approximately 61 MJ/m<sup>3</sup> crude feed for each 1 kg/m<sup>3</sup> sulfur and 44 MJ/m<sup>3</sup> for each 1 kg/m<sup>3</sup> density of crude refined. Differences in products, capacity utilized, and fuels burned were not confounding factors. Fuel combustion increments observed predict that a switch to heavy oil and tar sands could double or triple refinery emissions and add 1.6–3.7 gigatons of carbon dioxide to the atmosphere annually from fuel combustion to process the oil.

## Introduction

Replacing limited conventional crude oil (1) with heavy oil and natural bitumen (tar sands) resources could have substantial energy and environmental costs (2). Physical and chemical properties of the lower quality, heavier, more contaminated oils predict the combustion of more fuel for the energy necessary to convert them into product slates dominated by light hydrocarbon liquids (3–8). Preliminary estimates from fuel cycle analyses suggest that a switch to heavy oil and tar sands could increase the greenhouse gas emission intensity of petroleum energy by as much as 17–40%, with oil extraction and processing rather than tailpipe emissions accounting for the increment (3, 4). This raises the possibility that a switch to these oils might impede or foreclose the total reduction in emissions from all sources that is needed to avoid severe climate disruption. Accurate prediction of emissions from substitutes for conventional petroleum is therefore critical for climate protection. However, estimates of the emissions from processing lower quality oils have not been verified by observations from operating refineries.

Crude oils are extremely complex, widely ranging mixtures of hydrocarbons and organic compounds of heteroatoms

and metals (2, 7). Refiners use many distinct yet interconnected processes to separate crude into multiple streams, convert the heavier streams into lighter products, remove contaminants, improve product quality, and make multiple different products in varying amounts from crude of varying quality (5–11). Factors that affect emissions from refinery process energy consumption include crude feed quality, product slates, process capacity utilization, fuels burned for process energy, and, in some cases, preprocessing of refinery feeds near oil extraction sites. Estimates that construct process-by-process allocations of emissions among these factors have not been verified by observations from operating refineries in part because publicly reported data are limited for refinery-specific crude feeds and unavailable for process-level material and energy inputs and outputs (4–6). Research reported here distinguishes effects of crude feed quality on processing from those of the other factors using refinery-level data from multiple operating plants to estimate and predict the process energy consumption and resultant fuel combustion emissions from refining lower quality oil.

## Experimental Section

Refinery crude feed volume, density, and sulfur content, process capacity, capacity utilization, yield, and fuels were reported annually for each U.S. Petroleum Administration Defense District from 1999 to 2008 (9, 10). See the Supporting Information for this data (Table S1, Supporting Information). Districts 1 (East Coast–Appalachia), 2 (Midwest), 3 (Gulf Coast and vicinity), and 5 (West Coast, AK, and HI) each refined diverse crude feeds (19–41 source countries) at multiple facilities. Smaller, landlocked District 4 (Rocky Mountain states) refined nondiverse crude feeds (2–3 source countries).

At concentrations 4–8 times those of nitrogen and 160–500 times those of nickel and vanadium, sulfur is the major process catalyst poison in crude by mass (2, 11). In addition, for diverse blends of whole crude oils from many locations and geologic formations, distillation yield, and asphaltic, nitrogen, nickel, and vanadium content are roughly correlated with density and sulfur (2, 7). Variability in the effects of unreported crude feed characteristics on processing is thus constrained by the density and sulfur content of well-mixed crude feeds. Mixing analysis suggested that density and sulfur are reasonably reliable predictors of natural variability in unreported characteristics for annual crude feeds processed in Districts 1, 2, 3 and 5 but could not exclude the potential for unreported effects in processing the poorly mixed District 4 feed (Table S2, Supporting Information). The District 4 feed also was proportionately higher in synthetic crude oil (SCO) than those of other districts (Table S3, Supporting Information), and variant hydrogen production that was not predicted by crude feed density was found in District 4 (Table S4, Supporting Information). SCO may increase refinery hydroprocessing requirements (12, 13). High hydrogen capacity coincided with SCO refining in Districts 2 and 4 during 1999–2008, but the effect on refinery energy was minimal in District 2, while it was significant and more variable in District 4; other anomalies in the District 4 feed might cause this effect (Tables S2 and S4, Supporting Information). For these reasons, District 4 data were excluded from analysis of refinery observations and used only in estimates including upgrading for SCO. Districts 1, 2, 3, and 5 accounted collectively for 97% of U.S. refining capacity, 1999–2008. Analysis compared the reported data among these districts and years for interactions of the variables defined below.

