

# Toxic and fine particulate emissions from U.S. refinery coking and cracking of ‘tar sands’ oils

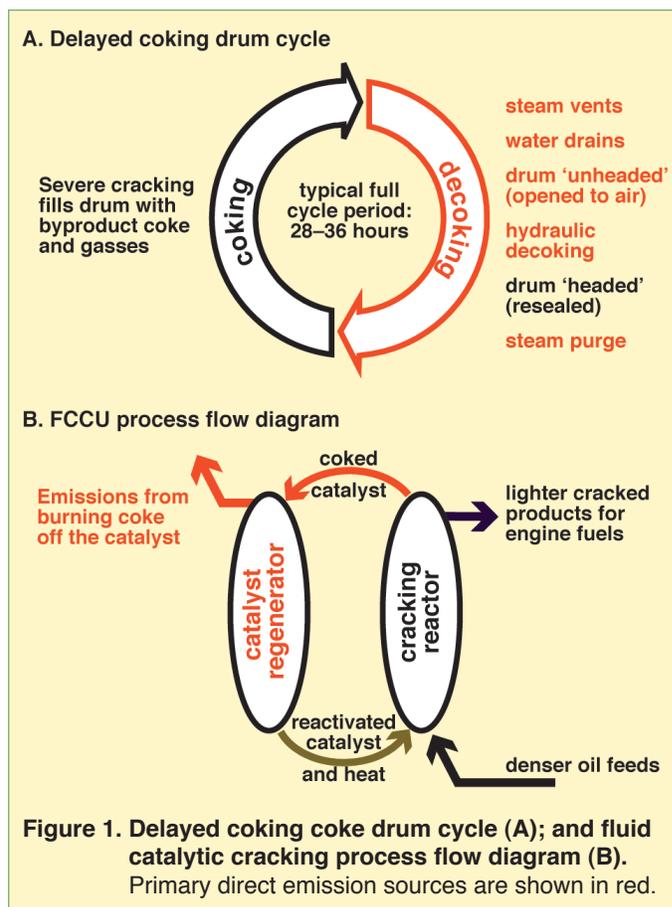
Greg Karras (2015).\*

Emissions of toxic and criteria air pollutants from delayed coking units (DCUs) and catalytic cracking units (CCUs) were assessed for scenarios in which 20–50% of current US refinery crude oil feed might be replaced by diluted bitumen (dilbit) oils. Refinery- and process-level data for feedstock properties, process capabilities, and emissions were compared across the US industry to estimate changes in processing needed to maintain transport fuels production from the changing feedstock, and in resultant emissions. The shift from mid-barrel to denser and more contaminated oils from crude distillation of dilbits could swing hydrocracking to diesel and jet fuel and would increase DCU and CCU feed rates and coke yields. Volatile emissions from DCUs could increase by 14–47% and coke combustion emissions from CCUs could increase by 14–25% in +20–50% dilbit scenarios. Condensable particulate matter emissions from CCUs could increase by 500–1,300 metric tons per year (t/y) in the +20% dilbit scenario and 900–2,400 t/y in the +50% dilbit scenario. Benzene emissions from DCUs, though poorly measured, might increase by 46–95 t/y, and 150–320 t/y, in the respective scenarios. These industry-wide estimates for US DCUs and CCUs assume a plausible but elective crude oil switch without mitigation, and are limited by a paucity of measurements for most of the >100 toxic chemicals found in emissions from these units. Future work might focus on feedstock-driven changes in storage tank, hydroprocessing, and coker byproduct emissions.

## Introduction

US refineries have gradually shifted to denser, more contaminated, lower quality crude feeds over three decades<sup>1</sup> and have begun to exploit vast potential supplies of still denser and more contaminated heavy oil and bitumen.<sup>2,3</sup> Bitumen—‘tar sands’ oil—is fundamentally different from conventional crude.<sup>3</sup> Processing lower quality oil is known to increase oil refining pollution intensity by increasing the pass-through of toxic elements in the oils,<sup>4</sup> the fuel combustion for energy needed to refine them<sup>5–10</sup> and the frequency and magnitude of plant upsets, spills, fires and flaring.<sup>11–13</sup> However, relatively little has been done to characterize feedstock-driven emissions from some high-emitting refinery processes—including the delayed coking and catalytic cracking processes.

Delayed coking units (DCUs) account for ≈95% of U.S. refining capacity to thermally crack residuum (resid),<sup>14</sup> the densest and most contaminated fraction (cut) of crude from atmospheric or vacuum distillation. DCUs perform



severe thermal cracking at ≈415–515 °C and ≈15–90 psi for hours to yield liquid oils and contaminated byproducts that are typically burned as fuels, including hydrocarbon gasses, and petroleum coke that can be 9–12% volatile chemicals.<sup>15–18</sup> This is a batch process that must interrupt feed to each reactor vessel (drum) to remove the coke, so DCUs typically have 2–8 drums in order to process resid semicontinuously. Decoking involves venting the drum, draining quench water from it, opening it to drill out the coke, and purging the drum after it is resealed—and all of that can introduce volatile chemicals to the atmosphere. *See* Figure 1. Direct measurements suggest that this inherently polluting design may place DCUs among the largest sources of volatile organic compounds such as benzene in refineries.<sup>19</sup>

Catalytic cracking units (CCUs) account for ≈83% of US refinery capacity to crack heavy gas oil (HGO).<sup>14</sup> HGO distills at ≈343–566 °C and is the second densest, second most contaminated cut of whole crude after resid.

\* This work was conducted for the Natural Resources Defense Council (NRDC) as part of a technical assistance contract. Author info., gkatche@gmail.com; c/o Communities for a Better Environment (CBE), 1904 Franklin St., Suite 600, Oakland CA 94612.

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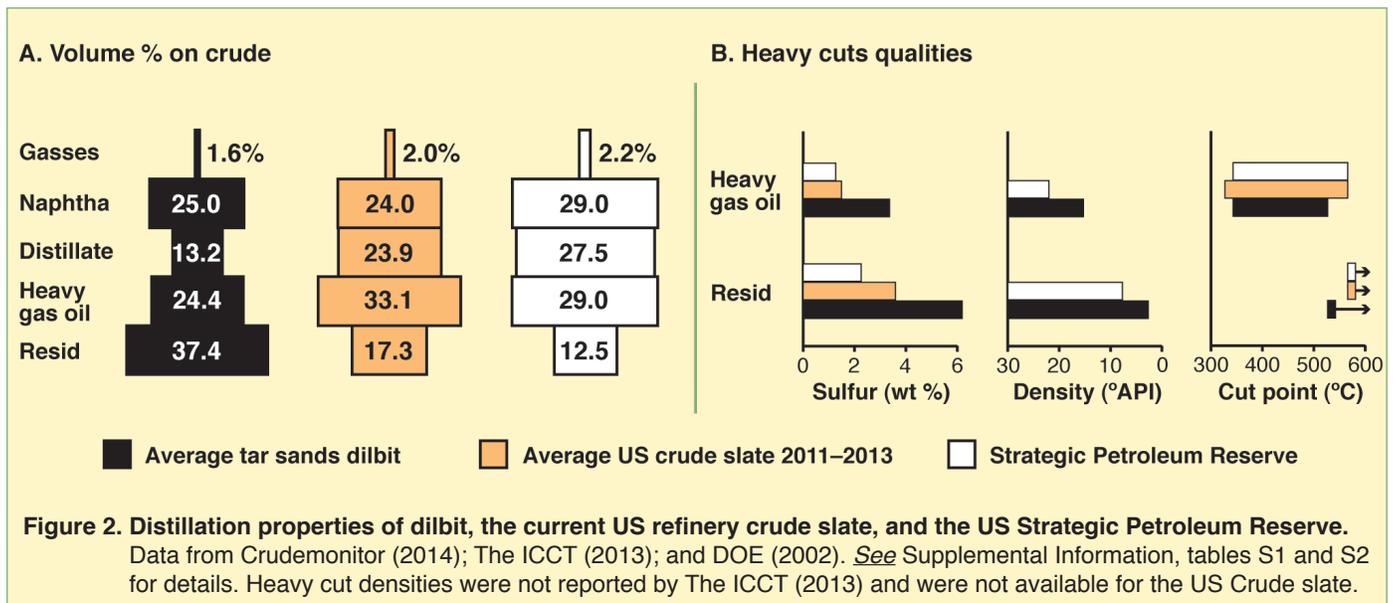
Famously developed and deployed to convert HGO into high-octane gasoline, the process also can run resid,<sup>15–17</sup> cycling the resid back into the reactor along with fresh feed, and many CCUs use this ‘recycle’ capacity.<sup>14,20</sup> Cracking occurs at  $\approx 480\text{--}540\text{ }^{\circ}\text{C}$  and  $\approx 10\text{--}20\text{ psi}$  in the presence of a catalyst to yield naphtha (gasoline feedstock), distillates (diesel and jet fuel feedstock), and byproduct gasses and coke.<sup>15–17,21</sup> The process is continuous. High-boiling hydrocarbons condense to deposit coke on the catalyst continuously, the catalyst cycles between the reactor and a ‘regenerator’ that reactivates the catalyst by burning the coke off of it continuously, and coke burn-off also heats the process. *See* Figure 1. Coke is high-emitting fuel. CCU ‘catalyst’ coke accounts for  $\approx 99\%$  of coke burned in US refineries.<sup>22</sup> CCUs are among the highest emitting refinery sources of combustion products such as condensable particulate matter (cPM).<sup>23,24</sup>

Bitumen is tar like or semi-solid petroleum that requires  $\approx 2\text{--}3$  times more energy to extract, and to refine for engine fuels, than conventional crude, making it inherently high-emitting oil.<sup>5–10</sup> Too viscous to transport by itself, bitumen is mixed with diluent oils such as naphtha in commercially exploited crude streams, and these diluent/bitumen blends are called dilbits. Distillation properties of dilbits differ markedly from those of the crude slate most US refineries were designed to process efficiently or process now. Figure 2 illustrates these differences. Dilbit distillation yield is low for HGO, especially low for mid-barrel distillates, and especially high for resid compared with the current average US crude slate and the Strategic Petroleum Reserve (SPR). Dilbit HGO

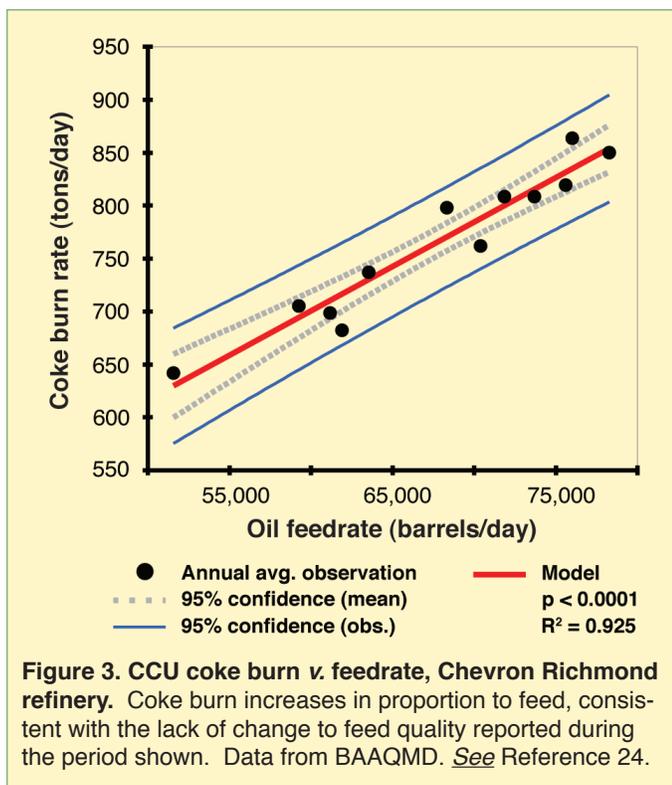
and resid cuts also are very dense (low API) and high in sulfur. Distillates are diesel and jet fuel feedstocks, while resid is fed to DCUs and CCUs to produce additional HGO that is added to CCU and hydrocracker feeds to produce distillate as well as naphtha. In other words, refining these high-resid, low-distillate oils means more DCU and CCU feedstock and more need for DCU and CCU products.

Process controls that are added onto the basic process design can capture or avoid a substantial part of process emissions, but technically feasible controls might not be deployed comprehensively, effectively, or at all, and in any case can control only a percentage of emissions generated by an inherently polluting design.<sup>18–20,24–26</sup> At any given level of such add-on controls, emissions are ultimately a function of process air pollutant generation. An example is increasing coke burn rate with increasing CCU feed rate, illustrated by data from a California plant in Figure 3: federal limits on PM emitted *per ton* coke burned in this CCU would not address its emissions from burning tons *per day* more coke. By increasing total DCU decoking cycle throughput, increasing CCU coke generation and burn-off, or both, changes in process feedstock associated with refining more dilbit would have the potential to increase emissions.

The work reported here compares publicly reported oil quality, processing, and emissions data to estimate refining sector-level changes in DCU and CCU processing, and emissions of toxic air pollutants and cPM, that could result from adding more dilbit oils to the US crude slate.



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**Figure 3. CCU coke burn v. feedrate, Chevron Richmond refinery.** Coke burn increases in proportion to feed, consistent with the lack of change to feed quality reported during the period shown. Data from BAAQMD. *See* Reference 24.

### Data and methods

Feedstock data for diluted bitumen (dilbit) oils and for the current average US refinery crude blend (slate) during 2011–2013 were reported by the oil industry, the International Council on Clean Transportation (ICCT), and the US Geological Survey, Department of Energy, and Energy Information Administration (EIA).<sup>1,3,27–33</sup> (Data summarized here are provided, along with methods details, in the Supplemental Information (SI).)

Crude density, sulfur content, and distillation properties varied little among dilbits,<sup>27</sup> reflecting the intentional blending of these oils, and supporting the calculation of the ‘average’ dilbit shown in Figure 2. Properties of the current average US refinery crude slate were based on whole crude volume, density and sulfur content in 2013 reported by the EIA<sup>1,30</sup> and distillation yields estimated for 2011 by The ICCT.<sup>28</sup> EIA did not report distillation yield for the US crude slate, but did report US refinery operating data that supported the ICCT estimate. These values for 2013 reported by EIA were within 0.2%, 2.2%, 0.0%, and 1.2% of the ICCT estimate for whole crude density, whole crude sulfur content, HGO distillation yield processed in downstream units, and resid yield processed downstream, respectively. (SI Table S2.)

Potential changes in distillation yields were calculated as weighted averages for barrel-for-barrel replacement of the current average US crude slate with 20%, and 50%,

more of the average dilbit. Results confirmed the potential for changes in the volume, density, and sulfur content of distillate, HGO, and resid yields from crude distillation that are suggested in Figure 2. *See* Table 1.