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Oil quality (*OQ*) was defined as the density (*d*) and sulfur content (*S*) of crude feeds in mass per cubic meter (1 m<sup>3</sup>, 6.29 barrels oil; 264 gallons). The density of crude oils is proportional to the fraction of higher molecular weight, higher boiling point, larger hydrocarbon compounds in the oils that are distilled in a vacuum, then cleaved (cracked) into fuel-size compounds to make light hydrocarbon fuels. The larger hydrocarbons have lower hydrogen/carbon ratios that require hydrogen addition to improve product quality and higher concentrations of sulfur and other catalyst poisons that are freed by cracking and bonded with hydrogen to remove them from the oil and protect process catalysts (2, 11). This hydrocracking and hydrotreating of gas oil and residua uses several times more hydrogen than does hydrotreating of lighter streams such as naphtha (11). These processing characteristics require increased capacity for vacuum distillation, cracking, and hydroprocessing of gas oil and residua in refineries designed to make light liquid products from heavier, higher sulfur crude oils (4, 8, 14).

Crude processing intensity (*PI*) was thus defined as the ratio by volume of vacuum distillation capacity, conversion capacity (catalytic, thermal, and hydrocracking), and crude stream (gas oil and residua) hydrotreating capacity to atmospheric crude distillation capacity. These processes account for the primary processing acting on the crude and “reduced crude” that *Speight* distinguishes from secondary processes acting on product streams such as gasoline, naphtha, and distillate oils (7). *PI* measures the increasing portion of the crude input fed to these processes that is predicted by worsening *OQ* (increasing *d*, *S*, or both) and indicates the additional energy needed for heat, pressure, and reactants such as hydrogen to process those increasing feed volumes. It also defines an operational distinction between “crude stream” processing that acts on crude, gas oils, and residua and the subsequent “product stream” processing that acts on the unfinished products from crude stream processing. This distinction was useful in the absence of reported data for more detailed process-level analyses of material and energy flows. *PI* was analyzed with refinery-level crude feed, fuel, capacity utilization, and product yield data to verify the refinery process energy predicted by *OQ*.

Energy intensity (*EI*) was defined as total refinery process energy consumed per volume crude feed, based on reported fuels consumed (Table S1, Supporting Information). Purchased fuels consumed by refiners, such as electric power from the transmission grid, were included in *EI*. Energy used by hydrogen production plants was estimated based on 90% of production capacity and data for new natural gas-fed steam methane reforming facilities (10, 15, Table S1, Supporting Information). *EI* integrates all factors in refineries that consume fuel energy, allowing analysis of *EI* with *OQ* and processing to account for refinery capacity utilized and yield.

Effects of variable product slates on refinery energy consumption were distinguished from those of *OQ* in five ways. First, product slate effects on the relationships observed among crude feed quality, crude stream processing, and energy were estimated directly. This was done by including the products ratio, defined as the volume of gasoline, kerosene, distillate, and naphtha divided by that of other refinery products, as an explanatory variable in comparisons of *OQ*, *PI*, and *EI*. Second, the products ratio, combined yield of gasoline and distillate, and combined yield of petroleum coke and fuel gas were analyzed with *EI* and *OQ*. This quantified changes in refinery energy with yield and changes in yield with crude feed quality for key conversion products and byproducts. Third, energy use was analyzed with product stream process capacities to estimate changes in *EI* that could be explained by changes in product processing rates. Fourth, effects of product stream processing on energy for hydrogen were compared with those of crude stream processing by

analyzing hydrogen production capacity with product hydrotreating capacity, hydrocracking capacity, and *OQ*. Finally, estimated total energy for processing product slates (Eproducts) was analyzed with *OQ*. Eproducts was estimated based on product-specific factors developed by Wang et al. (6) and yield data (Tables S1 and S5, Supporting Information). Refinery capacity utilization was included as an explanatory variable in all comparisons.

Analysis was by partial least squares regression (PLS, XLSTAT 2009). PLS was used based on the expectation that explanatory (*x*) variables may be correlated, the primary interest in prediction of *y* (e.g., *EI*) and a secondary interest in the weights of *x* variables (e.g., *S* and *d*) in predicting *y*. Distributions of PLS residuals appeared normal (Shapiro-Wilk; Anderson-Darling; Lilliefors; Jarque-Bera tests,  $\alpha$  0.05).

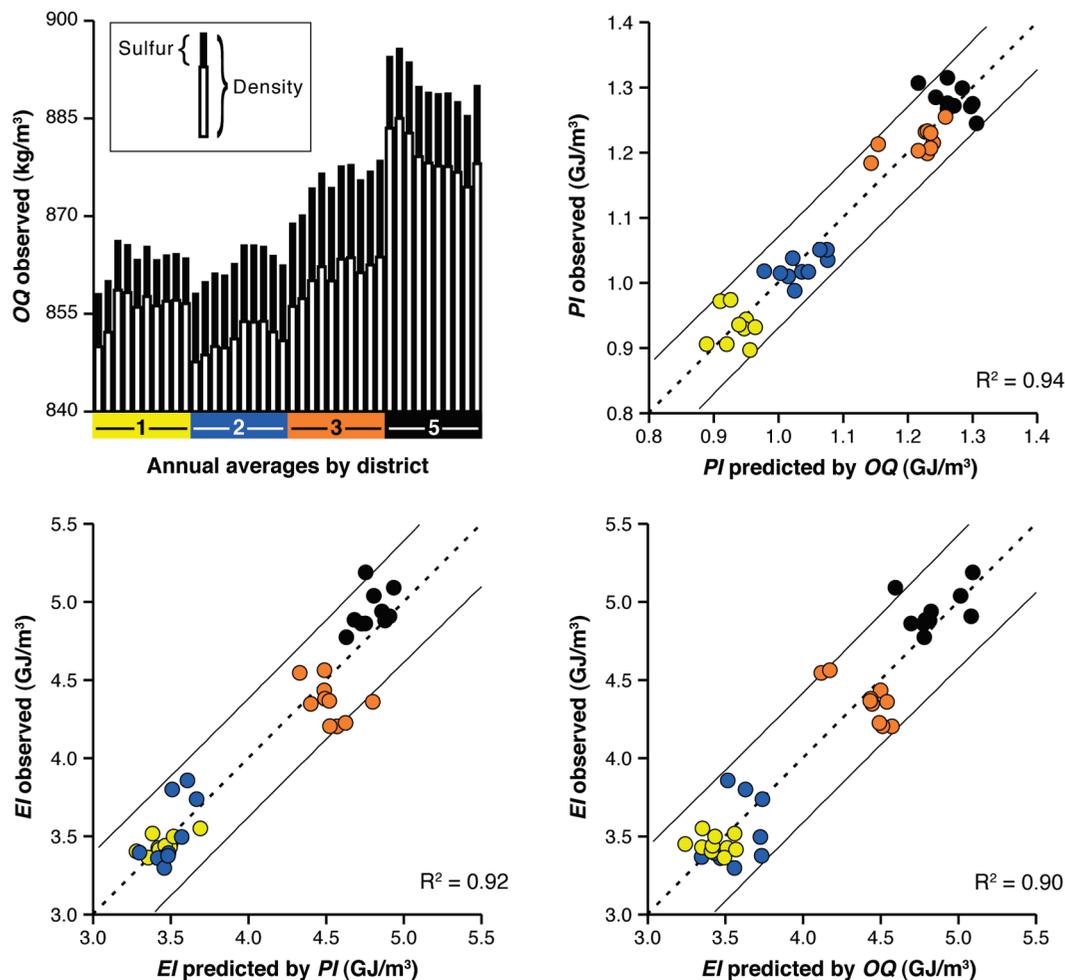
**Synthetic Crude Oil (SCO).** Coking- and hydrocracking-based upgrading of bitumen in Western Canada uses energy to yield SCO that has poor gas oil and distillate qualities but lower density and sulfur than the bitumen (12, 13). Refinery crude feeds and energy consumption do not reflect the original bitumen quality for this SCO or the energy used in its upgrading. SCO comprised appreciable fractions of annual crude feeds in Districts 2 (2–8%) and 4 (2–12%), based on limited estimates that may exclude SCO in some blended oil streams (Table S3, Supporting Information). Process modeling data for energy consumed and density and sulfur lost in coking- and hydrocracking-based upgrading (16) were applied to the estimated SCO volume in refinery feeds (Table S3, Supporting Information). Districts and years were compared for total processing (upgrading and refining) energy estimated and that predicted by including estimated original oil quality (*d*, *S*) in the prediction mode of the PLS model based on refinery observations (Table S6, Supporting Information).