Processing data for the conversion of resid and HGO into feedstocks for gasoline, diesel and jet fuel finishing (naphtha and distillate) were reported by the EIA and the petroleum engineering literature.<sup>15–17,21,31–34</sup> Observed process capacities and oil feed rates confirmed the dominance of DCUs and CCUs among US refinery conversion (cracking) processes, and also the significant role played by hydrocracking units (HCUs).<sup>31,33,34</sup> HCU capacity to crack gas oil was 1.297 million barrels/day (MMb/d), or 64% of total US HCU capacity, in 2014. (SI Table S4.) The HCU process differs from those of DCUs and CCUs in its use of hydrogen addition rather than carbon subtraction chemistry to accomplish cracking,<sup>15–17</sup> and in its ability to ‘swing’ between naphtha (gasoline) and distillate (diesel and jet fuel) production targets.<sup>21</sup> That ability would be important in addressing the loss of distillate from crude distillation of dilbits revealed in Table 1. For these reasons, gas oil HCUs were included in the analysis of conversion process changes that could result from adding more dilbit to the US crude slate.

Comparisons of +20–50% dilbit scenario distillation yields with current process capacities and rates revealed limited capacity to convert the additional resid into lighter feedstocks unless CCUs processed some of this resid or new coking capacity was built. (SI tables S3–S7.) While both solutions are technically feasible and each likely would be used in some cases, it was judged more likely overall that existing capacity would generally be used first before adding new capacity. Thus processing of resid in both DCUs and CCUs, with feed recycling to improve conversion in CCUs, was analyzed for these scenarios. Greater densities and sulfur contents of unit feeds containing more dilbit-derived resid is one important implication for processing in these scenarios.

Process design and operating data showed that, while product yields vary with unit design and operating details, when other factors were optimized, denser and higher sulfur feeds reduce liquid yields and increase coke yields from DCUs and CCUs. (SI Table S5.) Conversion process yield data that were found to best represent current and +20–50% dilbit scenario average process capacities and feeds are summarized in Table 2.

The DCU yields shown in Table 2 for 8.2 °API, 3.4% sulfur feed were applied to both the current slate and the +20–50% dilbit slates. However, dilbit-derived resid (Figure 2) is denser than 8.2 °API and exceeds 3.4% sul-

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**Table 1. Potential changes in distillation yields from 20–50% more dilbit in the US crude slate.**

		Current (2011-13) Crude slate	20/80 dilbit/current scenario Crude slate      Change ( $\Delta$ )		50/50 dilbit/current scenario Crude slate      Change ( $\Delta$ )	
<b>Crude</b>						
Volume	(MMb/d)	15.312	15.312	None	15.312	None
Density	(kg/m <sup>3</sup> )	872	883	Denser	899	Denser
Sulfur	(wt. %)	1.4%	1.9%	More sulfur	2.6%	More sulfur
<b>Yield volumes</b>						
Gasses	(MMb/d)	0.306	0.295	-0.011	0.279	-0.027
Naphtha	(MMb/d)	3.675	3.707	0.032	3.754	0.079
Distillate	(MMb/d)	3.660	3.332	-0.328	2.840	-0.820
HGO	(MMb/d)	5.068	4.801	-0.267	4.399	-0.669
Resid	(MMb/d)	2.649	3.264	0.615	4.188	1.539

Data from references 1 and 27–33. See SI Table S3 for details.

fur. If actual DCU yield in the dilbit scenarios is closer to that shown in Table 2 for the 4°API, 5.3% sulfur feed, this analysis might underestimate DCU and CCU feed rate increments in those scenarios. Similarly, although CCU yield data for the lighter feed shown in Table 2 was applied in the current baseline while that for the denser, 15.1 °API (3.3 % sulfur) feed was applied in the dilbit scenarios, CCUs would feed denser, higher sulfur resid derived from dilbit in those scenarios. If actual yields in the dilbit scenarios are lower than this 15.1 °API, 3.3% sulfur feed data estimate for light liquids, or if they are higher for coke, or both, this might underestimate CCU feed rate increments and coke-burn emissions in those scenarios. The use of these process yields for dilbits thus represents a conservative assumption.

These process yield data were applied to the crude distillation volume changes shown in Table 1 to estimate the changes in DCU, CCU, and gas oil HCU process feeds and rates that would be needed to maintain naphtha and distillate production in the +20–50% dilbit scenarios. The estimates were further constrained by an additional

objective to use existing DCU and CCU capacity before adding conversion capacity. As stated, this approach used existing CCU capacity for resid as well as HGO feed. Gas oil HCU ‘swing’ capacity was used to balance naphtha and distillate production so that both fuel feedstocks were maintained at current production volume. Other approaches are feasible but the cost of new capacity and value of motor fuel products was judged to support this approach. A check on this approach showed that, without changing CCU feeds, substantially more coking capacity was needed to approach current product yields even in the +20% dilbit scenario (SI Table S7), and growing or stable US refinery production rates with growing exports of these key products (SI Table S8) also supported this approach. Various changes in equipment (e.g., pumps, distillation internals) and product shifts among plants would be needed in any case.

Emissions were estimated relative to current conditions in percent, and as mass-rates for selected pollutants. The incremental emissions from DCUs were based on the volume of volatile material processed in the coke drums

**Table 2. Representative conversion process yields by unit feed quality or product target.**

Product target Feed quality	Delayed coking <sup>a</sup>		Catalytic cracking <sup>b</sup>		Gas oil hydrocracking <sup>c</sup>	
	—	—	—	—	naphtha	distillate
density (°API)	8.2	4.0	20.1	15.1	22	22
sulfur (wt. %)	3.4	5.3	0.5	3.3	2.5	2.5
<b>Process yields</b>						
naphtha (vol. %)	19	24	58	51	90	29
distillate (vol. %)	—	—	18	21	—	69
HGO (vol. %)	45	30	—	—	—	—
coke (wt. %)	25	35	7.0	10.3	—	—

(a) Data from reference 15. (b) Data from reference 17. (c) Data from reference 21. See SI Table S5 for details.

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and thus exposed to the atmosphere during decoking. This was estimated as the increase in DCU feed volume rate for each dilbit scenario by the analysis of process changes described above. Incremental emissions from CCUs were based on the mass of coke burned in CCUs. This was estimated from the increments for CCU coke yield (wt. %), feed vol./day, and feed density (current HGO  $\approx 922 \text{ kg/m}^3$ ; dilbit resid  $\approx 1,055 \text{ kg/m}^3$ ) found by the analysis of process changes. (*SI Table S6.*)

Mass emission rates were estimated by applying these relative increments to available measurements of specific pollutants in current ‘baseline’ DCU and CCU emissions.

Direct measurements of emissions were reported by Chambers et al.,<sup>19</sup> US EPA,<sup>20</sup> the Bay Area Air Quality Management District,<sup>35,36</sup> and Sánchez de la Campa et al.<sup>37</sup> Some 114 toxic chemicals were found in emissions from DCUs, CCUs, or both.<sup>20</sup> (*SI Table S9.*) But only a handful of these pollutants were measured above method detection levels (MDLs) consistently at multiple plants.<sup>20</sup>

DCU source tests for a 2011 Information Collection Request (ICR) used sampling methods for other sources that often collected too little sample for analysis.<sup>20</sup> Source tests were reported for 5 DCUs. Multiple tests were below MDLs in all runs for nearly every analyte except VOC, methane, and benzene (measured in 5, 5, and 4 of the tests, respectively). Emissions/barrel DCU feed reported for VOC, methane and benzene ranged by more than two orders of magnitude, but only DCU vents—not coke drilling or other decoking steps—were measured.<sup>20</sup>

Direct measurements of DCU decoking emissions by differential absorption light detection and ranging (DIAL)<sup>19</sup> found VOC and benzene emissions that exceeded the ICR vent emissions maxima by 1–2 orders of magnitude. (*SI Table S12.*) These DIAL measurements were validated and close to the median results from 16 other refineries.<sup>19</sup> Based on these data, vent tests alone may understate DCU emissions substantially. The DIAL data were judged more representative of DCU emissions, but only one unit was measured and  $\approx$  half of its emissions were from coke water handling. DIAL data were scaled to the minimum decoking frequency for DCUs and minimum decoking emission period measured, and coke water emissions were removed from the lower bound values, in the estimate derived from these data. (*SI tables S11, S12.*) This estimate, shown in Table 3, was judged to be the most conservative available based on the limited data from direct measurements of total decoking emissions. A check against benzene emissions in the Toxic Chemical Release Inventory (TRI) that were self-reported by refiners (*SI Table S15*) found that this estimate accounted for

**Table 3. Delayed coker emission rates estimate.**

*Emissions per barrel (b) of coker feed*

	Lower bound	Upper bound
Benzene (mg/b)	390	810
Methane (grams/b)	38	78
C <sub>2+</sub> VOC (grams/b)	63	130

Upper bound estimates include emissions from coke water handling. Data from reference 19 and SI tables S11, S12.

60% of total TRI benzene emissions from US refineries at the lower bound and 125% of them at the upper bound, suggesting DCUs are a strong source, and that either TRI emissions are underestimated, or that US refiners handle coke water differently from the refinery tested by DIAL.

Source tests of 11 refiners’ CCUs were reported.<sup>20,35,36</sup> Emissions were measured above MDLs in one or more test runs at 10 of these CCUs for cPM, 6–8 CCUs for various metals, and 8 CCUs for hydrogen cyanide (HCN). (*SI Table S14.*) Data distributions suggested that median values may better represent the central tendency of the emissions data than arithmetic averages. (*Id.*) However, correlations among pollutants and operating parameters that were consistent with cPM-boosting effects of ammonia injection, together with the potential that the small data set may under-represent high emitting units, supported 90<sup>th</sup> Percentile values as an upper bound on emissions estimated from these data. (*Id.*) A check against self-reported TRI emissions (*SI Table S15*) supported this estimate for metals but suggested the possibility that the source tests might not accurately represent average CCU emissions of HCN. Other data show that CCUs are strong emission sources of various pollutants including cPM and metals.<sup>23,37</sup> Table 4 shows the CCU ‘baseline’ emission rates estimate for cPM and metals.

**Table 4. Catalytic cracking unit (CCU) current ‘baseline’ emission rates estimate.**

*Emissions per barrel (b) of CCU feed*

	Lower bound	Upper bound
Fine particulate (g/b)	2.04	5.28
Chromium ( $\mu\text{g/b}$ )	158	243
Lead ( $\mu\text{g/b}$ )	130	284
Manganese ( $\mu\text{g/b}$ )	275	580
Nickel ( $\mu\text{g/b}$ )	481	3,630
Mercury ( $\mu\text{g/b}$ )	22.8	66.1

Lower bound: median value; upper bound: 90<sup>th</sup> Percentile. Data from references 20, 35, 36 and SI Table S14.

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## Results

US refining sector-level conversion processing changes needed to maintain naphtha and distillate production in the +20–50% dilbit scenarios are shown in Table 5.

Generally, Table 5 shows changes in oil feed flows and process rates for conversion of the additional resid from distillation of the crude slates containing more dilbit into enough gas oil and distillate to maintain gasoline, diesel, and jet fuel production despite the shortfalls in GO and distillate from crude distillation of the dilbit. Incremental changes from current ‘baseline’ are shown.

In the +20% dilbit (20/80 dilbit/current slate) scenario, coking rate increases to 98% of capacity, producing 0.065 million barrels/d (MMb/d) of additional naphtha and 0.153 MMb/d of gas oil—not enough GO to erase the deficit from crude distillation, but resid feed to CCUs increases more than GO feed drops. Recycling this new resid feed the equivalent of 0.86 times boosts the CCU recycle rate by 0.235 MMb/d, or 5.5 vol. % of total CCU fresh feed. Together with the overall increase in fresh feed (0.161 MMb/d), the net CCU feed rate increment is 0.396 MMb/d. Assuming the CCU yield on this increment for 15.1 °API, 3.3 % sulfur feed in Table 2, these coking and CCU changes boost naphtha to 0.299 MMb/d above baseline while distillate remains 0.245 MMb/d below baseline, allowing HCUs to swing from naphtha to distillate production and make up those differences. This swings 0.355 MMb/d or 27% of GO HCU capacity from naphtha to distillate production.

Net changes in processing for this 20/80 dilbit/current crude slate scenario boost coking and CCU feed rates by an estimated 0.340 and 0.396 MMb/d, respectively, but both processes remain within their nominal capacities while those rate increments achieve essentially zero net change in gasoline, diesel, and jet fuel feedstock.

In the +50% dilbit (50/50 dilbit/current slate) scenario, processing changes follow the same pattern but are larger with coking and CCU feed rates increasing by 1.138 and 0.723 MMb/d, respectively, and achieve similar net-zero changes in naphtha and distillate production, but at a coking rate that exceeds current capacity.

Total utilization of 2014 coking capacity is 128% for the 50/50 dilbit/current crude slate scenario in Table 5. This suggests that new conversion capacity would be built in the +50% dilbit scenario. That finding is consistent with refinery engineering knowledge—and, in fact, the coking capacity of US refineries has doubled since 1987.<sup>34</sup>

Results indicating < 100% utilization of capacity should be interpreted in the context of the capacity ‘optimiza-

tion’ approach discussed in the methods section. New capacity could be built for various reasons, and if built, could be used at rates greater than those conservatively estimated in Table 5. For example, plants that lack DCU, CCU, or HCU capacity may build it instead of transferring intermediate products to other plants that have these capacities. Also, lower yields from boosting CCU recycle rates may force new capacity for the increased fresh feed rates needed to meet product targets. In any case, the differences in distillation properties from a switch to 20–50% more dilbit in the crude slate could require changes to pumps, exchangers, distillation unit internal configurations and piping, and other refinery equipment.

CCU coke yield increments estimated in Table 5 reflect increased feed rate *and* the increase in coke burn rate per barrel of CCU feed that would be driven by the lower quality of the new dilbit resid feed increments processed in CCUs. These increments represent a coke burn rate of  $\approx 17.3$  kg/b, based on the coke yield of 10.3 wt. % in Table 2 and the average density of the dilbit resid (1,055 kg/m<sup>3</sup>; *SI Table S1*). This compares with  $\approx 10.3$  kg/b for current ‘baseline’ coke yield (7 wt. %) and HGO feed ( $\approx 922$  kg/m<sup>3</sup>; *SI Table S2*). Thus, the dilbit scenarios would result in burning  $\approx 68\%$  more catalyst coke per barrel for the new feed processed by CCUs. Emissions per barrel of the new CCU resid feed would be greater than baseline emissions per barrel by this amount, on average. Emission per barrel estimates applied to the new CCU resid feed increments are shown in Table 6.