**Emissions.** Emissions were assessed for carbon dioxide (CO<sub>2</sub>), the predominant greenhouse gas emitted by refineries (Table S7, Supporting Information). Direct measurements for all emission vents were not reported. Observed fuel consumption and fuel-specific emission factors developed by the U.S. Energy Information Administration (17, 18) were used to estimate “observed” emissions, and estimation details were documented (Table S1, Supporting Information). Fuel energy consumed ranged more widely among districts and years than the emission intensity of the fuel mix. Emissions predicted by *OQ* were based on *EI* predicted by *OQ* results from PLS and the emission intensity of the fuel mix. Observed and predicted emissions were compared among districts and years by PLS. Emissions estimates by government agencies (5, 19–21) that could be matched to data for *OQ* were superimposed on this comparison by including their *OQ* and predicted *EI* values in the prediction mode of the PLS models for the districts data (Tables S8 and S9, Supporting Information).

For heavy oil and natural bitumen, *OQ* data reported by the U.S. Geological Survey (2) and the average (1999–2008) U.S. refinery capacity utilization and products ratio were used in the prediction mode of the PLS model for observed *EI* versus *OQ* to predict *EI* (Table S8, Supporting Information). Predicted emissions from heavy oil and natural bitumen were derived from the products of these *EI* predictions (95% confidence for observations) and the emission intensity of the average (1999–2008) U.S. refinery fuel mix.

## Results

Figure 1 shows results from comparisons of *OQ*, *PI*, and *EI* among districts and years from 1999 to 2008. Observed *OQ* ranges by 7.85 kg/m<sup>3</sup> crude feed (kg/m<sup>3</sup>) for *S* and 37.6 kg/m<sup>3</sup> for *d*. Observed *PI* ranges by 0.42, or 42% of atmospheric crude distillation capacity. Observed *EI* ranges by 1.89 GJ/m<sup>3</sup> crude feed. *PI* is strongly and positively associated with



**FIGURE 1. Increasing crude processing intensity and energy intensity with worsening oil quality. *OQ*: Crude feed oil quality. *PI*: Crude processing intensity. *EI*: Refinery energy intensity. Observations are annual weighted averages for districts 1 (yellow), 2 (blue), 3 (orange), and 5 (black) in 1999–2008. Diagonal lines bound the 95% confidence of prediction for observations.**

worsening *OQ* (increasing  $d$ ,  $S$ , or both). *EI* is strongly and positively associated with worsening *OQ* and increasing *PI*. *EI* increases by approximately 44 MJ/m<sup>3</sup> for each 1 kg/m<sup>3</sup>  $d$  and 61 MJ/m<sup>3</sup> for each 1 kg/m<sup>3</sup>  $S$  based on the PLS regression analysis for *EI* versus *OQ*. The equation of the model (*EI* vs *OQ*) can be expressed as

$$EI = 0.044d + 0.061S + 0.010(\text{Capacity utilized}) - 0.159(\text{Products ratio}) - 35.092 \quad (1)$$

where *EI* is the central prediction in GJ/m<sup>3</sup>,  $d$  is in kg/m<sup>3</sup>,  $S$  is in kg/m<sup>3</sup>, capacity utilized is in percent, products ratio is expressed as a quotient, and the last term is the coefficient for the intercept.

Table 1 shows additional results from analysis of refinery observations. *PI* increases strongly with  $d$  and  $S$  (95% confidence for observations). *EI* increases strongly with  $d$  and  $S$  and with vacuum distillation, conversion, and crude stream hydrotreating capacities. Hydrogen production capacity increases strongly with  $d$  and hydrocracking capacity. Sulfur recovery capacity increases strongly with  $S$ . These observations describe increasing portions of crude feeds processed by crude stream capacity and resultant effects on total refinery energy consumption as crude density and sulfur content increase.

In contrast to crude stream processing, except for cracking byproducts and two processes that treat them, product slate indicators are not significant or decrease with increasing *OQ* and *EI*. The products ratio is not significant in the strong relationships among *EI*, *PI*, and *OQ*, perhaps in part because

light liquids yield is less variable than  $S$  or *EI* among these districts and years. However, the ratio of light liquids to other products decreases with increasing  $d$  (products ratio vs *OQ*) and *EI* (*EI* vs products processing), and yield shifts, from gasoline and distillate to coke and fuel gas, as *OQ* worsens and *EI* increases.

Products processing reflects this shift from light liquids to cracking byproducts. Product stream hydrotreating, reforming, asphalt, aromatics, and polymerization/dimerization capacities decrease as *EI* increases. Those five processes account for 83–90% of total product stream processing capacity among districts (Table S1, Supporting Information). Among products processes, only alkylation and isomerization (7–13% of products capacity), which receive light streams from conversion processes, are positively associated with *EI*. Product hydrotreating cannot explain the observed increase in hydrogen production with increasing  $d$ . Estimated refinery energy use for products processing (*Eproducts*) decreases with increasing  $d$ . These results appear to measure the decreasing fraction of crude inputs converted to light liquid product streams and increasing creation of cracking byproducts such as coke and fuel gas that result from incomplete conversion as crude feed density and sulfur increase.

A weak inverse association of hydrogen production with product hydrotreating capacity (Table 1) results from a strong increase in H<sub>2</sub> capacity with  $d$  and hydrocracking, a steady decrease in the hydrotreating/hydrocracking ratio with increasing H<sub>2</sub> capacity, and lower hydrotreating at high

**TABLE 1. Results from Refinery Crude Feed Quality, Processing, Energy, Yield, and Emission Comparisons<sup>a</sup>**

effects of crude feed oil quality (OQ)					
y vs x	R <sup>2</sup>	standardized coefficients of x variables (coeff)			
		density	sulfur	cap. utilized	products ratio
process intensity (PI) vs OQ	0.94	<b>0.73</b>	<b>0.42</b>	<b>0.09</b>	-0.02
energy intensity (EI) vs OQ	0.90	<b>0.80</b>	<b>0.23</b>	0.05	-0.10
hydrogen production vs OQ	0.91	<b>1.09</b>	-0.01	0.05	<b>0.35</b>
sulfur recovery vs OQ	0.94	-0.01	<b>0.95</b>	-0.06	<b>-0.15</b>
pet. coke + fuel gas vs OQ	0.95	<b>0.80</b>	<b>0.34</b>	-0.04	
gasoline + distillate vs OQ	0.75	<b>-0.85</b>	-0.07	-0.04	
products ratio vs OQ	0.26	<b>-0.40</b>	-0.12	0.17	
Eproducts vs OQ	0.74	<b>-0.61</b>	0.13	<b>0.49</b>	

effects of oil quality (OQ) and fuels on CO <sub>2</sub> emissions			
y vs x	R <sup>2</sup>	standardized coefficients of x variables (coeff)	
		EI predicted by OQ	fuel mix emission intensity
observed vs predicted CO <sub>2</sub>	0.85	<b>0.88</b>	-0.04