Results for emission increments in the dilbit scenarios are summarized in Table 7. Volatile pollutant emissions from decoking operations exposing larger throughputs to the atmosphere at DCUs in US refineries could increase by  $\approx 14\%$  in the +20% dilbit scenario and by  $\approx 47\%$  in the +50% dilbit scenario. This estimate is based on the 0.340–1.138 MMb/d increments over the 2.303 MMb/d current feed rate shown in Table 5, conservatively scaled downward to the portion of total coking capacity represented by DCUs (94.6%). Estimated average benzene and volatile organic compound (VOC) emission increments for US refinery DCUs are based on these scaled increments applied to the DCU emission-per-barrel rates in Table 3. Benzene emissions from the DCUs could increase by an estimated 46–95 metric tons per year (t/yr) in the +20% dilbit scenario and by 150–320 t/yr in the +50% dilbit scenario. VOC emissions from the DCUs could increase by an estimated 7,400–15,300 t/yr in the +20% dilbit scenario and by 24,700–51,100 t/yr in the +50% dilbit scenario. These pollutant-specific DCU increments are based on a conservative interpretation of

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**Table 5. Estimated changes in conversion processing to maintain US gasoline, diesel and jet fuel production in scenarios with 20–50% more dilbit entering the current US crude slate.**

Values in millions of barrels per day (MMb/d) or as noted

	20/80 dilbit/current scenario	50/50 dilbit/current scenario
<b>Change in crude dist. unit (CDU) yield</b>		
Naphtha, change from crude distillation	0.032	0.079
Distillate, change from crude distillation	−0.328	−0.820
Gas oil, change from crude distillation	−0.267	−0.669
Resid, change from crude distillation	0.615	1.538
<b>Changes in coking rate and yield</b>		
Net change in coking feed rate	0.340	1.138
Change in coker naphtha yield	0.065	0.216
Change in coker gas oil (GO) yield	0.153	0.512
Change in GO from CDU + coking	−0.114	−0.157
Change in resid from CDU + coking	0.275	0.400
<b>Changes in CCU rate and yield</b>		
Change in CCU fresh feed input	0.161	0.243
Change in CCU recycle rate	0.235	0.480
New resid feed % of total CCU fresh feed	5.5%	7.9%
Equivalent times new resid feed is recycled	0.86	1.20
Net change in CCU total feed rate	0.396	0.723
Change in CCU naphtha yield	0.202	0.369
Change in CCU distillate yield	0.083	0.152
Change in CCU coke yield (MM kg/day)	6.84	12.5
Change in CDU+coking+CCU naphtha	0.299	0.664
Change, CDU+coking+CCU distillate	−0.245	−0.668
<b>Changes in GO-HCU rate and yield</b>		
Net change in HCU GO feed input	0.000	0.000
Δ in GO-HCU feed input for naphtha	−0.355	−0.970
Δ in GO-HCU feed input for distillate	0.355	0.970
Change in GO HCU naphtha yield	−0.216	−0.592
Change in GO HCU distillate yield	0.245	0.669
<b>Net changes in processing and key yields</b>		
Coking capacity in 2014 (MMb/cd)	2.687	2.687
Coking feed rate in 2013 (MMb/d)	2.303	2.303
Net Δ in coking feed rate (MMb/d)	0.340	1.138
Total utilization of 2014 capacity (%)	98%	128%
CCU capacity in 2014 (MMb/cd)	5.616	5.616
CCU feed rate in 2013 (MMb/cd)	4.811	4.811
Net Δ in CCU feed rate (MMb/d)	0.396	0.723
Total utilization of 2014 capacity (%)	94%	98%
GO-HCU capacity, 2013 (MMb/cd)	1.297	1.297
GO-HCU feed swung to distillate (%)	27%	75%
<b>Naphtha (gasoline feedstock)</b>		
Net Δ from CDU, coking, CCU and HCU	0.082	0.072
Net Δ v. baseline CDU yield (%)	2%	2%
<b>Distillate (diesel, jet fuel feedstock)</b>		
Net Δ from CDU, coking, CCU and HCU	0.000	0.001
Net Δ v. baseline CDU yield (%)	0%	0%

Data from tables 1 and 2, except current process capacities and rates from refs. 31, 33, 34. See SI Table S1–S7 for details.

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**Table 6. Catalytic cracking unit (CCU) potential emission rates estimate for dilbit oil increments.**

*Emissions per barrel (b) of CCU feed*

		Lower bound	Upper bound
Fine particulate	(g/b)	3.43	8.89
Chromium	(µg/b)	266	409
Lead	(µg/b)	219	478
Manganese	(µg/b)	463	976
Nickel	(µg/b)	810	6,110
Mercury	(µg/b)	38.4	111

Based on data from Table 4, 10.3 wt. % coke yield for denser 1,055 kg/m<sup>3</sup> resid feed; rates for resid feed increments only.

the limited available data from direct measurements of DCU emissions and are subject to the caveats regarding the available DCU data discussed in the methods section.

CCU emissions from US refineries could increase by an average of ≈ 14% in the +20% dilbit scenario and by an average of ≈ 25% in the +50% dilbit scenario. These increments are based on burning more coke in CCUs and are estimated based on the coke yields in Table 5 and that calculated from the baseline data cited above at the 4.811 MMb/d baseline feed rate in Table 5. (SI Table S6.)

Changes in CCU feed volume and coke yield account for ≈ 59% and 41% of these increments, respectively. (*Id.*) CCU emission increments for specific pollutants are based on the emission-per-barrel rates in Table 6 and the CCU dilbit scenario feed rate increments in Table 5.

Average US refinery CCU emissions of condensable particulate matter could increase by 500–1,300 t/yr in the +20% dilbit scenario and by 900–2,400 t/yr in the +50% dilbit scenario. For metals, these estimates suggest that average US refinery CCU emissions could increase, in the +20% and +50% scenarios, respectively, by 38–59 and 70–110 kg/yr for chromium, by 32–69 and 58–130 kg/yr for lead, by 67–140 and 120–260 kg/yr for manganese, by 120–880 and 210–1,600 kg/yr for nickel, and by 5.5–16 and 10–29 kg/yr for mercury.

Because they are based on changes in the processes generating volatile chemical emissions from DCUs and coke combustion product emissions from CCUs, the relative percent increments in Table 7 also apply to the (large) subsets of those pollutants that are not yet quantified well by direct measurements of these emissions. At least 114 toxic chemicals have been identified in DCU emissions, CCU emissions, or both. (SI Table S9.)

## Discussion

This work confirms that replacing more of the current US refinery crude slate with ‘tar sands’ dilbit oil has the potential to increase emissions of air pollutants that have local and regional environmental health implications from delayed coking and catalytic cracking units. DCUs and CCUs would process denser and lower quality oils in greater amounts, boosting the amounts of volatile chemicals entering the air from decoking and the amounts of combustion products from burning more coke in CCUs.

**Table 7. Potential increase in delayed coking and catalytic cracking unit emissions estimated for scenarios in which 20–50% of the baseline US crude slate is replaced by tar sands dilbit oil.**

*Increments in percent and mass rate*

		20/80 dilbit/current scenario	50/50 dilbit/current scenario
<b>Delayed Coking</b>			
Emission increment	%	+ 14 %	+ 47 %
Benzene	tons/yr	46 – 95	150 – 320
Volatile organic carbon (C <sub>2+</sub> )	tons/yr	7,400 – 15,300	24,700 – 51,100
<b>Catalytic Cracking</b>			
Emission increment	%	+ 14 %	+ 25 %
Particulates (condensable)	tons/yr	500 – 1,300	900 – 2,400
Chromium	kg/yr	38 – 59	70 – 110
Lead	kg/yr	32 – 69	58 – 130
Manganese	kg/yr	67 – 140	120 – 260
Nickel	kg/yr	120 – 880	210 – 1,600
Mercury	kg/yr	5.5 – 16	10 – 29

Total increments from these units at U.S. refineries—individual plant emissions will vary. DCU increments from greater decoking throughputs. CCU increments from greater coke-burn rates caused by increased feed rates and coke yields. [See](#) SI for details.

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Direct measurement data are limited, especially for DCUs, but available data suggest that these emission increments would be significant. Benzene increments estimated for the US fleet of DCUs are 9–18% of benzene emissions reported from all US refinery sources by the Toxic Chemical Release Inventory (*SI Table S15*) in the +20% dilbit scenario and 29–62% of that TRI estimate in the +50% dilbit scenario. Emission increments reported here are US averages—individual plant emissions will vary—but if these VOC and cPM increments were realized at a ‘notional’ refinery with a 50,000 b/d DCU and 80,000 b/d CCU (*SI Table S16*), the resultant emissions could exceed the environmental significance thresholds applied in the San Francisco Bay Area (10 short tons/yr) for both pollutants.

Future work should consider feedstock-driven emissions from other refinery sources. The diluents in dilbit could boost volatile ‘fugitive’ emissions from crude oil storage tanks in amounts that, DIAL measurements suggest,<sup>19</sup> may be underestimated by traditional emission modeling. Substantial CO<sub>2</sub> emission from hydrogen production for the extra gas oil hydrocracking and hydrotreating needed to process bitumen has been documented,<sup>6–10</sup> but flaring from gas oil hydroprocessing warrants more attention. This exothermic, high pressure, hard-to-control process<sup>21</sup> can dump sulfur-rich gasses in amounts that overwhelm flare gas recovery systems when reactors depressure during upsets. Feedstock-driven expansion of gas oil hydroprocessing could thus increase the frequency and magnitude of flare emission incidents at refineries.

Emissions associated with DCU byproducts also warrant more attention. Most of the coke yield from DCUs is burned after it leaves the refinery gate,<sup>22</sup> much of it is exported overseas (*SI Table S8*), and coke by-production rises predictably as denser, higher sulfur crude is processed (*SI Table S17*), but the resultant emissions often are ignored by refinery and fuel cycle assessments. The byproduct gasses that are collected before venting starts in the decoking part of the DCU drum cycle are burned as fuel gas throughout refineries, and these coker gasses contain sulfur compounds that are uniquely resistant to the amine scrubbing typically used by refinery fuel gas systems.<sup>23</sup> Emissions from increased by-production of this ‘dirtier’ fuel gas as cokers process more resid should be considered in assessments of refining dilbit oils.

Ultimately, there are alternatives to refining bitumen, and the most important uncertainty in estimates of future emissions from refining more of this ‘tar sands’ oil involves public policy choices among these alternatives.

### Acknowledgments

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### Supporting Information Available

Data and details of methods; 34 pages including references and 17 annotated tables.

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# Supplemental Information (SI) *for*

## Toxic and fine particulate emissions from U.S. refinery coking and cracking of ‘tar sands’ oils

Greg Karras (2015)\*

Thirty-four (34) pages including references and seventeen (17) annotated tables:

Table S1.	Feedstock quality data for diluted bitumen ‘dilbit’ oils.	page S-2
Table S2.	Feedstock data for the US refinery crude slate with comparisons to the Strategic Petroleum Reserve and observed feedstock processing.	S-3
Table S3.	Estimation details for crude slate blends and potential changes in crude distillation yields in 20/80 and 50/50 dilbit/baseline blend scenarios.	S-5
Table S4.	Oil feed capacities and actual feed rates reported for US coking, catalytic cracking, and hydrocracking units, 2011–2014.	S-7
Table S5.	Design capacity data for delayed coking unit (DCU), catalytic cracking unit (CCU), and gas oil hydrocracking unit (HCU) oil feeds and yields.	S-9
Table S6.	Estimate calculation for changes in DCU and CCU feed rate and CCU coke burn in 20/80 and 50/50 dilbit/baseline US crude feed scenarios.	S-11
Table S7.	Estimate of additional capacity costs to maintain US gasoline, diesel, and jet fuel production by a coking and <i>hydrocracking</i> alternative.	S-13
Table S8.	US production and export data for selected refined products.	S-16
Table S9.	Toxic pollutants detected in EPA ICR source tests of DCUs and CCUs.	S-17
Table S10.	VOC, methane and benzene emissions measured from DCU vents.	S-19
Table S11.	VOC, methane and benzene emissions measured from DCU decoking.	S-21
Table S12.	Benzene, methane, and VOC emissions measured from DCUs.	S-22
Table S13.	Concentrations of selected elements measured in a CCU emission stack.	S-23
Table S14.	Emission data for toxic pollutants detected in source tests of multiple CCUs, with calculations for median and 90 <sup>th</sup> Percentile emissions/barrel.	S-24
Table S15.	Comparison of DCU and CCU emissions estimated in this work and US refinery Toxic Chemical Release Inventory emissions.	S-27
Table S16.	Comparison of potential emission increments with CEQA thresholds.	S-29
Table S17.	Association of coke yield with crude feed quality details (CBE, 2011).	S-30
References		S-32

\* This work was conducted for the Natural Resources Defense Council (NRDC) as part of a technical assistance contract. Author info., [gkatchbe@gmail.com](mailto:gkatchbe@gmail.com); c/o Communities for a Better Environment (CBE), 1904 Franklin St., Suite 600, Oakland CA 94612.

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**Table S1. Feedstock quality data for diluted bitumen ('dilbit') oils.**

Dilbits	WCS	AWB	BHB	CDB	CL	KDB	Average
Whole crude							
Density (kg/m <sup>3</sup> )	929	923	925	924	928	927	926
Sulfur wt. %	3.5%	3.9%	3.7%	3.9%	3.8%	3.9%	3.8%
Distillation vol. fraction							
Gasses	0.024	0.015	0.016	0.012	0.016	0.015	0.016
Naphtha IBP–190C	0.197	0.279	0.276	0.274	0.230	0.246	0.250
Distillate 190–343C	0.174	0.113	0.107	0.123	0.152	0.122	0.132
Gas oil 343–527C	0.263	0.237	0.247	0.246	0.226	0.242	0.244
Resid 527+ °C	0.366	0.371	0.369	0.356	0.392	0.390	0.374
Cuts density (kg/m <sup>3</sup> )							
Naphtha IBP–190C	690	688	681	687	688	672	684
Distillate 190–343C	880	882	892	880	883	892	885
Gas oil 343–527C	955	964	976	964	958	966	964
Resid 527+ °C	1,055	1,062	1,061	1,059	1,052	1,039	1,055
Cuts sulfur (wt. %)							
Naphtha IBP–190C	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	ND	<0.1%
Distillate 190–343C	1.3%	1.4%	1.5%	1.3%	1.6%	1.5%	1.4%
Gas oil 343–527C	2.9%	3.5%	3.6%	3.3%	3.3%	3.5%	3.4%
Resid 527+ °C	5.6%	6.5%	6.5%	6.2%	6.3%	6.0%	6.2%

**Table S1 notes:** Data shown were reported publicly by the Canadian oil industry for these crude streams, which are commercially available to US refiners. Dilbits, shown in the table by their acronyms, are: Western Canadian Select (WCS), Access Western Blend (AWB), Borealis Heavy Blend (BHB), Christina Dilbit Blend (CDB), Cold Lake (CL), and Kearl Lake (KDB). Data for distillation cuts are averages of the two most recent assays for each stream reported, where available; data for whole crude are averages for the most recent five-year period reported. *See* reference RS1, and Figure 2 in the main report for a graphic illustration of these data.

The densities, sulfur contents, and distillation yields of these oils are similar, reflecting the intentional blending of diluents—lighter cuts—with bitumen to facilitate transport of these commercial crude streams. Thus, differences from the average US crude slate (Table S2) would exist for these oils individually as well as on average. Blending with diluent also moderates the extreme density, contamination, and dearth of light yields from crude distillation that characterize the average pure bitumen (RS2). Volume expansion on distillation is  $\approx 1\%$ . Sulfur data were converted from wt. % to mass in calculating the weighted averages shown (this is because the same wt. % sulfur is a different mass of sulfur in an oil of different density).

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**Table S2. Feedstock data for the US refinery crude slate with comparisons to the Strategic Petroleum Reserve and observed feedstock processing.**

	Current US crude slate	Strategic Pet. Reserve		Observed in 2013	
	Estimate (Est.) <sup>a</sup>	Data <sup>b</sup>	Δ from Est.	Data <sup>c</sup>	Δ from Est.
Whole crude					
Density (kg/m <sup>3</sup> )	873	853	-2.3%	872	-0.1%
Sulfur wt. %	1.41%	0.89%	-36%	1.44%	-2.1%
Distillation vol. fraction					
Gasses	0.020	0.022	+10%		
Naphtha IBP-190C	0.240	0.290	+21%		
Distillate 190-327C	0.239	0.275	+15%		
Gas oil 327-566C	0.331	0.290	-12%	0.331	0.0%
Resid 566+ °C	0.173	0.125	-28%	0.171	-1.1%
Cuts density (kg/m <sup>3</sup> )					
Gas oil 327-566C	NR	922			
Resid 566+ °C	NR	1,017			
Cuts sulfur (wt. %)					
Gas oil 327-566C	1.5%	1.3%	-13%		
Resid 566+ °C	3.6%	2.3%	-36%		

### **Table S2 notes:**

(a). The International Council on Clean Transportation (ICCT, 2013; *RS3*) estimated the current US crude slate for the year 2011 based on reported data for the major crude streams processed. The ICCT reported including data for domestic crude from the Bakken, Eagle Ford, Alaska, California and other sources; Canadian conventional and oil sands light, medium and heavy crude; and Mexican, Atlantic Basin, and rest-of-world light, medium, and heavy crude in this analysis (*Id.*). Cut points shown in the table (e.g., 327-566 °C for gas oil) are for the current US crude slate estimate (*Id.*).

(b). The US Department of Energy (DOE) reported assays for pooled crude blends of the Strategic Petroleum Reserve (SPR) in 2002 (*RS4*). Weighted averages of these ‘pools’ data are shown. Oils in SPR blends assayed included Isthmus, Iranian Light, Maya, Gulf of Suez Blend, Dubai Fateh, Arab Light, Alaska North Slope, Oman, Gabon Mandji, Ninian, Es Sider, Forties, Brent, Zarzaitine, Kole Marine, Sitica, Palanca, Oseberg, US Naval Reserve California (Stephens Zone), Bonny Light, Forcados, Ecofisk, Escravos, and Saharan Blend (*Id.*).

The SPR oil appears lighter and lower in sulfur than the ICCT estimate for the current US refinery crude slate. In general, SPR crude quality is specified and managed for the ability of

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most US refiners to process it efficiently when needed (*Id.*). The ongoing trend to denser, higher-sulfur crude feeds (*RS5*), and refiners' incentive to run price-discounted lower quality oil when it can be processed efficiently, could explain these results suggesting a denser and higher-sulfur crude slate now than the blends acquired for the SPR before these 2002 DOE assays.

(c). The US Energy Information Administration (EIA) reported the volume (15.312 MMb/d; *RS6*), density (*RS5*), and sulfur content (*RS5*) of crude processed by US refiners in 2013. These data are used as current 'baseline' data herein. EIA does not report distillation properties of the US crude slate directly, however, it reports actual feed rates of 'downstream' processes that feed the gas oil and resid cuts from the crude slate actually processed. 'Observed' gas oil and resid fractions are based on these downstream feed observations for the US industry (*RS7–RS9*). The sum of fresh feed inputs to delayed and fluid cokers (2.303 MMb/d; *RS7*) and production of asphalt and road oil (representing resid that is not converted in cokers; 0.322 MMb/d; *RS8*) in 2013 provides an indication of resid distillation yield.<sup>1</sup> Similarly, the sum of catalytic cracking and gas oil hydrocracking fresh feed (4.811 and 1.297 MMb/d; *RS7 and RS9*) minus gas oil yield from coking resid ( $\approx 1.036$  MMb/d) provides an indication of 2013 gas oil distillation yield.<sup>2</sup> The 1.036 MMb/d subtracted is from coking, not distillation yield, and is estimated at the coker gas oil yield from Table S5 for resid feeds that are closest in density and sulfur content to the ICCT and SPR averages (45% vol. on coker feed; *see* Table S5).

The estimate values for properties of the 2011 US crude slate by the ICCT compare well to the observed values for actual operations in 2013 reported by EIA. *See* Table. Measured as percent change from the ICCT values, observed values are within  $\approx 0.1\%$  for crude density (872 v. 873 kg/m<sup>3</sup>), within  $\approx 2.1\%$  for crude sulfur content (1.44 v. 1.41 wt. %), identical within  $\approx 0\%$  for gas oil distillation yield (0.331 volume fraction on crude), and within  $\approx 1.1\%$  for residuum yield (0.171 v. 0.173 vol. fraction). This close agreement of estimated and observed values supports the ICCT distillation properties estimate as reasonably representative of the current (2011–2013) 'baseline' US crude slate.

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<sup>1</sup> Calculated as  $(2.303 + 0.322) / 15.312 = 0.171$  (the volume fraction of 2013 crude input for resid yield).

<sup>2</sup> Calculated as  $(4.811 + 1.297 - 1.036) / 15.312 = 0.331$  (the vol. fraction of 2013 crude for gas oil yield).

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**Table S3. Estimation details for crude slate blends and potential changes in crude distillation yields in 20/80 and 50/50 dilbit/baseline blend scenarios.**

*Volume in millions of barrels per day (MMb/d)*

	Baseline slate <sup>a</sup>		Dilbit <sup>b</sup> fraction	20/80 dilbit/ baseline <sup>c</sup>			50/50 dilbit/ baseline <sup>c</sup>		
	fraction	MMb/d		dilbit	base	slate	dilbit	base	slate
Crude vol.	1.000	15.312	1.000	3.062	12.250	15.312	7.656	7.656	15.312
<i>d</i> (kg/m <sup>3</sup> )	872	872	926	926	872	883	926	872	899
sulfur (wt %)	1.44%	1.44%	3.8%	3.8%	1.44%	1.9%	3.8%	1.44%	2.6%
Cuts vol.									
Gasses	0.020	0.306	0.016	0.050	0.245	0.295	0.126	0.153	0.279
Naphtha	0.240	3.675	0.250	0.767	2.940	3.707	1.917	1.837	3.754
Distillate	0.239	3.660	0.132	0.404	2.928	3.332	1.010	1.830	2.840
Gas oil	0.331	5.068	0.244	0.746	4.055	4.801	1.865	2.534	4.399
Resid	0.173	2.649	0.374	1.145	2.119	3.264	2.863	1.325	4.188

### **Table S3 notes:**

Crude slate volume (15.312 MMb/d) is reported 2013 US volume (*RS6*). (a) Current US crude slate fractions from Table S2 are applied to 100% of crude slate volume to derive these ‘baseline’ values. (b) Average dilbit fractions from Table S1 are applied to 20% and 50% of this crude volume in the 20/80 and 50/50 dilbit/baseline scenarios, respectively. (c) The remaining volume of the current crude slate is 80% and 50% in the 20/80 and 50/50 dilbit/baseline scenarios, respectively. These columns in the table show the resultant volumes of dilbit and current crude that are added together to arrive at the cut volumes for each scenario, and the distillation yield of the total crude slate in each scenario. The +20–50% dilbit scenario crude densities (kg/m<sup>3</sup>) and sulfur contents (wt. %) are weighted averages calculated from the ‘dilbit’ and ‘base’ column crude data for each scenario.

Some of the volumetric differences in yields indicated in the table are dramatic. Distillate yields are ≈328,000–820,000 barrels/day lower than the current US crude slate yield and resid yields are ≈615,000–1,538,000 b/d higher than that baseline yield in the +20–50% dilbit scenarios. Crude distillation naphtha yields are ≈32,000–79,000 b/d higher, and gas oil yields from crude distillation are ≈267,000–669,000 b/d lower in the +20–50% dilbit scenarios. Supplying current product markets at rate despite these large differences in distillation yield would require changes to process operations and equipment in many and perhaps virtually all parts of existing refineries. Conversion (cracking) processes, the focus of this analysis, are addressed in tables S4–S7.

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The data in Table S3 may represent a conservative estimate of actual distillation differences, in part because of differences between dilbit and current slate data with regard to the cut points used to generate the available distillation data. *See* tables S1 and S2. Using identical crude distillation cut points would likely further amplify the difference in distillation yields, especially for mid-barrel distillates, which have a more generous cutpoint range in the dilbits data reported than in the US crude slate data reported.

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**Table S4. Oil feed capacities and actual feed rates reported for US coking, catalytic cracking, and hydrocracking units, 2011–2014.**

*Volume in millions of barrels/day (MMb/d)*

	2011		2012		2013		2014	
	CD <sup>a</sup>	SD <sup>a</sup>						
<b>Coking<sup>b-d</sup></b>								
Delayed coking cap.	2.307	2.487	2.410	2.578	2.451	2.692	2.542	2.773
Fluid coking capacity	0.145	0.159	0.145	0.159	0.145	0.159	0.145	0.159
Delayed & fluid cap.	2.453	2.646	2.555	2.737	2.596	2.851	2.687	2.932
Fresh feed input	2.094		2.177		2.303		NR	
<b>Catalytic cracking<sup>b,c</sup></b>								
Fresh feed capacity	5.794	6.220	5.611	6.032	5.682	6.089	5.616	6.032
Recycle capacity		0.096		0.085		0.084		0.076
Fresh feed input	4.952		4.901		4.811		NR	
<b>Hydrocracking<sup>b-d</sup></b>								
Distillate feed capacity	0.484	0.540	0.543	0.596	0.559	0.621	0.633	0.686
Gas oil feed capacity	1.081	1.170	1.070	1.161	1.230	1.337	1.297	1.400
Resid feed capacity	0.123	0.145	0.094	0.122	0.098	0.122	0.105	0.122
Total HCU capacity	1.688	1.855	1.707	1.879	1.887	2.080	2.035	2.208
Fresh feed input	1.467		1.529		1.670		NR	

**Table S4 notes:** (a) Capacities are shown in two ways: stream day (SD) capacity is the amount of input that can be processed in 24 hours when running at full capacity under optimal crude and product slate conditions with no allowance for downtime. Calendar day (CD) capacity is the amount that can be processed under usual operating conditions in 24 hours, accounting for the capabilities of a refinery’s interconnected processing (e.g., “bottlenecks”), the types and grades of inputs processed, environmental constraints, and downtime. (b) Observed fresh feed input rates were reported through 2013 by the US Energy Information Administration (EIA), in its *U.S. Downstream Processing of Fresh Feed Input (RS7)*. (c) Catalytic cracking capacity data, and stream-day capacities for the other processes are from EIA’s *U.S. Number and Capacity of Petroleum Refineries (RS10)*. (d) Calendar-day coking and hydrocracking capacities are from EIA’s *Refinery capacity data by individual refinery as of Jan. 1 (RS9)*.

Delayed coking units (DCUs) and catalytic cracking units (CCUs) dominate US refinery conversion capacity. DCU capacity is  $\approx 17$  times fluid coking capacity, and CCU capacity is 4–5 times hydrocracking (HCU) capacity for gas oil feeds. Process capacity is not fully utilized. Comparisons of 2014 unit capacities with 2013 unit input baseline conditions indicate that 0.384

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MMb/d, 0.805 MMb/d, and 0.365 MMb/d of available coking, CCU, and total HCU calendar-day capacity, respectively, is currently not utilized.

Note that the CCU recycle capacity data in Table S4 are incomplete. At least 25 CCUs were reported to EPA as having CCU resid recycle capacity (*RS11*) that were still operating in 2014 as reported to EIA (*RS9*) but were not reported to EIA as having any recycle capacity (*RS9*). The resid recycle capacity for those 25 CCUs reported to EPA (*RS11*) but not to EIA in 2014 (*RS9*) ( $\approx 0.174$  MMb/d) exceeds the *total* CCU recycle capacity EIA reported that year. Taken together, these data suggest a current CCU recycle capacity of  $\approx 0.250$  MMb/d,<sup>3</sup> however, publicly reported EPA data do not include recycle rates for many CCUs, and some of those units report recycle capacity to EIA, so this (250 MMb/d) figure also may underestimate total current US recycle capacity.

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<sup>3</sup> Based on the *additional* EPA CCU reports, EIA 2014 data, and  $0.076 + 0.174 = 0.250$  MMb/d.