effects of processing and products yield					
y vs x	R <sup>2</sup>	coeff.	y vs x	R <sup>2</sup>	coeff.
EI vs PI	0.92		EI vs yield	0.93	
vacuum distillation		<b>0.35</b>	pet. coke + fuel gas		<b>0.59</b>
conversion capacity		<b>0.35</b>	gasoline + distillate		<b>-0.42</b>
csHydrotreating		<b>0.22</b>	capacity utilized		-0.01
capacity utilized		<b>-0.16</b>	products ratio		-0.02
products ratio		-0.14			
H <sub>2</sub> production vs hydrocracking	0.97		EI vs psProcessing	0.91	
hydrocracking		<b>1.02</b>	psHydrotreating		<b>-0.17</b>
capacity utilized		-0.06	reforming		<b>-0.19</b>
products ratio		<b>0.14</b>	asphalt		<b>-0.30</b>
			aromatics		<b>-0.33</b>
H <sub>2</sub> production vs product-stream hydrotreating			polym./dimerization		<b>-0.25</b>
	0.18		lubricants		0.04
psHydrotreating		<b>-0.33</b>	alkylation		<b>0.30</b>
capacity utilized		-0.09	isomerization		<b>0.24</b>
products ratio		<b>-0.17</b>	capacity utilized		-0.06
			products ratio		<b>-0.33</b>

<sup>a</sup> R-squared values and standardized coefficients from PLS regressions on annual data from refining districts 1, 2, 3 and 5, 1999–2008. **Boldface:** significant at 95% confidence. Eproducts: estimated energy use to process a given product slate. Prefix cs (ps): crude stream (product stream) processing.

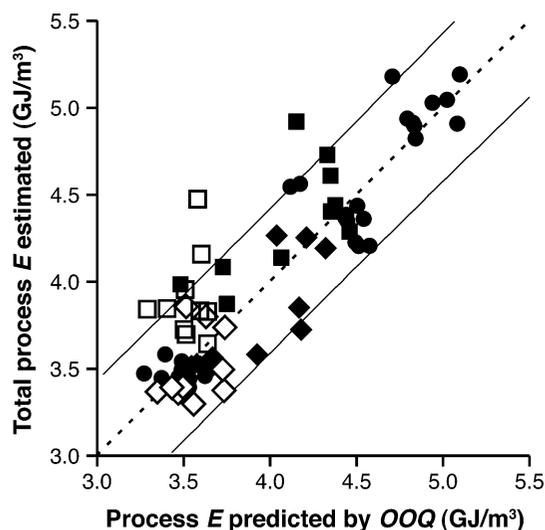
H<sub>2</sub> capacity among these districts and years (Figure S1, Supporting Information). Refinery capacity utilization was not significant in the effects of OQ on EI and affected the relationships between PI and OQ and between PI and EI only marginally, possibly because capacity utilization varied little among districts and years (Table S1, Supporting Information). Significant capacity utilization results are consistent with marginally increased energy consumption and decreased flexibility to process lower quality crude when refineries run closer to full capacity.

Rough estimates including the energy, *d*, and *S* lost in bitumen upgrading for SCO refined reveal greater effects of total processing for crude feeds refined in Districts 2 and 4 and follow the relationships observed in refining (Figure 2). Estimated total processing energy falls within the prediction based on OQ from refinery observations in 43 of 50 cases and exceeds the 95% confidence of prediction by more than 2% only in two cases explained by District 4 hydrogen anomalies discussed above. Oil quality–energy relationships observed in refining can predict those for total processing because upgrading and refining use similar carbon rejection, hydrogen addition, and utility technology.

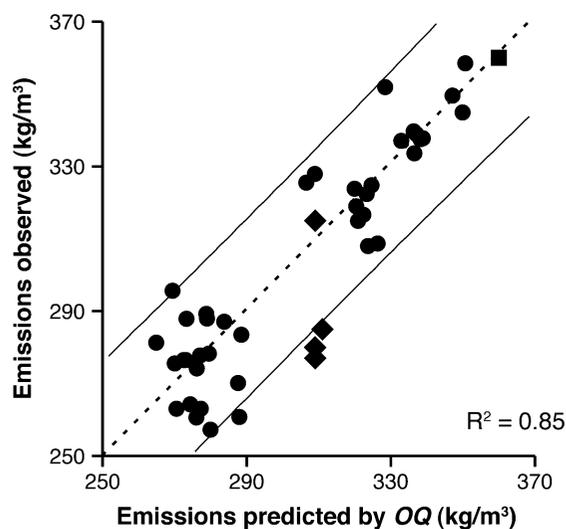
Emissions calculated from observed fuels consumed are strongly and positively associated with EI predicted by OQ (Table 1) and range by 39%, from 257 to 358 kg/m<sup>3</sup> crude