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**Table S5. Design capacity data for delayed coking unit (DCU), catalytic cracking unit (CCU), and gas oil hydrocracking unit (HCU) oil feeds and yields.**

<b>Delayed coking<sup>a</sup></b>									
Feed API and wt % sulfur	17.1 API, 0.5%		12.8 API, 0.6%		8.2 °API, 3.4%		4 °API, 5.3%		
Yield (vol. fraction)									
LPG	0.11		0.10		0.14		0.16		
Naphtha	0.22		0.21		0.19		0.24		
Gas oil	0.52		0.60		0.45		0.30		
Coke	0.15		0.09		0.22		0.30		
<b>Catalytic cracking<sup>b</sup></b>									
Feedstock	UR	UR	UR	UR	HGO	UR	UR	HGO	UR
Density (°API)	24.1	22.8	22.3	21.3	20.1	19.2	18.2	15.1	13.4
Sulfur (wt. %)	0.8	NR	1.0	NR	0.5	NR	1.1	3.3	1.3
Yield (vol. %) (wt. %)									
Naphtha	61	59	60	57	58	56	49	51	46
Distillate	17	16	17	15	18	16	20	21	19
Gas oil/heavy cycle oil	5.6	6.2	6.6	9.0	NR	9.6	5.9	NR	11
Resid	NR	NR	NR	NR	7.2	NR	NR	9.7	NR
Coke	7.1	8.4	7.8	9.1	7.0	10.8	5.9	10.3	7.6
<b>Gas oil hydrocracking<sup>c</sup></b>									
	Feedstock: 340–550 °C Straight-run vacuum gas oil; 22°API, 2.5 wt. % sulfur								
HCU product objective:	Naphtha			Jet Fuel			Diesel		
Yield (vol. % fresh feed)									
Butanes	11			8			7		
Pentanes	25			18			16		
Naphtha	90			29			21		
Distillate	—			69			77		

**Table S5 notes:** (a) Available delayed coking unit (DCU) data are from Meyers, 1986 (*RS12*). Mass/volume yield conversions used naphtha and gas oil API reported by Meyers and densities of 539 and 967 kg/m<sup>3</sup> for LPG and coke, respectively, from Karras, 2010 (*RS13*). DCU yields follow the expected trend of increasing byproducts (gasses and coke) and decreasing liquids (naphtha+gas oil) with increasing feed (resid) density and sulfur. Sulfur content of the 8.2 °API feed shown (3.4%) is close to that of resid in the baseline shown in Table S2 (3.6%), and its density (8.2 °API ≈ 1,013 kg/m<sup>3</sup>) is close to that of resid in the average SPR crude (1,017 kg/m<sup>3</sup>). The 8.2 °API, 3.4% sulfur yield was chosen as representative for the analysis herein. This results in conservative coker yield estimates because the baseline crude slate is denser than the SPR average, and dilbit resid density and sulfur content are greater still.

(b) Available catalytic cracking unit (CCU) yield data are from Speight, 2013 (*RS14*). UR: Unspecified resid feed. HGO: Heavy gas oil with an initial boiling point of 370 °C. Yields shown in red are in wt. %. CCU yields also follow expected trends with feed quality; naphtha

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yields generally decline and coke yields increase as CCU feed becomes denser and higher in sulfur. Data for the 20.1 API/0.5% sulfur and 15.1/3.3% sulfur yields are more complete than those for the other yields (which lack feed cut-point, and in many cases, sulfur content data), and are the most representative of US refineries on average, because unlike the other data, these data are for fluid catalytic cracking (*RS14*). FCCUs are the most common type of CCU in the US.

Sulfur in the 20.1 API feed (0.5%) is lower than in GO distilled from the baseline crude slate shown in Table S2 (1.5%), but its density (20.1 API  $\approx 933 \text{ kg/m}^3$ ) is high relative to GO distilled from the average SPR crude shown in Table S2 ( $922 \text{ kg/m}^3$ ), and a portion of current US CCU feed is pretreated to lower its sulfur content (*RS11*). Thus, the 20.1 API/0.5% sulfur yield shown provides the most representative available data for baseline average US CCU yield. The 15.1 API ( $\approx 965 \text{ kg/m}^3$ ), 3.3% sulfur feed is very close to the average GO distilled from dilbits ( $964 \text{ kg/m}^3$ , 3.4 wt. % sulfur). The data for this HGO feed are the most representative available for CCU yield from US refining of additional dilbit, and are used in the scenario analysis herein. This results in conservative estimates of potential CCU yield because CCUs would process more resid blended with HGO in these scenarios, there is relatively little CCU *resid* pretreatment capacity in the US, and this relatively high CCU distillate yield (21 vol. %) may underestimate the processing impacts of low distillate yield from dilbit crude distillation (*see* tables S1, S2).

(c) Available hydrocracking unit (HCU) data are from Robinson and Dolbear, 2007 (*RS15*). First, note the volume expansion from aggressive hydrogen addition in the cracking process (yields substantially exceed 100% of feed volume). Equally important, different HCU yields result from the same HGO feed when the HCU is operated for different product objectives. This ability to ‘swing’ from making naphtha for gasoline to making distillate for diesel or jet fuel is used to supply seasonally changing product demand and explains in part why substantial HCU capacity has been built despite its relatively high capital and operating costs (*RS15*). Indeed, investment in HCU capacity has been called a ‘stay in business’ cost for some refiners (*Id.*) HCU capacity to swing from naphtha to distillate production would be used to mitigate the low crude distillation distillate yield from replacing more of the US crude slate with dilbit (Table S3), especially since DCU and CCU capacity is available to make up the lost HCU naphtha yield (tables S4, S5). The HCU ‘Jet Fuel’ yield estimate in Table S5, which conservatively minimizes the amount of HCU naphtha yield lost in such a swing, is used by the analysis herein.

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**Table S6. Estimate calculation for changes in DCU and CCU feed rate and CCU coke burn in 20/80 and 50/50 dilbit/baseline US crude feed scenarios.<sup>a</sup>**

Scenario	20/80 dilbit/baseline crude blend	50/50 dilbit/baseline crude blend
<b>Change in DCU cycle number, volume, or both</b>		
Baseline feedrate (MMb/d) <sup>b</sup>	2.303	2.303
Feed increment (MMb/d) <sup>a,c</sup>	0.340	1.138
DCU increment (MMb/d) <sup>d</sup>	0.322	1.076
DCU rate increase (%)	14%	47%
<b>Change in CCU yield and combustion of catalyst coke</b>		
2013 fresh feed (MMb/d) <sup>b</sup>	4.811	4.811
2013 recycle feed (MMb/d) <sup>b</sup>	0.084	0.084
Baseline feedrate (MMb/d)	4.895	4.895
Feed increment (MMb/d) <sup>a,c</sup>	0.396	0.723
<b>CCU coke burned</b>		
2011–2013 (M tons/d) <sup>e</sup>	50.2	50.2
Feed increment (M t/d) <sup>e</sup>	6.84	12.5
Cokeburn rate increase (%)	14%	25%

**Table S6 notes:** (a) Based on cracking process changes due to dilbit scenario shifts in crude distillation from distillate and gas oil (GO) to resid that would be needed to maintain gasoline, diesel, and jet fuel feedstock production at the current baseline crude rate, and the data in tables S1–S5 and S7. Scenario process flows and rates are detailed and tabulated in the main report. Briefly, available conversion capacity (Table S4) would be utilized before building new capacity; DCUs would convert more resid to naphtha and GO (Table S5); CCUs would convert more resid and GO to naphtha and distillate (*Id.*); and the new DCU and CCU naphtha would allow GO HCU to swing from naphtha to distillate (*Id.*) until these rate changes and shifts produce naphtha and distillate at baseline volume rates from the new crude blend.

(b) Feed rates for DCU and CCU fresh feed and CCU recycle feed in 2013 from Table S4.

(c) Additional DCU fresh feed resid and CCU fresh feed and recycle feed gas oil and resid increments under scenario conditions described in note “a” and detailed and tabulated in the main report. Crude distillation yields at current crude rate are  $\approx 0.328$ – $0.820$  MMb/d and  $0.267$ – $0.669$  MMb/d lower in distillate and gas oil, respectively, and  $\approx 0.032$ – $0.079$  and  $0.615$ – $1.538$  MMb/d higher in naphtha and resid, respectively, in the +20–50% dilbit scenarios. (Table S3.) Even after swinging 27% of gas oil HCU capacity to distillate yield, coking must run near capacity on increased resid and shift  $0.275$  MMb/d of resid ( $\approx 5\%$  of CCU runs) to be blended

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into CCU feed; and CCU rate increases to 94% of capacity, recycling an additional 5% of CCU feed, to maintain naphtha and distillate production in the +20% dilbit scenario. In the +50% dilbit scenario 75% of GO HCU capacity swings to distillate, coking rate exceeds current capacity by  $\approx 28\%$ , and recycling 0.48 MMb/d more CCU feed than in the baseline (recycling new CCU resid feed  $\approx 1.2$  times) increases total CCU feedrate to  $\approx 98\%$  of 2014 CCU capacity.<sup>4</sup> These estimates are based on the changes in crude distillation yields from Table S3 stated above, the unit rate and capacity baselines from Table S4, and the conversion yields from Table S5.<sup>5</sup> Process rate and feed/product flows maintaining the scenario crude and product slate conditions as described in note “a” are detailed and tabulated in the main report.

(d) DCU portion of the total coking capacity as of 2014 (94.6%) from data in Table S4.

(e) Coke yield per barrel CCU feed would increase because dilbit GO and resid is denser and more contaminated (tables S1, S2), and CCUs would run more recycle resid of even lower quality (this table). The 7 wt. % (baseline) and 10.3 wt. % (scenarios) feed-related coke yields from Table S5 are applied to the amount of CCU throughput equal to the baseline, and to the incremental CCU throughput exceeding the baseline, respectively. The total throughput amount up to baseline (4.895 MMb/d) is further assumed to remain at baseline density as represented by the SPR average from Table S2 (922 kg/m<sup>3</sup>) while only the portion of the new CCU resid feed in the increment exceeding baseline is represented by the dilbit resid from Table S1 (1,055 kg/m<sup>3</sup>). Thus, the coke yield/barrel increase is conservatively applied only to the new increments of CCU feed. This estimate is conservative, also, because the resid that CCUs would run in greater amounts is of lower quality than the gas oil the 0.7–10.3% coke yield data are based upon, so that running this additional resid throughput could further boost CCU coke yield. This estimate implies adjusting baseline emissions per barrel CCU feed by a factor of  $\approx +0.69$ .

CCU feed rate change and coke-burn (mass/b) change components account for  $\approx 59\%$  and 41%, of the estimated potential CCU coke combustion emissions increments, respectively.

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<sup>4</sup> Note that HCU rate could increase instead of CCU rate, but at greater capacity addition cost, as explored in Table S7 below.

<sup>5</sup> Table S5 yields, as vol. % on feeds: DCU yields, 19% and 45% for naphtha and gas oil; CCU yields, 51% and 21% for naphtha and distillate; HCU yields (accounting for capacity swung from naphtha to distillate production target), -61% and +69% for naphtha and distillate, respectively.

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**Table S7. Estimate of additional conversion capacity costs to maintain US gasoline, diesel, and jet fuel production by a coking and hydrocracking alternative.**

Values in millions of barrels per day (MMb/d) or percent (%)

Scenario	20/80 dilbit/baseline crude blend scenario	
	A: Use existing capacity 1st	B: DCU & GO HCU alternative
<b>Case</b>		
<b>Change in crude dist. unit (CDU) yield<sup>a</sup></b>		
Naphtha, change from crude distillation	0.032	0.032
Distillate, change from crude distillation	-0.328	-0.328
Gas oil, change from crude distillation	-0.267	-0.267
Resid, change from crude distillation	0.615	0.615
<b>Changes in coking rate and yield</b>		
Net change in coking feed rate <sup>b</sup>	0.340	0.615
Change in coker naphtha yield <sup>c</sup>	0.065	0.117
Change in coker gas oil (GO) yield <sup>c</sup>	0.153	0.277
Change in GO from CDU + coking	-0.114	0.010
Change in resid from CDU + coking	0.275	0.000
<b>Changes in CCUs rate and yield</b>		
Change in CCU fresh feed input <sup>b</sup>	0.161	—
Change in CCU recycle rate <sup>d</sup>	0.235	—
New resid feed (% total CCU fr. feed) <sup>d</sup>	≈5.5%	—
Eq. times new resid feed is recycled <sup>d</sup>	0.855	—
Net change in CCU total feed rate <sup>d</sup>	0.396	0.000
Change in CCU naphtha yield <sup>c</sup>	0.202	—
Change in CCU distillate yield <sup>c</sup>	0.083	—
Change in CDU+coking+CCU naphtha	0.299	0.149
Change, CDU+coking+CCU distillate	-0.245	-0.328
<b>Changes in GO-HCU rate and yield</b>		
Net change in HCU GO feed input <sup>e</sup>	0	0.010
Δ in GO-HCU feed input for naphtha <sup>e</sup>	-0.355	-0.465
Δ in GO-HCU feed input for distillate <sup>e</sup>	0.355	0.475
Change in GO HCU naphtha yield <sup>c</sup>	-0.216	-0.284
Change in GO HCU distillate yield <sup>c</sup>	0.245	0.328
<b>Net changes, processing and key yields</b>		
US coking capacity in 2014 (MMb/cd) <sup>f</sup>	2.687	2.687
US coking feed rate in 2013 (MMb/d) <sup>f</sup>	2.303	2.303
Net Δ in coking feed rate (MMb/d)	0.340	0.615
Total utilization of 2014 capacity (%)	98%	109%
US CCU capacity in 2014 (MMb/cd) <sup>f</sup>	5.616	5.616
US CCU feed rate in 2013 (MMb/cd) <sup>f</sup>	4.811	4.811
Net Δ in CCU feed rate (MMb/d)	0.396	0.000
Total utilization of 2014 capacity (%)	94%	86%
US HCU capacity in 2014, (MMb/cd) <sup>f</sup>	2.035	2.035
US GO-HCU capacity, 2013 (MMb/cd) <sup>f</sup>	1.297	1.297
Net Δ in GO-HCU feed rate (MMb/d)	0	0.010
Δ in GO-HCU feed swung to distillate	0.355	0.465
<b>Naphtha (gasoline feedstock)</b>		
Net Δ from DCU, coking, CCU and HCU	0.082	-0.135
Net Δ v. baseline CDU yield (%)	2%	-4%
<b>Distillate (diesel, jet fuel feedstock)</b>		
Net Δ from DCU, coking, CCU and HCU	0.000	0.000
Net Δ v. baseline CDU yield (%)	0%	0%

Figures may not add due to rounding.

See Table S7 notes, next page.

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### *Table S7 notes:*

(a) Data from Table S3. (b) Cokers and CCUs process resid; CCUs and GO HCUs process gas oil. The change in CCU fresh feed is the net change from CDUs and coking, minus any new GO fed to HCUs. (c) From yields on feed vol. identified in Table S5: DCU naphtha (19%) and gas oil (45%); CCU naphtha (51%) and distillate (21%); GOHCU (naphtha/dist-‘jet’ / swing to distillate ‘jet’): naphtha (90% / 29% / -61%) and distillate (0% / 69% / +69%).

(d) These Case A CCU rate increments are based on replacing naphtha production lost from CDUs (after coker yield is accounted for) and from GO HCUs that swing to distillate; future CCU recycle rates are not objectively known. However, the CCU process has the capability to feed resid and clearly would recycle some of its residue and GO to crack more light product. (*RS12–RS15*.) Case ‘A’ recycle rates are  $\approx 5.5\%$  and  $7.9\%$  of CCU fresh feed in the +20% and +50% dilbits scenarios, respectively, and represent recycling  $\approx 16\text{--}17\%$  more of the *new* resid feed volume back into CCUs the equivalent of 0.86–1.2 times in the +20–50% dilbit scenarios. The recycle rate increments appear reasonable—and may be achievable without capacity addition in the +20% dilbit scenario, based on public reports that each omit recycle data from some CCUs.<sup>6</sup> In any case, total (fresh+recycle) feed is 94%–100% of 2014 CCU fresh feed capacity in Case A +20–50% dilbit scenarios, supporting these results.