feed (Figure 3). Observed emissions fall within the 95% confidence of prediction based on OQ in 36 of 40 cases and are within 3% of the confidence of prediction in all cases. Despite emission differences among fuels, the fuel mix is not significant in this prediction. The emission intensity of the fuel mix varies much less than EI and decreases slightly with decreasing petroleum coke contributions and a shift in cracking processes as EI, *d*, and *S* increase (Table S1 and Figure S1, Supporting Information). Refinery emission estimates by government agencies that could be matched to OQ differ from each other by as much as 12–30% but fall within 2% of the central prediction based on OQ or within 4% of its confidence interval (5, 19–21, Table S8, Supporting Information). The 2008 San Francisco Bay Area estimate in Figure 3 (360 kg/m<sup>3</sup>) is close to estimated 2008 California refinery emissions (354 kg/m<sup>3</sup>) (21), for which matching OQ data were not available. California gasoline and diesel production may account for 56% (197.2 kg) and 22% (78.7 kg) of this 354 kg/m<sup>3</sup>, respectively, based on fuel-specific estimates for the average California crude feed (21–23, Table S8, Supporting Information).

Predictions for heavy oil (957.4 kg/m<sup>3</sup> *d*; 27.8 kg/m<sup>3</sup> *S*) and natural bitumen (1 033.6 kg/m<sup>3</sup> *d*; 45.5 kg/m<sup>3</sup> *S*) (USGS average) (2) reflect their low quality compared with crude feeds observed (Figure 1). On the basis of the PLS model for



**FIGURE 2.** Estimated process energy for bitumen upgrading and refining versus that predicted by oil quality ( $\text{GJ}/\text{m}^3$  crude), 1999–2008. *OQ*: original oil quality including bitumen quality for synthetic oil inputs. Black diamonds: District 2. Black squares: District 4. Black circles: Districts 1, 3, and 5. White diamonds (squares): District 2 (District 4) refinery energy and oil quality only. Diagonal lines bound the 95% confidence of prediction for refinery observations.



**FIGURE 3.** Refinery  $\text{CO}_2$  emission intensity observed versus predicted by oil quality. *OQ*: Oil quality. Black circles: District 1, 2, 3, or 5 annually, 1999–2008. Black diamonds: United States in 2002, 2005, 2006, 2007. Black square: San Francisco Bay Area in 2008. Diagonal lines bound the 95% confidence of prediction for observations.  $R^2$  value shown is for the comparison among districts and years.

observations from Districts 1, 2, 3, and 5 (*EI* vs *OQ*) and the emission intensity of the U.S. refinery fuel mix ( $73.8 \text{ kg}/\text{GJ}$ ), processing the range of heavy oil/bitumen blends could use  $8.23\text{--}14.13 \text{ GJ}/\text{m}^3$  fuel (Table S8, Supporting Information) and emit  $0.61\text{--}1.04 \text{ t}/\text{m}^3 \text{ CO}_2$ .

## Discussion

Strongly coupled increases in energy and crude stream processing intensities with worsening oil quality (Figure 1) describe energy for carbon rejection, aggressive hydrogen addition, and supporting processes acting on larger portions of heavier, higher sulfur crude feeds to yield light liquid product streams. The creation of cracking reaction byproducts that limits conversion of heavier oils to light liquid

product streams is observed in the shift from gasoline and distillate to coke and fuel gas yield as *OQ* worsens and *EI* increases. Observed decreases in light liquids yield and most major product stream processes as *EI* increases are consistent with this rising reliance on incomplete conversion. Differences in product slates cannot explain increasing *EI* as *OQ* worsens because capacities of processes comprising 83–90% of product stream processing capacity decrease as *EI* increases, and estimated energy use for products processing decreases as *OQ* worsens. Hydrogen production increases with crude density and hydrocracking. *EI* drives emissions variability. *OQ* predicts 94% of *PI*, *PI* predicts 92% of *EI*, and *OQ* predicts 90% of *EI* and 85% of emissions variability. These observations from operating plants across the four largest U.S. refining districts over 10 years provide evidence that crude feed density and sulfur content predict processing, energy, and  $\text{CO}_2$  emission intensities for large groups of refineries with diverse feeds.