(e) In Case A, GO HCUs stay below current capacity but make more GO into distillate instead of naphtha, and achieving baseline distillate volume drives this swing (while CCU rate increases to balance naphtha at baseline, accounting for changes in CDU+coker+HCU yield. In Case B, there is no change in CCU operation or feed, and GO HCUs increase rate *and* swing from naphtha to distillate production seeking to balance naphtha and distillate at baseline (accounting for changes in CDU+coker+HCU yield).

(f) Fresh feed calendar-day capacities as of January 2014 from Table S4. Stream-day capacities are greater than calendar-day capacities, and CCU fresh+recycle feed capacities are greater than fresh feed capacities (Table 4). For this reason, from the standpoint of estimating potential needs for capacity additions, the capacity utilization results shown in the table based on fresh feed and c/d capacities may be conservative. Also note that ‘net change’ rates for CCUs,

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<sup>6</sup> Based on 0.235 MMb/d (Table S7) v. 0.250 MMb/d based on two sources of incomplete data noted in Table S4.

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including fresh *and* recycle feed changes, are compared with CCU fresh feed capacity that does not include recycle feed capacity,<sup>7</sup> so CCU capacity utilization results are conservative in this respect for another reason as well. Total coking capacity, including delayed and fluid coking, is shown; the scale of resid yield changes versus current coking capacities in some cases or scenarios strongly suggests all types of coking could increase rate in these scenarios, and in any case, data were not available to calculate DCU-specific capacity utilization in the US (e.g., EIA did not report DCU feed inputs publicly). Capacity for fresh feed of *gas oil* to hydrocracking (GO-HCU;  $\approx 64\%$  of total 2014 HCU capacity in Table 4) is used instead of total HCU capacity. In essence, this makes the assumption that HCUs designed for other types of feed (*esp.* hydrocracking of distillate feed;  $\approx 31\%$  of total 2014 HCU capacity in Table 4), would not be able to switch over or would not switch over to gas oil feeds—another potentially conservative assumption in the analysis. EIA did not report US feed rates for GO-HCUs publicly, so capacity utilization for GO-HCUs (separately from all HCUs) were not available.

Results support the ‘analysis’ case (Case A) as it may achieve product targets within existing DCU, CCU and HCU capacities while the HCU alternative (Case B) nearly achieves product targets only by clearly adding to existing coking capacity, even in the less extreme, +20% dilbit scenario. Because Case B assumes no change in CCU operation, coking must expand to run the excess resid from crude distillation of dilbit and to convert enough of the resid to GO so that GO-HCUs can make distillate *and* naphtha. But even coking all of the excess resid in the +20% dilbit scenario provides only  $\approx 10,000$  b/d more gas oil feed to the HCUs, not quite enough extra feed to meet both the distillate and the naphtha baseline targets in the Case B +20% scenario. In sum, adjusting all three types of conversion capacity provides more flexibility to convert the new crude slate, and it does not seem plausible that refiners would forego that existing flexibility and commit additional capital to capacity expansions that would not achieve superior product yields.

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<sup>7</sup> Data suggest CCU recycle capacity is underestimated and poorly quantified (*see* Table S4 notes, note ‘d’ above).

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**Table S8. US production and export data for selected refined products.**

Annual data in thousands of barrels per day (Mb/d)

	Finished mtr. gasoline		Kerosene jet fuel		Distillate fuel oil		Petroleum coke	
	Production	Export	Production	Export	Production	Export	Production	Export
1983	6,338	10	817	5	2,456	64	420	195
1984	6,453	6	919	7	2,680	51	439	193
1985	6,419	10	983	12	2,686	67	455	187
1986	6,752	33	1,097	16	2,796	100	506	238
1987	6,841	35	1,138	23	2,729	66	512	213
1988	6,956	22	1,164	27	2,857	69	544	231
1989	6,963	39	1,197	23	2,899	97	542	233
1990	6,959	55	1,311	39	2,925	109	552	220
1991	6,975	82	1,274	39	2,962	215	568	235
1992	7,058	96	1,254	33	2,974	219	596	216
1993	7,304	105	1,309	43	3,132	274	619	258
1994	7,181	97	1,410	16	3,205	234	622	261
1995	7,459	104	1,407	23	3,155	183	630	277
1996	7,565	104	1,513	46	3,316	190	664	285
1997	7,743	137	1,554	35	3,392	152	689	306
1998	7,892	125	1,525	24	3,424	124	712	267
1999	7,934	111	1,565	29	3,399	162	713	242
2000	7,951	144	1,606	32	3,580	173	727	319
2001	8,022	133	1,529	29	3,695	119	767	336
2002	8,183	124	1,514	8	3,592	112	781	337
2003	8,194	125	1,489	20	3,707	107	798	361
2004	8,265	124	1,547	40	3,814	110	836	350
2005	8,318	136	1,546	53	3,954	138	835	347
2006	8,364	142	1,481	41	4,040	215	848	366
2007	8,358	127	1,448	41	4,133	268	823	366
2008	8,548	172	1,493	61	4,294	528	818	377
2009	8,786	195	1,396	69	4,048	587	799	391
2010	9,059	296	1,418	84	4,223	656	812	449
2011	9,058	479	1,449	97	4,492	854	843	499
2012	8,926	409	1,471	132	4,550	1,007	853	503
2013	9,234	373	1,499	156	4,733	1,134	871	524

**Table S8 notes:** Refinery and blender net production (RS16) and US exports (RS17) of finished motor gasoline, kerosene jet fuel, distillate fuel oil, and petroleum coke from US EIA. Production continues to grow or is stable, and exports have grown, especially in recent years, helping to explain continued production growth despite lower domestic demand for some of these products. While it is not possible to know future international demand or market conditions, these data support *forecasting* scenarios with the potential for stable US refinery gasoline, diesel, and jet fuel feedstock production.

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**Table S9. Toxic pollutants detected in EPA ICR source tests of DCUs and CCUs.**

Pollutant	Detected from	Pollutant	Detected from
1,2-Dibromoethane	DCU and CCU	Fluorene	DCU and CCU
2,2,4-Trimethylpentane	DCU	Formaldehyde	DCU and CCU
2,4-Dimethylphenol	DCU and CCU	Hexane	DCU and CCU
2-Methylnaphthalene	DCU and CCU	Hexavalent chromium	CCU
2-Methylphenol	CCU	Hydrogen chloride	CCU and CCU
2-Nitropropane	DCU and CCU	Hydrogen cyanide	DCU & CCU
3-Methylcholanthrene	DCU	Hydrogen fluoride	CCU
Acenaphthalene	DCU and CCU	Hydrogen sulfide	DCU
Acenaphthene	DCU and CCU	Indeno(1,2,3-cd)pyrene	DCU and CCU
Acetaldehyde	DCU and CCU	Lead	DCU and CCU
Acetone	DCU and CCU	m&p-Xylenes	DCU
Acetonitrile	CCU and CCU	Manganese	DCU and CCU
Acrolein	DCU and CCU	Mercury (elemental)	DCU and CCU
Acrylonitrile	CCU	Mercury (oxidized)	DCU and CCU
Ammonia	CCU	Mercury (total)	DCU and CCU
Aniline	DCU and CCU	Methanol	DCU and CCU
Anthracene	DCU and CCU	Methyl iso-Butyl Ketone	DCU
Antimony	DCU and CCU	Methyl t-Butyl Ether (MTBE)	DCU
Arsenic	DCU and CCU	Methylene Chloride	DCU and CCU
Benzene	DCU and CCU	Naphthalene	DCU and CCU
Benzo(a)anthracene	DCU and CCU	Nickel	DCU and CCU
Benzo(a)pyrene	DCU and CCU	Nitric oxide	DCU
Benzo(b)fluoranthene	DCU and CCU	Nitrobenzene	DCU and CCU
Benzo(e)pyrene	DCU and CCU	o-Toluidine	DCU
Benzo(ghi)perylene	DCU and CCU	o-Xylene	DCU
Benzo(k)fluoranthene	DCU and CCU	Particulates (condensable)	DCU and CCU
Beryllium	DCU and CCU	Particulates (filterable)	DCU and CCU
Biphenyl	DCU and CCU	Particulates (total PM)	DCU and CCU
Cadmium	DCU and CCU	Pentane	DCU
Carbon disulfide	CCU	Perylene	DCU and CCU
Carbon monoxide	DCU and CCU	Phenanthrene	DCU and CCU
Chlorine	CCU	Phenol	DCU and CCU
Chlorine gas	DCU	Propanal	DCU and CCU
Chlorobenzene	DCU	p-Xylene	DCU
Chromium	DCU and CCU	Pyrene	DCU and CCU
Chrysene	DCU and CCU	Selenium	DCU and CCU
Cobalt	DCU and CCU	Styrene	DCU
Cresols	DCU and CCU	Sulfur dioxide	DCU and CCU
Cumene	DCU	Tetrachloroethane	DCU
Dibenzo(a,e)pyrene	DCU	Toluene	DCU and CCU
Dibenzo(a,h,)anthracene	DCU	PCBs (total)	CCU
Dibenzofuran	DCU and CCU	PCBs (dioxins)	CCU
Ethylbenzene	DCU	PC dibenzo-p-dioxins	CCU
Fluoranthene	DCU and CCU	PC dibenzofurans (dioxins)	CCU

**Table S9 notes:** Data from DCU and CCU source tests reported to and summarized by EPA in its ICR public data reports (*RS11*; *see esp.* Goehl, 2012 summaries of delayed coking unit and fluid catalytic cracking unit emission source test reports). Pollutants reported as detected in one or more test runs are included: note, however; the vast majority of pollutants detected were not

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measured above method detection limits in some—and typically most—of the total DCU or CCU source tests. ‘Dioxins’ listings in this table includes 29 polychlorinated dibenzo-*p*-dioxin, dibenzofuran, and biphenyl compounds with dioxin-like activity (binding to dioxin receptor). Including these 29 dioxins, 114 toxic chemicals were detected in these source tests.

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**Table S10. VOC, methane, and benzene emissions measured from DCU vents.**

Site <sup>a</sup>	Marathon Garyville LA	BP-Husky Oregon OH	ExxonMobil Baytown TX	Houston Refining Houston TX	Hovensa St. Croix VI
Coker drums <sup>a</sup>	2	2	4	4	4
Unit capacity (Mb/d)	44.00 <sup>a</sup>	27.00 <sup>a</sup>	51.50 <sup>b</sup>	82.87 <sup>c</sup>	73.60 <sup>b</sup>
Test rate (Mb/d)	38.00 <sup>d</sup>	24.30 <sup>a</sup>	46.35 <sup>e</sup>	74.58 <sup>a</sup>	59.66 <sup>a</sup>
Full cycle hours <sup>a</sup>	34	33	28.25	22	40
Cycles/yr (all drums) <sup>a</sup>	515	531	1,240	1,593	876
VOC emissions					
Data flags <sup>a</sup>	—	—	—	—	—
kg/hour (avg.)	3.39	10.4	1.59	0.573	51.9
lb/day (avg.)	179	548	83.9	30.3	2,748
short tons/year	32.7	100	15.3	5.53	502
lb/Mb feed	4.72	22.6	1.81	0.407	46.1
lb/drum cycle <sup>a</sup>	127	377	24.7	6.95	1,145
Methane emissions					
Data flags <sup>a</sup>	—	—	—	—	—
kg/hour (avg.)	7.01	8.83	4.84	0.423	99.0
lb/day (avg.)	371	467	256	22.4	5,239
short tons/year	67.7	85.2	46.7	4.09	956
lb/Mb feed	9.77	19.2	5.52	0.300	87.8
lb/drum cycle <sup>a</sup>	263	321	75.3	5.13	2,183
Benzene emissions					
Data flags <sup>a</sup>	DLL	DLL	DLL	DLL	BDL
kg/hour (avg.)	0.0203	0.0522	0.0219	0.0010	< 0.5
lb/day (avg.)	1.07	2.76	1.16	0.05	< 26
short tons/year	0.196	0.504	0.211	0.010	< 5
lb/Mb feed	0.0282	0.114	0.0250	0.0007	< 0.4
lb/drum cycle <sup>a</sup>	0.760	1.90	0.341	0.0120	< 11

**Table S10 notes:**

BDL: Analyte below method detection level in all test runs; data not used in statistical analysis for comparison of these measurements of delayed coking (DCU) vent emissions with measurements of emissions from the decoking cycle. DLL: Analyte below method detection level in one or more test runs and above MDL in one or more runs; data used in comparison.

(a) Data from ICR source test; for emission data *see esp.* Goehl (2012) summary of delayed coking unit emission source test reports (*RS11*). (b) Data from ICR ‘Component 1’ Non-CBI data tables (*RS11*). (c) Data from US EIA for this facility’s b/cd delayed coking capacity in 2011 (*RS9*). (d) Estimated based on ICR Source Test Report at page 2-3 (*RS11*). (e) Estimated at 90% of capacity based on EPA ICR protocol requirement to test at a minimum of 90% capacity. Note that the ranges of emissions expressed on a per-barrel basis are generally similar to or smaller than those expressed on a per-cycle basis. This result was expected because coke cycle volume

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can affect emissions per cycle. VOC, methane, and benzene results of all ICR source tests reported are shown (only five source tests of DCUs were reported) and VOC, methane, and benzene were detected in 5, 5, and 4 of these tests respectively. Only DCU vent emissions were reported in the ICR data, however, volatile chemicals also emit during coke cutting and byproduct handling; when the coke drum is opened, when the coke is ‘cut’ from the drum, and when the coke, which can be 9–12% volatile chemicals, as well as the cutting and quench water, is handled (*RS18–RS20*).

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**Table S11. VOC, methane, and VOC emissions measured from DCU decoking.**

Site	Canadian refinery <sup>a,b</sup>	Canadian refinery <sup>a,b</sup>
Coker drums <sup>a</sup>	2	2
Coker capacity (Mb/d) <sup>b</sup>	7.5	7.5
Test rate (Mb/d) <sup>c</sup>	7.5	7.5
Full cycle hours <sup>d</sup>	32 (range: 22–40)	32 (range: 22–40)
Cycles/yr (all drums) <sup>d</sup>	548 (range: 438–796)	548 (range: 438–796)
<b>Emission sources</b>	venting, coke cutting & coke water handling	venting and coke cutting
<b>C<sub>2+</sub> VOC (grams/b)</b>		
Lower bound <sup>e</sup>	132	63.4
Median <sup>f</sup>	206	99.1
Upper bound <sup>g</sup>	480	231
<b>Methane (grams/b)<sup>h</sup></b>		
Lower bound <sup>e</sup>	77.9	37.6
Median <sup>f</sup>	122	58.7
Upper bound <sup>g</sup>	283	137
<b>Benzene (mg/b)<sup>h</sup></b>		
Lower bound <sup>e</sup>	810	391
Median <sup>f</sup>	1,266	610
Upper bound <sup>g</sup>	2,945	1,421

**Table S11 notes:** (a) Chambers et al., 2008 reported direct measurements of hydrocarbon emissions from a delayed coker at a Canadian refinery using differential absorption light detection and ranging (DIAL) technology. All parts of the decoking cycle were measured; samples were 2–3 hours each; at least 12 samples of the coking area are described (*see* Chambers Table 5); and validation demonstrations (+5% to –15%) and closeness of the results to the median from 16 other refinery DIAL surveys support their accuracy (*RS20*). C<sub>2+</sub>VOC, methane, and benzene emissions from the coker venting, cutting and water handling operations averaged 206, 122, and 1.27 kg/hr, respectively (*RS20*; *see* also note h below). (b) Data from *Oil & Gas Journal* ‘Worldwide Refining Survey’ (*RS21*). These data (*RS21*) indicate that the only Canadian refinery operating at the crude and product capacities described by Chambers et al. (*RS20*) during their survey and publication had 7,500 b/cd of DCU capacity.<sup>8</sup> Note that the refinery measured used injection wells to handle some of its wastewater (*RS20*). Typical US refinery operations may differ from that approach; this difference is explored by breaking out water handling emissions from other DCU decoking emissions in Table S11. (c) Measurement during operation at 100% capacity is conservatively assumed. (d) Typical cycle times range from 28–36 hours (*RS18*) but the entire range from ICR data (22–40 hrs., median 32 hrs; *RS11*)

<sup>8</sup> *See RS21* data for Petro-Canada Products Ltd. Edmonton listing during 2005–2008.

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is conservatively assumed. Emitting activities (vents, water drains, unheading, hydraulic decoking ‘drilling’ and purging) are also conservatively assumed—at the low emitting end of this range—to last only 4 hours, which is the lowest assumption consistent with Chambers et al.’s samples of venting *and* coke drilling samples at 2-hour-minimum sampling times (RS20).

(e) Based on 40-hour cycle or 438 cycles/year with emission during 4 hours/cycle. (f) Based on 32-hour cycle or 548 cycles/year with emission during 5 hours/cycle. (g) Based on 22-hour cycle or 796 cycles/year with emission during 8 hours/cycle. (h) Methane and benzene emissions fractions from venting, coke cutting, and coke water handling based on VOC emissions breakdowns reported by Chambers et al. (RS20).

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**Table S12. Benzene, methane and VOC emissions measured from delayed coker units (DCUs).**

*Emissions per barrel (b) of coker oil feed*

	Coker vents <sup>a</sup>		Vents & coke cutting <sup>b</sup>		Vents, cutting & proc. H <sub>2</sub> O <sup>b</sup>	
	median	(range)	median	(range)	median	(range)
Benzene (mg/b)	19	(<1–52)	610	(390–1,400)	1,270	(810–2,900)
Methane (g/b)	11	(<1–40)	59	(38–140)	122	(78–280)
C <sub>2+</sub> VOC (g/b)	7	(<1–21)	99	(63–230)	206	(130–480)

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**Table S12 notes:** Data summarized from tables S10 and S11. Decoking emissions estimated from direct measurements of vents, coke cutting, and coker process water handling exceed those estimated from ICR source tests of vents alone by  $\approx$  1–2 orders of magnitude, especially for benzene. These results demonstrate the inaccuracy of relying solely on the vent emission measurements from the ICR source tests (Table S10) to estimate emissions of volatile chemicals from DCUs. Only a single DCU is represented, however, very conservative assumptions for the low-end and median emissions (Table S11) notes d–g compensate for this weakness in the data to the extent possible—especially for in the case of ‘venting and coke cutting’ estimates, which do not assume similar water handling emissions by the average US refinery DCU operation.

The low end of the ‘vents & coke cutting’ emissions, and the low end of the ‘vents, cutting & process water’ emissions (e.g., 390 and 810 mg/barrel, respectively, for benzene) are conservatively chosen to represent lower bound and upper bound DCU emissions herein.

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**Table S13. Concentrations of selected elements measured in a CCU emission stack.**

*Stack concentrations in micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ )*

Antimony	0.41	Lanthanum	865
Arsenic	1.63	Lead	6.41
Beryllium	0.15	Nickel	819
Cadmium	2.92	Selenium	0.58
Cesium	0.04	Thorium	2.14
Chromium	962	Uranium	0.55
Cobalt	24.8	Vanadium	145

**Table S13 notes:** Data from Sánchez de la Campa et al., 2011 (RS22). Concentrations of beryllium, chromium, lanthanum, and uranium in the stack of this CCU in were the highest of those in any stack measured by this survey of a Spanish refinery and petrochemical complex (*Id.*) Metals in CCU emissions originate from both CCU catalysts (e.g., lanthanum; nickel) and from the oils fed to the CCUs (e.g., nickel; vanadium). Indeed, vanadium, nickel and lanthanum have been used tracers for CCU particulate emissions. This information provides ancillary support for the ICR source tests of CCU metal emissions.

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**Table S14. Emission data for toxic pollutants detected in source tests of multiple CCUs, with calculations for median and 90<sup>th</sup> Percentile emissions/barrel—page 1 of 2.**

Site	ExxonMobil Torrance CA <sup>a</sup>	Chevron Kapolei HI <sup>a</sup>	Marathon Robinson IL <sup>a</sup>	BP Whiting IN <sup>a</sup>	Citgo Lake Charles LA <sup>a</sup>	Motiva Norco LA <sup>a</sup>	Flint Hills Rosemount MN <sup>a</sup>
Feed HTU	102 Mb/d <sup>c</sup>	0% <sup>d</sup>	0% <sup>d</sup>	89.1 Mb/d <sup>c</sup>	0% <sup>d</sup>	0% <sup>d</sup>	100% <sup>d</sup>
PM control	ESP <sup>d</sup>	ESP <sup>d</sup>	WS <sup>d</sup>	ESP & Inj. <sup>d</sup>	venturi/WS <sup>d</sup>	venturi/WS <sup>d</sup>	ESP <sup>d</sup>
Coke burn	NR	169 <sup>a</sup>	310 <sup>d</sup>	NR	314 <sup>a</sup>	960 <sup>d</sup>	451 <sup>a</sup>
Capacity	83.5 Mb/d <sup>f</sup>	21.0 Mb/d <sup>f</sup>	54.45 Mb/d <sup>d</sup>	115 Mb/d <sup>g</sup>	49.0 Mb/d <sup>d</sup>	118.8 Mb/d <sup>d</sup>	81.0 Mb/d <sup>d</sup>
Test rate	75.15 Mb/d <sup>h</sup>	18.9 Mb/d <sup>h</sup>	49.01 Mb/d <sup>h</sup>	103.5 Mb/d <sup>h</sup>	52.42 Mb/d <sup>a</sup>	106.9 Mb/d <sup>h</sup>	74.23 Mb/d <sup>a</sup>
PM flags	no flags	no flags	no flags	no flags	no flags	no flags	NR
PM (lb/h)	22.1	6.13	31.2	22.7	4.23	43.5	
PM (g/b)	3.20	3.53	6.94	2.39	0.88	4.42	
cPM flags	no flags	no flags	no flags	no flags	no flags	no flags	NR
cPM (lb/h)	20.8	1.68	8.53	9.49	2.61	21.8	
cPM (g/b)	3.01	0.969	1.89	1.00	0.542	2.22	
PM lb/t coke		0.873	2.42		0.323	1.09	
cPM/PM (%)	94%	27%	27%	42%	62%	50%	
NH <sub>3</sub> flags	no flags	no flags	no flags	no flags	no flags	no flags	no flags
NH <sub>3</sub> (lb/h)	5.49	0.120	0.723	0.450	0.639	0.270	5.50
NH <sub>3</sub> (mg/b)	795	69.1	161	47.3	133	27.5	807
Cr flags	no flags	no flags	BDL	no flags	DLL	no flags	NR
Cr (lb/h)	1.09E-03	4.07E-04		2.44E-03	1.11E-03	7.30E-04	
Cr (μg/b)	158	234		257	231	74.3	
Pb flags	DLL	no flags	no flags	no flags	DLL	BDL	NR
Pb (lb/h)	4.64E-04	1.50E-04	1.15E-03	3.11E-03	6.27E-04		
Pb (μg/b)	67.2	86.4	255	327	130		
Mn flags	no flags	no flags	no flags	no flags	no flags	no flags	NR
Mn (lb/h)	7.54E-04	9.88E-04	2.40E-03	9.46E-04	7.70E-04	3.84E-03	
Mn (μg/b)	109	569	533	99.5	160	391	
Ni flags	DLL	no flags	no flags	no flags	no flags	no flags	NR
Ni (lb/h)	6.08E-04	1.63E-02	4.61E-03	3.33E-03	2.18E-03	1.14E-02	
Ni (μg/b)	88.1	9,390	1,020	350	453	1,160	
oHg flags	BDL	DLL	DLL	no flags	DLL	BDL	NR
oHg (lb/h)		1.50E-05	7.24E-05	6.78E-05	1.54E-06		
oHg (μg/b)		8.64	16.1	7.13	0.320		
eHg flags	BDL	DLL	no flags	BDL	DLL	no flags	DLL
eHg (lb/h)		3.00E-05	1.04E-04		3.86E-05	2.42E-05	2.73E-05
eHg (μg/b)		17.3	23.1		8.02	2.46	4.00
HCN flags	no flags	no flags	no flags	no flags	no flags	BDL	no flags
HCN (lb/h)	12.0	5.36	2.07	0.460	32.2		3.33
HCN (mg/b)	1,740	3,090	460	48.4	6,690		488

**KEY** Feed HTU: CU feed hydrotreating in percent or Mb/d. ESP: electrostatic precipitator. WS: wet scrubber  
Inj.: ammonia injection. Coke burn rate in short tons/calender day. PM: total particulate matter. cPM: condensable  
particulate matter. NH<sub>3</sub>: ammonia. Cr: chromium. Pb: lead. Mn: manganese. Ni: nickel. oHg: oxidized/organic  
mercury. eHg: elemental mercury. HCN: hydrogen cyanide. DLL: detection level limited; analyte was below method  
detection level in one or more test runs. BDL: analyte was below MDL in all test runs; data not used quantitatively.

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**Table S14 (continued). Emission data for toxic pollutants detected in source tests of multiple CCUs, with calculations for median and 90<sup>th</sup> Percentile emissions/barrel—page 2 of 2.**

Site	Sunoco Philadelphia PA <sup>a</sup>	Valero Port Arthur TX <sup>a</sup>	Hovensa St. Croix VI <sup>a</sup>	Chevron Richmond CA <sup>b</sup>	Number of the 11 CCUs where analyte was positively detected	Median emissions per barrel for CCUs where analyte was detected	90 <sup>th</sup> Percentile emissions per barrel for CCUs where analyte was detected
Feed HTU	0% <sup>d</sup>	95% <sup>d</sup>	0.4% <sup>d</sup>	80% <sup>e</sup>			
PM control	venturi/WS <sup>d</sup>	venturi/WS <sup>d</sup>	venturi/WS <sup>d</sup>	ESP & Inj. <sup>e</sup>			
Coke (t/d)	879 <sup>a</sup>	570 <sup>a</sup>	782 <sup>a</sup>	812 <sup>b</sup>			
Capacity	90.0 Mb/d <sup>g</sup>	73.5 Mb/d <sup>d</sup>	160 Mb/d <sup>d</sup>	80.0 Mb/d <sup>e</sup>			
Test rate	79.29 Mb/d <sup>a</sup>	52.21 Mb/d <sup>a</sup>	113.1 Mb/d <sup>a</sup>	76.02 Mb/d <sup>b</sup>			
PM flags	no flags	no flags	no flags	DLL			
PM (lb/h)	116	8.51	38.2	78.0			
PM (g/b)	16.0	1.77	3.68	11.2	10	3.60	11.7
cPM flags	no flags	no flags	no flags	no flags			
cPM (lb/h)	34.2	2.29	22.8	73.4			
cPM (g/b)	4.70	0.477	2.19	10.5	10	2.04	5.28
PM lb/t coke	3.17	0.358	1.17	2.31			
cPM/PM (%)	29%	27%	60%	94%			
NH <sub>3</sub> flags	BDL	no flags	no flags	no flags			
NH <sub>3</sub> (lb/h)		0.522	9.85	12.8			
NH <sub>3</sub> (mg/b)		109	948	1,830	10	147	1,040
Cr flags	NR	no flags	no flags	NR			
Cr (lb/h)		4.21E-04	1.40E-03				
Cr (μg/b)		87.8	135		7	158	243
Pb flags	NR	no flags	no flags	NR			
Pb (lb/h)		2.16E-04	1.90E+03				
Pb (μg/b)		45.0	183		7	130	284
Mn flags	NR	no flags	no flags	NR			
Mn (lb/h)		6.71E-04	6.30E-03				
Mn (μg/b)		140	606		8	275	580
Ni flags	NR	no flags	no flags	NR			
Ni (lb/h)		1.11E-03	5.30E-03				
Ni (μg/b)		231	510		8	481	3,630
oHg flags	NR	no flags	no flags	NR			
oHg (lb/h)		1.90E-05	2.92E-05				
oHg (μg/b)		3.96	2.81		6	5.55	12.4
eHg flags	no flags	BDL	no flags	NR			
eHg (lb/h)	7.09E-04		2.55E-04				
eHg (μg/b)	97.3		24.5		7	17.3	53.7
HCN flags	BDL	no flags	no flags	NR			
HCN (lb/h)		42.0	105				
HCN (mg/b)		6,540	10,100		8	2,410	7,710

**KEY** Feed HTU: CU feed hydrotreating in percent or Mb/d. ESP: electrostatic precipitator. WS: wet scrubber Inj.: ammonia injection. Coke burn rate in short tons/calender day. PM: total particulate matter. cPM: condensable particulate matter. NH<sub>3</sub>: ammonia. Cr: chromium. Pb: lead. Mn: manganese. Ni: nickel. oHg: oxidized/organic mercury. eHg: elemental mercury. HCN: hydrogen cyanide. DLL: detection level limited; analyte was below method detection level in one or more test runs. BDL: analyte was below MDL in all test runs; data not used quantitatively.