Slight, unexpected decreases in product hydrotreating at high hydrogen production and in fuel mix emission intensity with increasing *d* and *S* can be explained by a coincident shift from hydrotreating and catalytic cracking to hydrocracking with worsening *OQ*. Refiners can substitute hydrocracking for hydrotreating and catalytic cracking to some extent. *OQ*, along with other factors beyond this study scope, may influence those business decisions.

Energy increments predicted by density ( $44 \text{ MJ}/\text{kg}$ ) and sulfur ( $61 \text{ MJ}/\text{kg}$ ) in crude feeds (eq 1) compare to energy inputs of  $40\text{--}70 \text{ MJ}/\text{kg}$  density (including sulfur) lost from bitumen upgrading for *SCO*, based on process modeling of coking- and hydrocracking-based upgraders ((16), Table S6, Supporting Information). At an energy cost of  $16.4 \text{ MJ}/\text{m}^3$  (Table S1, Supporting Information), hydrogen for density reduction by hydrocracking could account for  $44 \text{ MJ}/\text{kg}$ , based on the  $\text{H}_2/\text{oil}$  feed ratio of  $308 \text{ m}^3/\text{m}^3$  Robinson and Dolbear report for  $22^\circ\text{API}$  feed and  $44^\circ\text{API}$  yield (11).

Results help to explain differences among government estimates of refinery emissions (Figure 3) and support the high case fuel cycle emission increments from a switch to heavy and tar sands oils reported for gasoline by Brandt and Farrel (+40%) (3) and for diesel by Gerdes and Skone (+17%) (4). Predicted emissions from processing heavy oil/natural bitumen blends ( $0.61\text{--}1.04 \text{ t}/\text{m}^3$ ) are 2–3 times the average of observed and estimated emissions in Figure 3 ( $0.30 \text{ t}/\text{m}^3$ ). Assuming this  $0.30 \text{ t}/\text{m}^3$  refining average and 2007 world petroleum emissions ( $11.27 \text{ Gt}$ ) (24) as a baseline, processing heavy oil/bitumen blends at 2009 world refining capacity ( $5.06 \times 10^9 \text{ m}^3$ ) (10) could increase annual  $\text{CO}_2$  emissions by  $1.6\text{--}3.7$  gigatons and total petroleum fuel cycle emissions by 14–33%. Extraction emissions would add to these percentages.

This prediction applies to average  $\text{CO}_2$  emissions from large, multiplant refinery groups with diverse, well-mixed crude feeds and appears robust for that application. However, the method used here should be validated for other applications. If it is applied to different circumstances, the potential for significantly different product slates, poorly mixed crude feeds, synthetic crude oil impacts on refining, and effects on fuel mix emission intensity and hydrotreating resulting from choices among carbon rejection and hydrogen addition technologies should be examined.

Several issues suggest future work. Other properties of crude feeds and incremental efficiencies from modernization of equipment and catalyst systems might explain up to 10% of the variability in *EI* observed among U.S. refining districts and years and could be more important for single plants and nondiverse crude feeds. Burning more fuel to refine lower quality oil emits toxic and ozone-precursor combustion products along with  $\text{CO}_2$ . Pastor et al. estimate that refinery emissions of such “co-pollutants” dominate health risk in nearby communities associated with particulate matter

emitted by the largest industrial sources of greenhouse gases in California and identify racial disparities in this risk as important in emission assessment (25). Better facility-level OQ data could improve local-scale pollutant assessment. Better crude quality predictions could improve energy, and climate protection, forecasts. Assessments of the need, scope, and timing for transition to sustainable energy should account for emissions from lower quality oil.

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## Supporting Information Available

Data and details of methods, analyses, and results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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