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**Table S14 notes:** (a) Data from EPA ICR source tests; for emission data *see esp.* Goehl (2012) *Summary of fluid catalytic cracking unit emission source test reports (RS11)*. (b) Data from Bay Area Air Quality Management District (BAAQMD) source tests (*RS23, RS24*). These source tests were performed before EPA revised cPM sampling protocol in 2011 and used a version of the previous protocol; BAAQMD has said it will not enforce cleanup based on these results, however, it has continued to rely upon them in its emissions inventory, and the company has provided source data supporting them as well (*RS25, RS26*). (c). Data from *Oil & Gas Journal (RS21)*. (d). Data from EPA public data reports for ICR ‘Component 1’ (*RS11*). (e). Data from Title V air permit issued by BAAQMD to the Chevron Richmond Refinery; BAAQMD: San Francisco, CA ([www.baaqmd.gov](http://www.baaqmd.gov)). (f). Data from US EIA *Refinery Capacity Data by Individual Refinery* for year-2011 (*RS9*). (g). Estimated by the author based on EPA ICR non-CBI data, per. comm. with E. Goehl (Dec. 2014; *RS11*). (h). Test rate estimated at 90% of unit capacity based on EPA ICR source test guidance to test at a minimum of 90% capacity.

Overall, these emissions data do not appear to follow a ‘normal’ or ‘Gaussian’ distribution, suggesting that median values may better represent the central tendency of the data.

Note that low cPM/PM ratios tend to occur with high nickel emissions/barrel (Kapolei and Robinson plants), while high cPM/PM ratios occur with high ammonia emissions (Torrance and Richmond plants). Nickel is a typical component of CCU catalyst, and catalyst fines are a source of coarser PM in CCU emissions. Excessive ammonia injection has been linked to high cPM emissions (*RS27, RS28*), and the three highest-NH<sub>3</sub>-emitting CCUs measured for cPM (Torrance; St. Croix; Richmond) each emits cPM in excess of the 2.04 grams/barrel median value for this data set. The ten CCUs reporting cPM in the table are a small fraction of all US CCUs, and NH<sub>3</sub> injection is a common practice. If this practice is underrepresented in the Table S14 data set, the median value for these data may underestimate cPM emissions from US CCUs industry-wide. These observations support carrying forward both the median and the 90<sup>th</sup> Percentile values (*see* Table S14 final columns) in estimates of potential CCU emissions of cPM.

Note also that the ‘baseline’ emissions/b in Table S14 would need to be adjusted as shown in Table S6 (+0.69x) to account for the greater density and CCU coke mass yields of CCU feeds in the +20–50% dilbit scenarios.

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**Table S15. Comparison of DCU and CCU emissions estimated in this work and US refinery Toxic Chemical Release Inventory emissions.**

	US refinery emissions from the Toxics Release Inventory (TRI) <sup>a</sup>	Lower bound process <sup>b,c</sup> baseline from this analysis		Upper bound process <sup>b,c</sup> baseline from this analysis	
		Emissions	(% of TRI)	Emissions	(% of TRI)
Benzene (tonnes/y) <sup>b</sup>	514	310	60%	644	125%
Metals (kg/y) <sup>c</sup>					
Chromium	1,064	277	26%	427	40%
Lead	1,941	228	12%	499	26%
Manganese	1,481	483	33%	1,018	69%
Nickel	8,456	845	10%	6,374	75%
Mercury	549	40	7%	116	21%
Hydrogen cyanide <sup>c</sup>					
HCN (tonnes/y)	1,965	4,232	215%	13,539	689%

**Table S15 notes:**

(a) Stack and fugitive emissions from all US refinery sources as reported by US EPA in the Toxic Chemical Release Inventory; retrieved from [www.epa.gov](http://www.epa.gov) Dec. 2014. Benzene data are the average from 2011–2013. Metals data include all records from 2013 containing the name of the metal (e.g., ‘chromium and chromium compounds’). Hydrogen cyanide data are from 2013. Note that TRI emission estimates are generally semi-quantitative at best, and their accuracy and precision should not be assumed or overestimated.

(b) DCU emissions of benzene, calculated based on a 2.18 MMb/d DCU feed rate<sup>9</sup> are compared with total refinery emissions of benzene from the TRI. Lower bound DCU emissions are based on the low end of the range for vents and coke cutting emissions in Table S12; upper bound DCU emissions are based on the low end of the range for vents, cutting and process water handling emissions in Table S12. The upper bound estimate of current DCU emissions based on these data exceeds the refinery wide TRI estimate. This is consistent with the underestimation based on vent emissions alone that is documented in Table S12, especially when one recalls that EPA has published no protocol for estimating DCU emissions of volatile chemicals from the other decoking operations of DCUs (*RS18*). Moreover, protocols for estimating fugitive emissions from other refinery sources (such as hydrocarbon storage tanks) have been shown to result in emission estimates roughly an order of magnitude lower than those found by direct measurements (*RS20*). It is thus reasonable to suspect that the TRI data might underestimate

<sup>9</sup> Table S4 data are scaled to DCU percent of coking capacity ( $2.303 \cdot 2.542/2.687 = 2.179$ ; rounded to 2.18).

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refinery benzene emissions, and even if that were not the case, the lower bound estimate (60% of TRI benzene emissions) would not appear unreasonable for a strong benzene source within refineries, such as DCUs.

(c) CCU emissions of metals and HCN, calculated based on the 2013 CCU feed rate (4.811 MMb/d; Table S4) are compared with total refinery emissions of benzene from the TRI. Lower bound CCU emissions/barrel are based on the median emission values calculated in Table S14; upper bound CCU emissions are based on the 90<sup>th</sup> Percentile emission/b values in Table S14. The estimates of current CCU metals emissions ranges from 7–33% of refinery wide TRI estimates at the lower bound and from 21–75% of those TRI estimates at the upper bound. These results are generally consistent with a strong metal emissions source within refineries. CCU emissions have been shown to have high metals concentrations relative to other refinery sources (*RS22*), and CCU vents are relatively high-volume refinery process sources (*RS18*).

Hydrogen cyanide (HCN) emissions estimated from the data in Table S14 at 2013 CCU feed rates exceed the 2013 TRI refinery emissions estimate for HCN by 115% at the lower bound of the estimate and by 589% at its upper bound. The reason for this discrepancy is not known: it may be that the TRI underestimates HCN emissions, or that the eight CCUs represented for HCN emissions in the Table S14 source tests overestimate sector wide HCN emissions, or both. Note that the three CCUs in Table S14 reporting results that drive the upper-bound HCN emission estimates are not the same units that drive the upper-bound cPM emission estimates.

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**Table S16. Comparison of potential emission increments with CEQA thresholds.**

Scenario	20/80 dilbit/baseline blend	50/50 dilbit/baseline blend
Notional CCU at a refinery		
Assumed baseline feed rate (Mb/d)	80.0	80.0
Feedstock-related rate increase (%)	8.09%	14.8%
Feedstock-related rate increase (Mb/d)	6.47	11.82
cPM lower bound (g/b)	3.45	3.45
cPM upper bound (g/b)	8.92	8.92
cPM lower bound (kg/day)	22.3	40.7
cPM upper bound (kg/day)	57.8	105
cPM lower bound in short tons (t/yr)	<b>9</b>	<b>16</b>
cPM upper bound in short tons (t/yr)	<b>23</b>	<b>42</b>
Air quality significance threshold (t/yr)	<b>10</b>	<b>10</b>
Notional DCU at a refinery		
Assumed baseline feed rate (Mb/d)	50.0	50.0
Feedstock-related rate increase (%)	14%	47%
Feedstock-related rate increase (Mb/d)	7.00	23.5
VOC lower bound (g/b)	63	63
VOC upper bound (g/b)	130	130
VOC lower bound (kg/day)	441	1,480
VOC upper bound (kg/day)	910	3,050
VOC lower bound in short tons (t/yr)	<b>177</b>	<b>595</b>
VOC upper bound in short tons (t/yr)	<b>366</b>	<b>1,230</b>
Air quality significance threshold (t/yr)	<b>10</b>	<b>10</b>

**Table S16 notes:** Results from tables S6,<sup>10</sup> S12 and S14 are applied to a notional refinery with a baseline CCU throughput of 80 Mb/d and a baseline DCU throughput of 50 Mb/d. ‘Notional’ means that this refinery does not necessarily exist, although units run at or near these rates, and the example is therefore reasonable for purposes of illustration. The purpose of this example is to illustrate the potential significance of CCU and DCU emissions in the +20–50% dilbits scenarios at the facility (community) level. The ‘air quality thresholds’ shown are for fine particulate and VOC emissions and are those recommended by the Bay Area Air Quality Management District (BAAQMD) for determining the significance of potential emissions from operating proposed projects pursuant to the California Environmental Quality Act (CEQA).

<sup>10</sup> Baseline CCU emissions/b were adjusted (+0.69x) for coke-burn mass increments as shown in Table S6 notes.

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**Table S17. Association of coke yield with crude feed quality details (Table 2 from CBE, 2011).**

**Table 2. Refinery coke yield observed and California coke yield predicted by crude quality ( $R^2$  0.97).**

U.S. data:		<u>y observed</u>	<u>x (explanatory variable) data observed</u>			<u>coke yield predicted (95% confidence)</u>		
PADD	year	total coke (% yield)	crude den- sity (kg/m <sup>3</sup> )	crude sul- fur (kg/m <sup>3</sup> )	capacity util- ization (%)	lower bound (% yield)	prediction (% yield)	upper bound (% yield)
1	1999	3.1	858.20	8.24	90.9	2.6	3.0	3.4
1	2000	3.0	860.18	8.00	91.7	2.7	3.1	3.4
1	2001	3.3	866.34	7.71	87.2	3.0	3.4	3.8
1	2002	3.1	865.71	7.45	88.9	2.9	3.3	3.7
1	2003	2.9	863.44	7.43	92.7	2.7	3.1	3.5
1	2004	3.1	865.44	7.79	90.4	3.0	3.3	3.7
1	2005	2.9	863.38	7.17	93.1	2.6	3.0	3.4
1	2006	3.0	864.12	7.17	86.7	2.7	3.1	3.5
1	2007	3.2	864.33	7.26	85.6	2.8	3.2	3.5
1	2008	3.3	863.65	7.08	80.8	2.7	3.1	3.5
2	1999	4.2	858.25	10.64	93.3	3.3	3.7	4.0
2	2000	4.3	860.03	11.35	94.2	3.6	4.0	4.4
2	2001	4.3	861.33	11.37	93.9	3.7	4.1	4.5
2	2002	4.1	861.02	11.28	90.0	3.7	4.0	4.4
2	2003	4.2	862.80	11.65	91.6	3.9	4.3	4.6
2	2004	4.3	865.65	11.86	93.6	4.1	4.5	4.9
2	2005	4.5	865.65	11.95	92.9	4.1	4.5	4.9
2	2006	4.4	865.44	11.60	92.4	4.0	4.4	4.8
2	2007	4.3	864.07	11.84	90.1	4.0	4.4	4.8
2	2008	4.3	862.59	11.73	88.4	3.9	4.3	4.7
3	1999	4.8	869.00	12.86	94.7	4.6	5.0	5.4
3	2000	4.8	870.29	12.97	93.9	4.7	5.1	5.5
3	2001	5.3	874.43	14.34	94.8	5.4	5.8	6.1
3	2002	5.7	876.70	14.47	91.5	5.6	6.0	6.4
3	2003	5.7	874.48	14.43	93.6	5.4	5.8	6.2
3	2004	5.9	877.79	14.40	94.1	5.6	6.0	6.4
3	2005	6.0	878.01	14.40	88.3	5.7	6.1	6.4
3	2006	6.2	875.67	14.36	88.7	5.5	5.9	6.3
3	2007	6.0	876.98	14.47	88.7	5.6	6.0	6.4
3	2008	6.0	878.66	14.94	83.6	5.9	6.3	6.7
5	1999	6.1	894.61	11.09	87.1	5.8	6.2	6.6
5	2000	6.3	895.85	10.84	87.5	5.8	6.2	6.6
5	2001	6.0	893.76	10.99	89.1	5.7	6.1	6.5
5	2002	6.0	889.99	10.86	90.0	5.4	5.8	6.2
5	2003	6.2	889.10	10.94	91.3	5.4	5.8	6.2
5	2004	6.1	888.87	11.20	90.4	5.5	5.9	6.2
5	2005	6.2	888.99	11.38	91.7	5.5	5.9	6.3
5	2006	6.0	887.65	10.92	90.5	5.3	5.7	6.1
5	2007	5.8	885.54	11.07	87.6	5.2	5.6	6.0
5	2008	6.1	890.16	12.11	88.1	5.8	6.2	6.6
California data:			<u>data inputs for California predictions</u>					
Cal. avg. 2004		7.4	899.23	11.46	93.0	6.2	6.6	7.0
Cal. avg. 2005		7.7	900.56	11.82	95.0	6.4	6.8	7.2
Cal. avg. 2006		7.4	899.56	11.73	91.5	6.3	6.7	7.1
Cal. avg. 2007		7.1	899.84	11.89	88.3	6.4	6.8	7.2
Cal. avg. 2008		7.4	902.00	12.85	91.0	6.8	7.2	7.6
Cal. avg. 2009		7.6	901.38	11.70	82.9	6.5	6.9	7.2
70/30 HO/CA blend			948.39	22.59	90.8	12.4	13.0	13.5
70/30 NB/CA blend			1001.73	34.98	90.8	19.1	20.0	20.8

Prediction for replacement by heavy oil (HO) and natural bitumen (NB) at avg. 1999–2008 U.S. capacity utilization. 70/30 HO/CA crude feed: 70/30 blend of heavy oil/Calif.-produced crude. 70/30 NB/CA crude feed: 70/30 blend of natural bitumen/Calif.-produced crude. California-produced crude quality is the 2004–2008 average (Ref. 7 at Table 2-3). Avg. heavy oil and natural bitumen qualities are from USGS (5, 9). All other data from Ref. 7 at Table 2-1. Total (market & catalyst) coke yield predicted by crude density and sulfur content and refinery capacity utilization; analysis by partial least squares regression on the U.S. (PADDs) data shown.

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**Table S17 notes:** Data from *RS13* and *RS29*, excerpted from comments regarding California’s Low Carbon Fuel Standard submitted to the California Air Resources Board in 2011 by Communities for a Better Environment (*RS30*). Both CCU ‘catalyst’ coke and DCU ‘marketable’ coke are shown. The table illustrates that a substantial increase in coke production is reasonably predictable from a switch to denser, more contaminated crude feeds, such as bitumen-derived dilbits. DCU ‘marketable’ coke production, which often is exported by US refineries (Table S8), is typically used as fuel in cement, metals, and electric power production and a fraction of this coke is calcined for manufacturing of carbon products such as graphite and charcoal briquettes. Each of these uses of pet coke is high-emitting, and at least some of them (e.g., power generation; outdoor grilling) place this high-emitting refinery byproduct in competition with less emitting alternatives. However, petroleum fuel cycle analyses do not always account for the emissions ‘exported’ by refiners with DCU-produced coke—or the potential that these emissions could grow if lower quality refinery feedstock is processed.

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